Single Aerosol Particle Composition Using Vibrational Spectroscopy

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Recently, we have performed two types of time-resolved optical spectroscopic measurements on individual aerosol particles. The first method is similar to direct infrared (IR) absorption spectroscopy, and the second, exploits spontaneous and enhanced Raman scattering spectroscopy. Our objective is to study single aerosol particles to determine compositional changes and their dependencies on environmental conditions to understand fundamental mechanisms for particle transformations. To achieve our research goals, we have refined an experimental approach for aerosol particle studies using a Linear Electrodynamic Quadrupole (LEQ) trap. It also provides a convenient platform to develop and evaluate optical measurement techniques on individual particles.

The LEQ apparatus suspends and confines charged aerosol particles using a combination of four vertical rod-shaped electrodes arranged on a square, and a ring electrode at the bottom. The rods are connected in diagonal pairs to a sinusoidal high voltage, which confines particles to the symmetry axis of the rods. The ring carries a stationary potential of the same polarity as the particles, providing an electrostatic force to balance gravity and aerodynamic drag. This arrangement is mounted in an enclosure with optical access windows so that the trapped particles can be exposed to controlled environmental conditions (temperature, gas phase composition and humidity). Advantages of the LEQ design include: easier procedures (semi-automated) for introducing particles at the top with very high capture efficiency, and an ability to capture either one or more particles simultaneously. When using a droplet generation method for aerosol production, essentially identical particles can be introduced, and since they all possess the same charge polarity, they naturally space themselves evenly along the LEQ axis. Figure 1 shows a photograph of several 5 μm polymer beads captured in an LEQ, which can be maintained stably for periods up to many hours. More detail on the LEQ design and operation can be found in Hart, *et al* (2015).

This talk describes measurements to determine particle composition using IR absorption and Raman scattering vibrational spectroscopy. While both of these general methods have a long history of use, challenges in applying them to individual particles have impeded wide-spread usage.

For IR spectroscopy, the extremely small sample size (picograms) precludes use of any commercial instrument that directly measures absorption using conventional continuum light sources. We capitalize on the relatively recent proliferation of both fixed wavelength and tuneable quantum cascades laser (QCL) sources in order make single particle measurements feasible. However, another challenge remains for signal detection since even with a laser source, the measurement of extinction of an aerosol particle includes both elastic scattering and absorption with the former typically comparable to (or greater than) the latter in magnitude. To overcome this obstacle, we collect elastically scattered light spectral intensities, and relate the material dispersion in the real part of the refractive index to the imaginary part via the Kramers-Kronig relationship. Details of this method will be described, as well as our latest results for single particle compositional change over time.

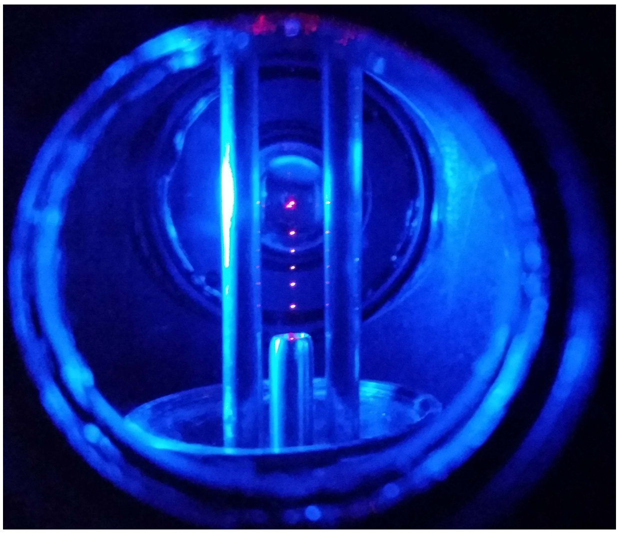

Figure 1. This is a photograph of 5 μm polymer spheres confined in an LEQ. Two of the four vertical electrode rods are visible.

Raman scattering measurements are performed on trapped particles of both neat and mixed composition, and can be compared and contrasted with IR absorption spectral measurements. The use of spontaneous Raman for environmental sampling is hampered by the low scattering cross-section, requiring long signal integration times. We are exploring a technique in which an enhanced signal may be obtained by presence of metallic nano-particles (MNPs) on the surface of, or inside, the aerosol particles (Sivaprakasam *et al* 2014), similar to surface enhanced Raman scattering (SERS). Spontaneous Raman spectra and MNP-enhanced Raman spectra will be measured on identical aerosol particless under controlled conditions. The dependence and repeatability of Raman enhancement factors on spectral response, MNP composition and aerosol material will be discussed.

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