Valenzuela Gutierrez, A., Chu, F., Haddrell, A. E., Cotterell, M. I., Walker, J. S., Orr-Ewing, A. J., & Reid, J. P. (2020). Optical Interrogation of Single Levitated Droplets in a Linear Quadrupole Trap by Cavity Ring-Down Spectroscopy. *Journal of Physical Chemistry A*, 125, 394 - 405. <https://doi.org/10.1021/acs.jpca.0c09213>

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Link to published version (if available):
[10.1021/acs.jpca.0c09213](https://doi.org/10.1021/acs.jpca.0c09213)

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This is the author accepted manuscript (AAM). The final published version (version of record) is available online via the American Chemical Society at <https://doi.org/10.1021/acs.jpca.0c09213>. Please refer to any applicable terms of use of the publisher.

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Optical Interrogation of Single Levitated Droplets in a Linear Quadrupole Trap by Cavity Ring-Down Spectroscopy

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ABSTRACT: Optical trapping is a well-established technique to manipulate and levitate micro- and nanoscale particles and droplets. However, optical traps for single aerosol studies are most often limited to trapping spherical non-absorbing droplets and a universal optical trap for the stable confinement of particles regardless of their absorption strength and morphology is not established. Instead, new opportunities arise from levitating droplets using electrodynamic traps. Here, using a combined Electrodynamic Linear Quadrupole trap and a Cavity Ring-Down Spectrometer, we demonstrate that it is possible to trap single droplets and simultaneously

measure their extinction cross sections and elastic scattering phase functions over extended periods of time. To test the novel setup, we evaluated the evaporation of 1,2,6-hexanetriol under low humidity conditions, and the evolution of aqueous $(\text{NH}_4)_2\text{SO}_4$ and NaCl droplets experiencing changing environmental conditions. Our studies extended beyond spherical droplets and we measured particle extinction cross sections after the efflorescence (crystallisation) of the inorganic salt particles. Comparison of measured cross sections for crystallised particles with light scattering model predictions (using Mie theory or T-Matrix/Extended Boundary-Condition Method (EBCM) implementations for random orientation, with either the spheroid or superellipsoid parameterisations) enables information on particle shape to be inferred. Specifically, we find that cross sections for dry $(\text{NH}_4)_2\text{SO}_4$ particles are accounted by Mie theory and, thus, particle shape is represented well by a sphere. Conversely, the cross sections for dry NaCl particles are only reconciled with light scattering models pertaining to non-spherical shapes. These results will have implications for accurate remote sensing retrievals of dry salt optical properties and for parameterisations implemented in radiative forcing calculations with changing humidity. Moreover, our new platform for precise and accurate measurement of optical properties of micron-scale and sub-micron particles has potential applications in a range of areas of atmospheric science, such as precise light scattering measurements for ice crystals and mineral dusts. It represents a promising step towards accurate characterisations of the optical properties for non-spherical and light absorbing aerosols.

1. INTRODUCTION

The social and economic impacts of rises in global temperatures over recent decades have brought climate change into the worldwide spotlight. According to the 2013 Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC), atmospheric aerosols cause a net cooling effect on the Earth's climate. However, an accurate quantification of this cooling is challenging because of large uncertainties in the estimation of the aerosol radiative forcing (RF).¹ A significant component of this uncertainty in RF derives from current levels of understanding of aerosol optical properties.²⁻⁴

Information about aerosol properties, such as particle size, morphology, and refractive index, can be obtained from measurements of the interaction of light with an aerosol sample.⁵⁻⁸ The scattering and absorption of light by aerosol particles are quantified by the scattering cross section, σ_{scat} , and the absorption cross section, σ_{abs} , respectively. The sum of these two parameters defines the extinction cross section, σ_{ext} .⁹ The σ_{ext} is a function of characteristic parameters of the particle such as the radius, r , the complex refractive index, m , the particle morphology, as well as the wavelength of the incident light, λ . The value of m is the sum of a real component, n , which describes the phase velocity of light inside a medium and influences the scattering of light, and an imaginary component, k , which describes the attenuation of light (light absorption). Knowledge of m is crucial to determining σ_{scat} and σ_{abs} values for aerosol particles and the collective impact of the aerosol on radiative forcing.

Aerosol optical properties are influenced by water uptake. For example, the ambient relative humidity (RH) is critical to determining the phase and refractive index of sulfate aerosols.¹⁰ $(\text{NH}_4)_2\text{SO}_4$ particles become aqueous spherical droplets at an RH (~80%) above the

deliquescence RH (DRH).¹¹ Subsequently, if the RH decreases, the droplets lose water, diminish in size and eventually undergo crystallisation (efflorescence) at their efflorescence RH point (ERH, which is ~35 % for $(\text{NH}_4)_2\text{SO}_4$ particles).¹² As a drying atmosphere passes through the ERH, an efflorescing particle may become non-spherical. Importantly, the ERH and DRH values are different for inorganic solutes, giving rise to hysteresis in the particle size and composition with humidity variations.

Climate studies and radiative transfer models commonly account for the chemical composition and size of particles, but the deliquescence and efflorescence behaviours which affect particle shape and morphology are neglected.^{7,8} Previous papers have shown that the spherical particle approximation is an oversimplified representation of the properties of ambient particles, leading to increases in the uncertainty of aerosol modelling and radiative transfer calculations.^{5,13,14} Wang et al. reported that the aforementioned hysteresis for sulfate-containing aerosol gives rise to a significant uncertainty of 20% in the direct climate forcing.¹⁵

The effects of non-spherical particle shape on aerosol optical and physical properties have been addressed in numerous studies through either laboratory measurements or computational modelling.^{5,16–24} However, controversy persists about the effects of particle-shape irregularity on the aerosol properties owing to the complexity of retrieving realistic experimental data to validate the models. For example, while computational studies have demonstrated a strong dependence of the scattering phase function on particle shape,^{21,25} some laboratory studies have reported this dependence to be weak.¹⁸

Mie theory is often used to model aerosol optical properties, but is limited in its analysis of laboratory measurements or remote sensing data by the implicit treatment of particles as

spherical in shape. Instead, approaches using T-Matrix calculations for spheroid morphologies offer an improved treatment of irregularity on particle shape.^{26,27} Compared to Mie theory, Dubovik et al. demonstrated that the spheroid approach provides superior retrievals of aerosol optical properties (refractive index, phase functions and particle size distributions) from remote sensing measurements in regions where aerosol loadings are dominated by desert dust.²⁷

Aerosol ensemble cavity ring-down spectroscopy (E-CRDS) is a well-developed technique for high precision measurements of aerosol extinction.^{28–33} A typical E-CRDS measurement uses an ensemble of particles with a known (or independently characterised) size distribution and concentration. Measurements are made of the time constants for exponential decay of light from the TEM₀₀ mode of a high-finesse optical cavity when the cavity is empty (τ_0) and when it contains particles (τ). The difference in the reciprocals of these ring-down times is proportional to the product of the extinction cross section, σ_{ext} , and the number density of particles N :^{31,33}

$$\sigma_{ext}N = \frac{L}{cl} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (1)$$

Here, c is the speed of light in air and L and l are the length of the optical cavity and the length occupied by the aerosol sample, respectively. However, the uncertainties in the aerosol size distribution and particle number density lead to significant uncertainties in the retrieved optical properties, particularly for absorbing aerosol.^{34–36}

A step-change improvement in both the accuracy and precision in CRDS-measured extinction, and subsequent determinations of refractive index, is achieved through CRDS measurements on a single confined aerosol particle in combination with independent size analysis techniques, enabling high-accuracy measurements of the aerosol size and optical constants over extended

time periods.^{37,38} The introduction of electrodynamic techniques³⁹ followed later by optical levitation methods⁴⁰ facilitates the confinement, levitation and monitoring of single airborne particles in real-time with high-speed spectroscopic data acquisition. Bessel beam (BB) optical traps enable trapping of particles over extended working distances and the control of particle location over macroscopic length scales. Our previous work has exploited this property of BB optical traps to optimise the position of trapped aerosol particles at the centre of the TEM₀₀ mode of a cavity ring-down spectrometer. In this way, single particle CRDS has provided refined values of parameters such as n with precisions of ± 0.0007 for measurements at $\lambda = 532 \text{ nm}$ ^{37,38} and of ± 0.0012 for measurements at $\lambda = 405 \text{ nm}$.^{41,42}

A drawback of BB optical traps is that they are restricted in their application to spherical non-absorbing particles. The unstable confinement of non-spherical particles in common optical traps arises from the force imbalance arising from the different faces of a non-spherical particle having different associated radiative scattering forces. Nonetheless, Redding and Pan demonstrated that it is possible to employ a hollow beam to create a stable optical trap for absorbing and non-absorbing particles with either spherical or spatially irregular shapes.⁴³ Yet, in the case of a light-absorbing aerosol, such a universal optical trap will heat the confined particle and thus modify its chemical composition and optical properties if particles contain internally mixed semi-volatile components. Moreover, optical traps can induce photobleaching of the light absorbing chromophores that are of direct interest to spectroscopic interrogations.⁴⁴ Therefore, the chemical and morphological complexity of aerosol particles in the atmosphere demands new analytical and experimental approaches capable of improving our understanding of the chemical and physical processes affecting aerosol composition that current single-particle optical trapping methods do not provide.

One opportunity arises from the manipulation of individual charged airborne particles by electric fields. Numerous studies have levitated single droplets using electrodynamic forces to evaluate different properties including hygroscopic growth and optical response.^{45–48} A few studies have even reported the retrieval of optical information during the transition of levitated droplets from spherical to non-spherical shapes.^{49–52} For spherical particles, particle information such as size and refractive index can be determined by fitting the dark and bright fringes in angularly resolved distributions of elastic light scattering intensity (phase functions) to an optical model (such as Mie theory). However, as efflorescence occurs, these typical dark and bright fringes disappear and the phase functions become incoherent; hence, phase function images offer only limited information on effloresced particles. Therefore, while ensemble measurements of extinction cross-sections for aqueous droplets and dry particles have been reported,^{30,32,36,53,54} continuous measurements of the changes in optical cross-section that occur on a phase transition from a solution droplet to a crystalline particle have not previously been performed for a single particle. Indeed, calculations of the optical cross-sections of realistic non-spherical crystalline scatterers are only now becoming available.²² Measurements with sufficient accuracy to test these calculations are thus required.

Recently, a linear electrodynamic quadrupole trap was used to manipulate particles,⁵⁵ providing rapid characterization of a wide range of aerosol particle properties and offering a new platform for aerosol optical-diagnostic measurements. Building on this recent development, we present a new experimental approach for the measurement of physical and optical properties of single aerosol particles in which an Electrodynamic Linear Quadrupole (ELQ) trap is coupled to a Cavity Ring-Down Spectrometer to determine the extinction cross sections, particle sizes and refractive indices of spatially confined particles under changing environmental conditions.

2. EXPERIMENTAL SETUP

2.1 Electrodynamic Linear Quadrupole Trap: Levitation of Particles

A new ELQ trap has been implemented to confine and levitate single, as well as multiple, aerosol particles across a range of particle sizes, with its performance demonstrated here for particles with diameters from 2 to 5 μm . The quadrupole confines particles using four parallel cylindrical electrodes spaced symmetrically to form a square pattern. Details of the fundamental principles of this methodology can be found elsewhere.^{55,56} The radius, r_e of the electrode rods is 3 mm and they are of length 15 cm, with a distance r_0 between the centre axis of the quadrupole and the individual rods of 3.2 mm; a schematic 3D-view is shown in Figure 1. The inset in Figure 1 indicates the Cartesian coordinate system (x , y and z) we use to describe the position of trapped particles with respect to the centre of the ELQ trap. Pairs of diametrically opposed cylindrical rods are connected to an AC voltage with amplitude of ~ 1 kV and frequency of ~ 1 kHz, with the AC voltages applied to each electrode pair differing in phase by 180° .

The variable electric field established by the voltage of 300 - 1000 V applied to the four electrodes at a frequency (Ω) of 400 - 1000 Hz confines particles along a vertical central axis. Control over the vertical position of particles inside the ELQ is achieved when the droplet weight and drag force (from a constant 50 sccm flow of humidified nitrogen) are balanced by the electrostatic force from a bottom electrode held at a selected DC potential. Particles are injected into the ELQ by applying a square voltage pulse (or sequence of pulses) to a droplet-on-demand micro-dispenser with a 30 μm orifice diameter (Microfab MJ-ABP-01). Droplets of opposite polarity to the voltage applied to an induction electrode (with voltage ranging from 50 to 600 V), placed between the droplet dispenser and the trap, are attracted and injected into the ELQ. Once

inside the ELQ, the motion and location of a particle are controlled by the electric fields. Two apertures in the side walls of the trapping cell allow passage of the optical cavity mode used for CRDS through the centre of the ELQ. An aperture at the base of the trapping cell allows access of a vertically propagating Gaussian laser beam of $\lambda = 532$ nm which illuminates the droplet for angularly resolved elastic scattering measurements of the droplet size. The relative humidity (RH) inside the ELQ is monitored using a capacitance probe.

The electric field $E_0(x,y)$ arising from the geometry of our ELQ was simulated using QuickField software (<https://quickfield.com>). The effective potential can be written as:⁵⁷

$$\Psi(x, y) = \frac{Q \times |E_0(x,y)|^2}{4m \Omega^2} \quad (2)$$

where Q and m are the charge and mass of the particle, respectively, and x and y are the particle's position in the radial direction averaged over one period $T = (2\pi/\Omega)$. A contour map of the square of the electric field is shown in Figure 2. The extrema on the x and y axes correspond to the rod centres. The arrows labelled by $\hat{v}$ and $\hat{u}$ indicate the radial electrical field gradients in directions towards the centre and between the electrode rods, respectively. The force generated from this effective potential causes harmonic motion of the particle characterized by the radial frequency ω_r , superimposed on a faster motion on a micrometre length scale due to the frequency Ω of the time-varying AC field. Additional information about the electrical field inside the ELQ can be found in Supporting Information (SI).

2.2 CRDS Measurements

We have previously demonstrated that the combination of a cavity ring-down spectrometer with a Bessel beam optical trapping method allows refined measurements of aerosol optical properties

at multiple wavelengths and over a wide range of RHs.^{42,58} By confining a single particle over an extended period, during which the particle size and composition evolve, the continuous variation of the extinction cross-sections can be measured. Here, individual particles are instead captured within the ELQ trap. We use a coordinate system X, Y, Z to describe the location of the particle within the CRD cavity, with X and Z orthogonal to the cavity mode axis Y . The vertical position of the particle (along the Z axis) is controlled by careful variation of the magnitudes of the bottom variable electrostatic (DC) potential of the ELQ trap, balancing the aerodynamic drag and gravitational forces acting on the particle. This feature is exploited to optimize the position of the particle at the centre of the optical cavity TEM_{00} mode excited by a $\lambda = 405$ nm laser (Power Technology Inc., IQ Series 36 mW) to retrieve accurate measurements of the extinction cross-section. A continuous wave $\lambda = 532$ nm laser passes through the centre of the bottom DC electrode and propagates vertically upwards collinearly to the centre axis of the ELQ trap to irradiate the trapped particle. Green ($\lambda = 532$ nm) light, elastically scattered by the particle, is collimated by a long working distance (numerical aperture $NA = 0.42$) objective and the perpendicular (s) polarisation is focussed onto a CMOS camera (Thorlabs DCC1645C). The collected image is the phase function describing the elastically scattered light over the angular range $\sim 69 - 111^\circ$. An example of a phase function image is shown in Figure 3. For spherical particles, these images are fit to Mie scattering theory during post-processing and the particle size and refractive index at $\lambda = 532$ nm are retrieved.^{31,59}

In addition to providing information about the particle microphysical properties, the location of the phase function in collected images informs us of the particle position. The vertical position of the particle is maintained at a fixed point within the centre of the TEM_{00} cavity mode by continuous adjustment of the DC voltage applied to the bottom electrode, with the DC voltage

regulated by computer-controlled feedback in combination with the positional information from the phase function images. The constant location of the evolving particle at the centre of the cavity TEM₀₀ mode provides continuous measurements of σ_{ext} . Meanwhile, the ELQ trap is mounted on a two-axis translation stage that allows fine adjustment of the particle's lateral trapping location in the remaining transverse (X) direction with respect to the CRDS optical axis. The experimental apparatus for 405-nm CRDS has been described elsewhere.⁴¹ The new instrument implementing CRDS in combination with the ELQ trap is summarised in Figure 3, in which the TEM₀₀ cavity mode and the levitated particle are shown schematically. The extinction cross section, σ_{ext} , is determined from ring-down times recorded without and with a particle positioned centrally in the TEM₀₀ cavity mode (τ_0 and τ respectively):⁶⁰

$$\sigma_{ext} = \frac{\pi L}{2c} w_0^2 \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (3)$$

where w_0 is the beam waist of the intra-cavity beam at the longitudinal (Y) position of the particle, c is the speed of light and L is the distance between the two highly reflective mirrors forming the high finesse optical cavity. A detailed explanation of the CRDS technique and analysis as applied to single particle measurements can be found in previous papers.^{38,41,42,61,62}

3. RESULTS

3.1 Particle Size and Refractive Index Retrievals from Angularly Scattered Light

A phase function pattern of bright and dark interference fringes is recorded as described in Sect. 2. The particle radius and real refractive index component n of the droplet are determined from the PFs by comparing to a computed library of Mie-theory simulated PFs over a defined radius range for a constant value of n at $\lambda = 532$ nm. Experimental PFs were recorded each second and

compared to simulated PFs during post-processing of recorded data. A Pearson correlation coefficient, C , was calculated to quantify the agreement between each phase function in the simulation library and a measured phase function. The highest C defined the radius of the particle for a given value of n . Once all the measured PFs were compared to those in the simulation library, the mean Pearson correlation coefficient $\bar{C}$ was calculated for the value of n input initially to the simulation library; $\bar{C} = 1$ indicates perfect agreement and lower values indicate a lower level of agreement. Then, n was iterated to a new value within a search range and the corresponding value of $\bar{C}$ calculated. The maximum in $\bar{C}$ over the refractive index search range defined the best fit value for n , and the corresponding values for $\bar{C}$ defined the final best fit radii. This fitting procedure was employed in previous publications.^{41,42} An example of the agreement between theory and experiment is shown in Figure 4 for a 1,2,6-hexanetriol droplet of radius 1778 nm.

Figure 5 illustrates the time-dependent trends in the radii for four different 1,2,6-hexanetriol droplets. 1,2,6-hexanetriol has a low hygroscopicity and absorbs little water, thus we assume a trapped droplet retains a well-defined composition. Moreover, we evaporated these individual droplets in a dry nitrogen gas flow and the RH was less than 10% as determined by a capacitance RH probe (Honeywell). The largest droplet is initially trapped at a radius of 2132 nm and evaporates to a size of 1567 nm. The smallest droplet is initially trapped at a radius of 1439 nm and evaporates to a radius of 1155 nm. The initial size of a droplet depends on the concentration of 1,2,6-hexanetriol in the aqueous solution loaded into the droplet-on-demand micro-dispenser.⁶³ Differences in the initial size between four droplets could be due to several reasons: droplets were studied on different days and were exposed to gas flows that might have differed, leading to differences in evaporation rates. Moreover, the temperatures at which experiments

were performed were not controlled and the temperature of the droplet will depend on the room temperature; these potential variabilities in droplet temperature would cause differences in evaporation rates. Also, small concentrations of impurities, and the time lag between droplet trapping and the beginning of data acquisition (owing to the requirement to optimise the particle position within the TEM₀₀ cavity mode) might cause differences in initial sizes.

We adopt the same fitting procedures used in our earlier work to retrieve the refractive index of the trapped droplet from the angular light scattering profiles.^{41,42} The fitting procedure yields an average value of n for these four droplets of 1.484 ± 0.003 at $\lambda = 532$ nm, with the stated uncertainty representing one standard deviation in the mean n . This value agrees within the mutual uncertainties with those reported by Mason et al. of 1.482 ± 0.001 and Cotterell et al. of 1.477 ± 0.004 for the same droplet composition.^{58,41} From the observed evaporation rates, the vapor pressure can be estimated and the average value for the four droplets is $(3.8 \pm 0.9) \times 10^{-4}$ Pa. This value is within the range of values established by Cai et al.⁶⁴ It also compares favourably to $(4.4 \pm 0.7) \times 10^{-4}$ Pa retrieved by Walker et al.⁶² Therefore, we have demonstrated the stable trapping of microdroplets over long times in the ELQ trap and the use of precise elastic scattering retrievals to estimate droplet size. These are essential steps in the validation of the new instrument and the results of these test measurements are comparable to those obtained with established optical trapping methodologies.

3.2 Variations in the Extinction Cross-Sections of Evaporating 1,2,6-Hexanetriol Droplets

1,2,6-hexanetriol droplets were also chosen to test and validate the use of single-particle CRDS in combination with the new trap. The particle radius, the V_{DC} of the bottom electrode, and the

evolution of the ring-down time τ during free evaporation of 1,2,6-hexanetriol over time are plotted in Figures 6a and b for a representative droplet. This analysis corresponds to the droplet labeled as 1 in Figure 5. The radius of the droplet is calculated from fitting the PFs, as described in the previous section. These measurements demonstrate the capabilities of the combined optical and electrostatic approach to determine particle size and ring-down time measurements. The proportionate scaling of the particle radius with V_{DC} suggests that electrostatic and Stokes drag forces are much larger than the particle weight; the electrostatic force is countered only by the Stokes drag (that scales linearly with particle radius) and the particle weight (which scales with particle volume). The τ_0 value is measured at the beginning and end of the experiment, and no drift in its value is observed. PFs are recorded and the droplet radius is retrieved with a 1 s time resolution. The ring-down time is recorded at ~ 10 Hz. Cotterell et al. established a mean beam waist of $(264.4 \pm 4.4) \mu\text{m}$ at the cavity resonator centre for the TEM_{00} mode at a probe $\lambda = 405 \text{ nm}$.⁴¹ According to Mason et al., τ is relatively insensitive to small excursions ($\pm 20 \mu\text{m}$) in particle position from the CRD beam centre because of the Gaussian profile of the TEM_{00} mode.³⁷ However, larger excursions in position (e.g. $\pm 100 \mu\text{m}$) can lead to significant changes in measured τ values. Although the droplet in the ELQ trap may plausibly undergo symmetric harmonic motion at a frequency ω_r over radial distances up to $\pm 0.5 \text{ mm}$, no significant deviations are observed in the ring-down time measurements suggesting the stability in position is considerably better than this. Nevertheless, this oscillatory motion is much greater than the wavelength of the 405-nm probe radiation, so the particle samples nodes and antinodes, and all phases in-between, of the standing wave associated with the cavity TEM_{00} mode. This particle motion is evident from the observed envelopes in the CRD time-constants, which are consistent

with our previous work using an optical trap, and with motion of the particle across the standing wave structure.^{58,65}

Figures 7a and b show σ_{ext} values inferred from CRDS measurements at $\lambda = 405$ nm as the particle radius varies, with the values of the radius determined from the experimental PF fitting. We include on these Figures the best-fits of the Cavity Standing Wave Generalised Lorenz-Mie Theory (CSW-GLMT) simulations of σ_{ext} for the particle placed at a node and anti-node of the standing wave of the intra-cavity ring-down beam (see Supporting Information of Cotterell et al.³⁸). These points represent the limiting cases for optical cross-section recorded from a particle in a standing wave.⁶⁵ The values of n at 405 nm and of the beam waist w_0 are varied during the fitting procedure, and a small particle radius offset can also be varied. A detailed explanation of the fitting procedure is given by Cotterell et al.⁴¹ Briefly, the parameters n and w_0 are varied using a grid search algorithm to maximise the number of measured σ_{ext} data points within the predicted cross-section envelope formed by the limiting cases of node and anti-node centred standing wave illumination.

The measured σ_{ext} values agree well with the CSW-GLMT simulations and there is a good description of the underlying contour of the data. Quantitative comparison of the measurement and simulations is evaluated using the computed residual corresponding to data lying outside the envelope of CSW-GLMT predictions, and this residual is plotted in terms of n at $\lambda = 405$ nm and w_0 values used in the CSW-GLMT simulations. A best fit corresponds to a minimum in this residual value. Figure 7c shows the corresponding 2D contour plot of residuals when n and w_0 vary, in which a minimum can be seen. A systematic radius offset was also allowed to vary during these fits (although we do not show the associated variations in the fit residual here) to

provide a correction for any systematic error in the radius determination from measured PFs (e.g. from systematic uncertainties in the angular range), with a best fit value of 3.4 nm. The optimized values of n and w_0 are 1.497 ± 0.006 and $271 \pm 3 \text{ } \mu\text{m}$, respectively, with the uncertainties determined using the same analysis methods described in our previous publications.

We determined w_0 and n at $\lambda = 405 \text{ nm}$ from the four experiments for which the radius evolutions are plotted in Figure 4, and the mean values are $(270 \pm 6) \text{ } \mu\text{m}$ and 1.492 ± 0.007 , respectively. This latter value for n at $\lambda = 405 \text{ nm}$ agrees with the previously reported value of 1.4906 ± 0.0012 for 1,2,6-hexanetriol within measurement uncertainty.⁴¹

3.3 CRDS Extinction Measurements for Efflorescing Aqueous Droplets Containing Inorganic Salts

Using our novel ELQ-CRDS setup, we demonstrate that it is now possible to measure the optical cross-section of a particle both prior to and after it has effloresced. Such measurements will enable us to explore optical cross sections with variability in particle morphology and refractive index under dry conditions. To the best of our knowledge, the current analysis represents the first single particle measurements of optical constants measured both at an RH higher than the ERH and under dry conditions once a particle has crystallised.

In the previous section, we analysed phase function and τ data for the single-component evaporation of 1,2,6-hexanetriol droplets with compositions that do not change over time. Now, we consider the analysis of the PF and τ data for particles containing the hygroscopic solutes NaCl or $(\text{NH}_4)_2\text{SO}_4$ as the ambient RH is varied. Both the particle size and the refractive index change with variation in RH; here, the PFs and RDTs from which these properties are deduced

are collected as the RH reduces steadily over time. The PF fitting strategy used to determine both radius and n values as the ambient conditions change is described by Cotterell et al.⁴¹

3.3.1 The Efflorescence of an $(\text{NH}_4)_2\text{SO}_4$ Droplet

An $(\text{NH}_4)_2\text{SO}_4$ droplet is initially trapped at ~65% RH; the ambient RH is subsequently lowered to ~38%, at which point the droplet crystallizes. Coherent bright and dark fringes are observed at high RH while the particle is spherical. However, after the droplet has crystallised, the PF fringes become incoherent. Figure 8a shows the measured radius and the retrieved value of n at $\lambda = 532$ nm with RH which is continuously reduced until efflorescence occurs. Over this measurement period, radius determination from the PFs is reliable, with the droplet evaporating from a radius of ~2451 to 2223 nm. The jumps in both curves are due to noise in the experimental PFs. Simultaneous ring-down time determinations are also reported in Figure 8b.

As the RH reduces and the ERH is passed, it is not possible to determine radius and n values from PF fitting because of the incoherence of the fringes. However, continuous τ measurements, even after the droplet has effloresced, can be made because the particle remains tightly confined by the ELQ trap. Figure 8b shows the τ envelope accompanied by the variation in the RH over time. As the droplet effloresces, it loses mass and volume which is immediately reflected in a substantial change in τ . After efflorescence, the droplet remains trapped and τ measurements remain constant, which indicates no further size change of the particle with continued reductions in the RH. We have evaluated the trapping method through and beyond efflorescence with multiple individual $(\text{NH}_4)_2\text{SO}_4$ droplets and these measurements exhibit consistent and reproducible trends (Figure S2, *SI*) in the extinction cross section with size and phase, with the cross section always invariant for the effloresced particle upon further reductions in RH.

Figure 9a shows the CRDS-measured σ_{ext} values (red dots) as a function of RH. This plot also includes σ_{ext} values (grey dots) when the particle effloresces, as calculated from Equation 3. Using the thermodynamic E-AIM model (<http://www.aim.env.uea.ac.uk/aim/aim.php>) and the change of droplet radius as a function of RH inferred from the PFs for the aqueous droplet, we estimated a dry radius of 1893 ± 15 nm for the $(\text{NH}_4)_2\text{SO}_4$ droplet assuming that it is spherical. For this salt, Cotterell et al. established a mean value for n of 1.549 with a range of uncertainty of 1.51 – 1.58.³⁶ A mean value of n of 1.54 and the estimated dry radius are used to model the σ_{ext} value (black dot) with CSW-GLMT predictions. The error bar in Figure 9a spans the extremes of σ_{ext} values for the range of uncertainty of n and also accounts for the distribution in σ_{ext} expected from the impact of the intra-cavity standing wave.

Comparison of the simulated and experimental σ_{ext} values for the dry droplet shows distinct differences. Whereas the simulated value for $n = 1.54$ falls within the measured range of σ_{ext} values, many of the CRDS-measured σ_{ext} values lie outside the range predicted for a spherical particle with values of the refractive index n between 1.51 and 1.58. These discrepancies could be explained either by an inaccurate dry radius estimation by the E-AIM model, particularly given the $\pm 5\%$ standard error in our RH probe measurement, or because the particle is not spherical after efflorescence and has a shape that is not reflected by a Mie scattering calculation. To test the second proposition, we applied a T-Matrix/Extended Boundary-Condition Method (EBCM) for random orientation spheroids to model σ_{ext} values at $\lambda = 405$ nm for an equivalent dry radius of 1893 nm and varying aspect ratios.⁶⁶ The shape of a spheroidal particle can be specified by its aspect ratio (the ratio of the largest to the smallest axes), whereas the volume of the particle can be specified by an equivalent-sphere radius, r_{eq} , for which we use the dry equivalent radius specified above (1893 nm). A mean value of $n = 1.54$ at 405 nm was used for

pure $(\text{NH}_4)_2\text{SO}_4$. The extinction cross section was also evaluated for the extreme values of n (1.51-1.58).

Figure 9b shows the dependence of predicted σ_{ext} values on the spheroid particle aspect ratio. These predictions are compared to the experimental σ_{ext} mean values (dash black line) and shaded area (experimental full range of σ_{ext} values) from CRDS measurements when the droplet has effloresced. The figure also shows the Mie theory predicted cross section (calculated using MiePlot) for the dry spherical radius inferred from the E-AIM model, with the associated error bars indicating the range of σ_{ext} predicted given the uncertainty in n over the range 1.51 – 1.58. For the CRDS mean σ_{ext} value of $2.29 \times 10^{-11} \text{ m}^2$, the coincident modelled σ_{ext} values occur in the aspect ratio range from 1.02 to 1.11, assuming a spheroidal shape.

Now, we consider the development from spheroid to superellipsoid particle shapes to improve the modelling of non-spherical particles. The advantage of the superellipsoidal model is that it can describe flexibly a wide range of shapes. The superellipsoidal equation is:^{67,68}

$$\left[\left(\frac{x'}{a} \right)^{2/e} + \left(\frac{y'}{b} \right)^{2/e} \right]^{e/l} + \left[\frac{z'}{c} \right]^{2/l} = 1 \quad (3)$$

in which a , b , and c are the three semiaxes of a superellipsoid particle along the particle-centred x' , y' , and z' directions in a Cartesian coordinate system. In this equation, e and l are roundness parameters, which determine the morphological variation of the particle with fixed aspect ratios (a/c and b/c). For simplicity, we only consider superellipsoids with one aspect ratio ($a = b = c$) and varying roundness parameters, with the constraint of $e = l$. Even superellipsoid particles with a unity aspect ratio can be irregular in shape.^{19,69} When the aspect ratio is equal to unity, Figure 10 shows that $l = e = 1$ corresponds to a sphere, while the particle shape becomes octahedral for l

$= e > 1$ and cubic like for $l = e < 1$. Figure 9c shows the dependence of predicted σ_{ext} values on the roundness parameter for an aspect ratio of unity. Clearly, the extinction cross section does not exhibit a clear trend with roundness parameter. The highly non-linear variation of σ_{ext} with roundness parameter, the additional impact of aspect ratio, and the wide distribution of measured σ_{ext} arising from measurement scatter and the effects of standing wave illumination, prevent additional information on particle shape being deduced from the superellipsoid model.

Although the aspect ratios from our comparisons with the spheroid model indicate a constrained range of 1.02 – 1.11, suggesting $(\text{NH}_4)_2\text{SO}_4$ aerosols adopt a non-spherical shape (as also evidenced by the incoherence in the recorded phase functions), they remain close to unity. Uncertainty in the exact value derives from the variance in the measured and predicted cross sections introduced by the effects of the intra-cavity standing wave, and uncertainties in the dry particle size and refractive index. Similarly, Radney and Zangmeister determined that $(\text{NH}_4)_2\text{SO}_4$ aerosols adopt near-spherical morphologies as indicated by the authors' measurements of particle mass-mobility relationships.⁷⁰

3.3.2 The Efflorescence of a NaCl Droplet

NaCl is another important salt which plays a significant role in both atmospheric chemical processing and radiative transfer.^{22,71} As far as we know, only a few studies have modelled light scattering from the irregular geometry expected for dry NaCl, using superellipsoid equations that include ellipsoids, cylinder-like, cube-like and octahedron-like shapes.²² These simulations now require experimental verification. In this section, we present the first report of optical constants for an NaCl particle both when aqueous and after crystallization induced by reduction in the ambient RH. We performed single particle CRDS measurements on a NaCl particle. For this

particle, the radius was determined from measured phase functions to decrease from 2192 nm to 2088 nm as the RH was reduced from 56%. The droplet effloresced at 49% RH.

Figure 11a shows the changes over time in CRDS-measured σ_{ext} (red dots) for the aqueous NaCl droplet held in a continuously decreasing RH environment. σ_{ext} values (grey dots) for the dry droplet are also included in the plot. A larger jump in the σ_{ext} values is observed as efflorescence occurs for NaCl in comparison to the $(\text{NH}_4)_2\text{SO}_4$ droplet discussed in Section 3.3.1. Moreover, this larger relative change in σ_{ext} upon efflorescence for NaCl compared to that for $(\text{NH}_4)_2\text{SO}_4$ is repeatable from multiple measurements, as evidenced in the Supporting Information. As described above, $(\text{NH}_4)_2\text{SO}_4$ particles are thought to adopt a near-spherical shape as they effloresce, whereas effloresced NaCl particles should adopt a cubic shape. Again, the thermodynamic E-AIM model was used to estimate the dry radius for NaCl, providing a value of 1430 ± 21 nm. Bi et al. used in their simulation a value of n of 1.50 for dry NaCl.²² However, other studies assume a value of 1.54 for the dry NaCl salt.⁷² Here, we consider n over the range 1.50 – 1.54 to model the σ_{ext} values (Figure 11a, error bars) with CSW-GLMT, accounting for the addition range in measured cross sections arising from the intra-cavity standing wave. Substantial differences are found between σ_{ext} values from CRDS measurements and those simulated by Mie theory for dry, hypothetically spherical NaCl particles. Lower σ_{ext} values are deduced from the CRDS measurements and relate to the irregular shape of the dry particles.

Again, as a first step in the analysis we use the spheroid T-Matrix model to calculate σ_{ext} values as function of the aspect ratio (Figure 11b). This figure shows that the spheroid model predicts that particles with aspect ratios between 1.2 and 1.4 give σ_{ext} values consistent with the mean values from CRDS measurements. Further, we increased the complexity in particle shape in our

T-Matrix model by using the superellipsoid model (Figure 11c). However, the scatter in the measurements and the number of degrees of freedom in the superellipsoid model prevent us from making any further determination of particle shape with the current data. Nevertheless, we can conclude that the dry NaCl particle is non-spherical.

4. CONCLUSIONS

We have demonstrated the stable trapping and the optical interrogation of 1,2,6-hexanetriol, $(\text{NH}_4)_2\text{SO}_4$ and NaCl droplets employing an electrodynamic linear quadrupole trap centred in a cavity ring-down spectrometer. The measured particle sizes and refractive indices of spherical droplets reproduce those previously achieved with optical traps, but we have advanced these studies further by interrogating particle optical properties after efflorescence at reduced relative humidity, allowing us to measure the optical extinctions of the solid particles and infer their shapes. The effloresced $(\text{NH}_4)_2\text{SO}_4$ particles are well approximated by a sphere (with an aspect ratio within the range 1.02 – 1.11). Although Mie theory offers a reasonable prediction of extinction cross sections, improvements can be made with a T-Matrix spheroid model, but extension to a superellipsoid model leaves the roundness parameter poorly constrained. However, for an effloresced NaCl particle, Mie theory is inadequate, overestimating the experimental extinction cross section by 43%, and a spheroid model treatment indicates an aspect ratio larger than unity. The data are not yet sufficiently rich to draw further conclusions about the particle shape from application of a superellipsoid model. Nonetheless, we conclude that the NaCl particle is non-spherical, in agreement with the consensus built up by other studies on super-micrometre and sub-micrometre sized particles.^{73–76} These results have important implications for accurate remote sensing retrievals of dry salt optical properties in the

atmosphere and for calculation of radiative forcing parameters in environments of changing humidity.

This new platform, with particle confinement in an ELQ trap, opens a wide range of research possibilities, including optical measurements on non-spherical aerosols such as mineral dusts and ice crystals, and light absorbing aerosols that are challenging to isolate in common optical traps.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at:

- Electrodynamic Linear Quadrupole Field (PDF)
- Efflorescence events for $(\text{NH}_4)_2\text{SO}_4$ and NaCl droplets (PDF)

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Notes

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ACKNOWLEDGMENTS

Antonio Valenzuela acknowledges financial support from the European Union Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 754446 and UGR Research and Knowledge Transfer Fund – Athenea3i. Michael I. Cotterell acknowledges support through a Natural Environmental Research Council Independent Research Fellowship (NE/S014314/1). The authors thank Prof Lei Bi of the Department of Atmospheric Sciences (Zhejiang University) for provision of superellipsoid data.

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FIGURES CAPTIONS

Figure 1. A schematic 3D view of the ELQ trap setup. The inset shows a front view of the ELQ with the Cartesian coordinate axes indicated. Note that the dimensions in this figure are not to scale, and the separation between the high reflectivity mirrors is much greater than this schematic implies.

Figure 2. Electrical field simulation within the ELQ with a 1 kV AC potential applied on the electrode rods, shown as a contour plot of $|E|^2$ in the x - y plane. The arrows labelled by $\hat{v}$ and $\hat{v}$ indicate radial electrical field gradients pointing towards the centre and between the electrode rods, respectively.

Figure 3. Schematic diagram of the apparatus used to perform CRDS on single aerosol particles in an ELQ trap. AOM is an acousto-optic modulator and piezo represents a piezoelectric ring actuator. An example is shown of a phase function image obtained by particle illumination with a laser beam of $\lambda = 532$ nm from the bottom of the ELQ.

Figure 4. The comparison of a modelled and measured phase functions for a levitated 1,2,6-hexanetriol droplet with a radius of 1778 nm.

Figure 5. Change in measured radius over time for four evaporating 1,2,6-hexanetriol droplets.

Figure 6. Evaporation of a 1,2,6-hexanetriol droplet, shown by change in a) radius and V_{DC} for the bottom electrode of the ELQ, and b) simultaneous ring-down time measurements.

Figure 7. a) and b) Measured extinction cross sections for an evaporating 1,2,6-hexanetriol droplet with change in particle radius. Simulations are shown assuming travelling wave

illumination (Mie theory, labeled ‘Sim σ_{ext} ’), and for a particle located in a node (‘Sim σ_{ext} ($kz_0 = 0$)’) or anti-node (‘Sim σ_{ext} ($kz_0 = \pi/2$)’) of the intra-cavity standing wave. c) A contour plot of the dependence of the fit residuals on values of two fit parameters, the refractive index n at $\lambda = 405$ nm and the CRDS beam waist w_0 . The colour scale indicates the value of the residual function used to define the goodness of fit (see Cotterell et al.⁴¹).

Figure 8. Evaporation and efflorescence of an aqueous $(\text{NH}_4)_2\text{SO}_4$ droplet held in an environment of decreasing RH. a) Changing radius (black dots) and derived n (red dots) values from PF fitting as function of RH; b) the ring-down time variation with RH for the aqueous droplet and for a solid particle after efflorescence. Note that the RH increases with increasing time.

Figure 9. Extinction cross sections for an initially aqueous $(\text{NH}_4)_2\text{SO}_4$ droplet in a drying environment. a) Experimental σ_{ext} values at $\lambda = 405$ nm for an aqueous droplet (red dots) and the effloresced particle (grey dots). The black star is a predicted σ_{ext} value obtained from Mie theory for the spherical dry radius estimated from the E-AIM model (see text) with the error bar reflecting the possible range of refractive index values and also including the effect of the standing wave on the measured distribution using CSW-GLMT. b) Variation of σ_{ext} with aspect ratio modelled with T-Matrix methods for a spheroid. This plot includes the experimental σ_{ext} mean values (black line), and the shaded area spans the full range of CRDS-measured σ_{ext} values for the dry particle, c) Superellipsoid T-Matrix of the dependence of σ_{ext} on the roundness parameter (constrained with $e = l$).

Figure 10. The geometries of superellipsoid particles for aspect ratio equal to unity and different roundness parameters ($l = e$).

Figure 11. Evaporation for an aqueous NaCl droplet in drying environment. a) CRDS-measured σ_{ext} values at $\lambda = 405$ nm from CRDS measurements for the aqueous droplet (red dots) and dry particle (grey dots). The star is a Mie theory prediction of σ_{ext} for a hypothetically spherical solid particle, and the associated error bars indicate the range of σ_{ext} predicted given the uncertainty in n over the range 1.50 – 1.54 for the spherical dry radius estimated from the E-AIM model (see text) and also including the effect of the standing wave on the measured distribution using CSW-GLMT. b) Variation of σ_{ext} with aspect ratio modelled with T-Matrix methods for a spheroid particle. This plot includes the experimental σ_{ext} mean value (dash black line), and the shaded area spans the full range of CRDS-measured σ_{ext} values for the dry particle. Mie theory predictions (star, and error range) are included as described for panel a). c) Variation of σ_{ext} with roundness parameter modelled with the T-Matrix method for superellipsoids. Other contents are as for panel b).

FIGURES

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Figure 11

TOC Graphic