Department of chemistry

Photoinitiated Chemistry in Single Levitated Aerosol Droplets using Cavity Ring-Down Spectroscopy

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Introduction

This project investigates the photobleaching kinetics of individual aerosol particles in the size range of 1-10 µm using a linear electrodynamic quadruple (LEQ) trap combined with cavity ring-down spectroscopy (CRDS), where the effects of particle size, viscosity, chemical composition and wavelength of illumination will be explored.

Background

Brown carbon:

- Atmospheric brown carbon (BrC) is a collective term for light absorbing organic compounds in the atmosphere.
- The light absorption by BrC is weak at long visible wavelengths but is strong at shorter visible wavelengths, giving BrC its characteristic brown appearance.
- BrC is produced in various ways, including direct emissions from biomass burning, anthropogenic emissions, and secondary oxidation reactions in the atmosphere.

Interaction of aerosols with light :

- extinction cross section (σ_{ext}): quantifies how much power is removed from the incident light.
- σ_{ext} is a combination of the scattering cross sections (σ_{sca}) and absorption cross sections (σ_{abs}).
- The extinction cross section can be measured by many spectroscopic techniques, e.g. cavity ring-down spectroscopy (CRDS) .

Single particle cavity ring-down spectroscopy:

- Able to complete a sequential (continuous) measurement on particles with changing size.
- By comparing with the Lorentz-Miens theory, the refractive index of the particles and chemical composition can be determined.

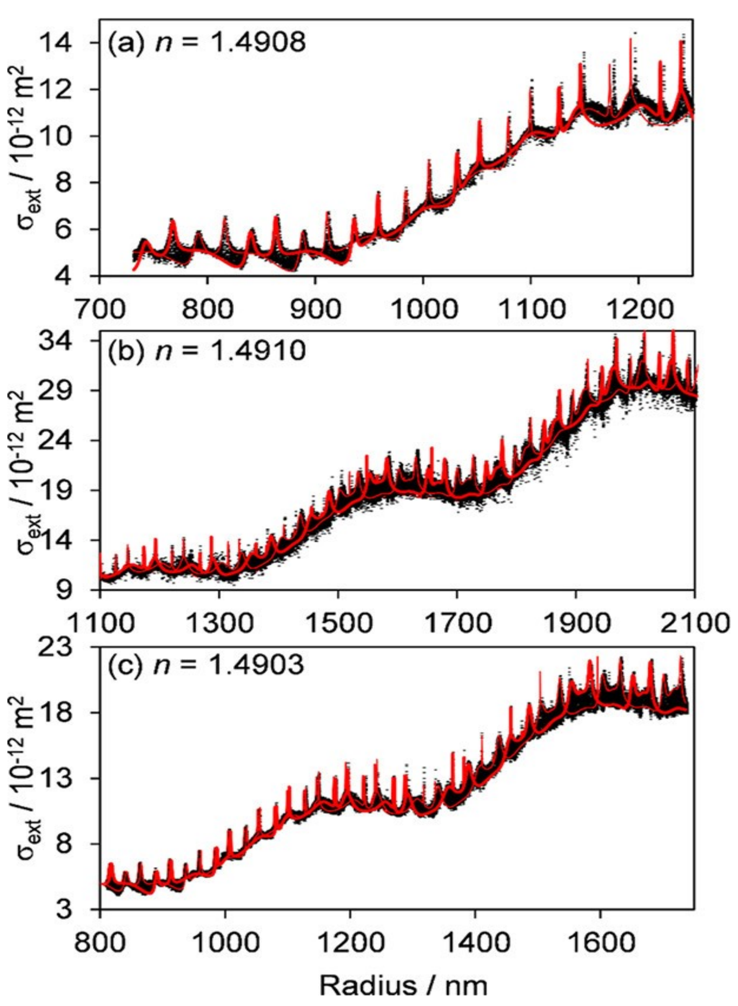

Figure 1 - Repeated measurements (black dots) of the extinction cross sections of three separate, non-absorbing 1,2,6-hexanetriol droplets as a function of particle radius; the red line shows the best fit to the extinction range predicted by the Mie theory of standing waves in the cavity. Adapted from Ref.1.

Methodology

- To enable the optical properties of individual light-absorbing aerosol droplets to be interrogated over an indeterminate time scale, this project uses a linear electrodynamic quadrupole (LEQ) balance to levitate a single droplet at the centre of a CRDS probe beam, as shown in Figure 2.

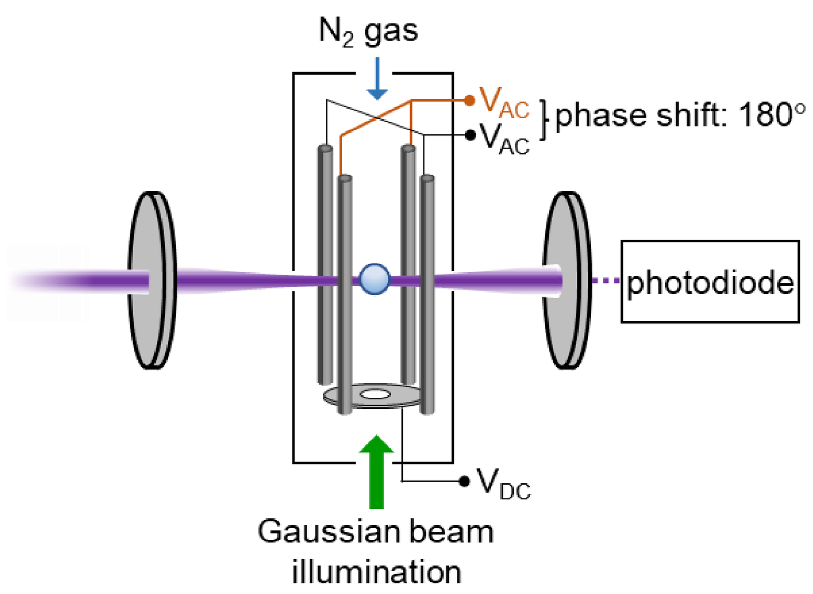

Figure 2 - Schematic of CRDS and quadrupole electrodynamic trap. Figure is adapted from Ref.1

- Once the ring-down event start, The intensity of the intracavity beam then decays exponentially. The characteristic time for the light intensity to decay by 1/e is called the ring-down time, τ. And the characteristic time of the empty cavity is called τ0.
- Based on knowledge of τ and τ0, σ_{ext} can be calculated using the following equation,

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

where L is the length of the optical cavity and c is the speed of light, provided that the focal beam waist w is known for the fundamental (TEM00) mode

Research Programme

The research programme will be guided by the following three Work Packages (WP). WP1 will start with exploring the effects of different initial sizes. WP2 will focus on the effect of molecular diffusivity with different viscosities.WP3 will explore the photobleaching effects of light-absorbing organic chemical systems that are directly related to atmospheric. chemistry.

References

1. Cotterell, M. I.; Knight, J. W.; Reid, J. P.; Orr-Ewing, A. J. Accurate Measurement of the Optical Properties of Single Aerosol Particles Using Cavity Ring-Down Spectroscopy. The Journal of Physical Chemistry A 2022, 126 (17), 2619-2631.
2. Knight, J. W.; Orr-Ewing, A. J.; Cotterell, M. I. Evaluating the accuracy of absorbing aerosol optical properties measured using single particle cavity ring-down spectroscopy. Aerosol Science and Technology 2023, 1-19. DOI: 10.1080/02786826.2023.2185500.

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