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

Size dependent photochemistry:

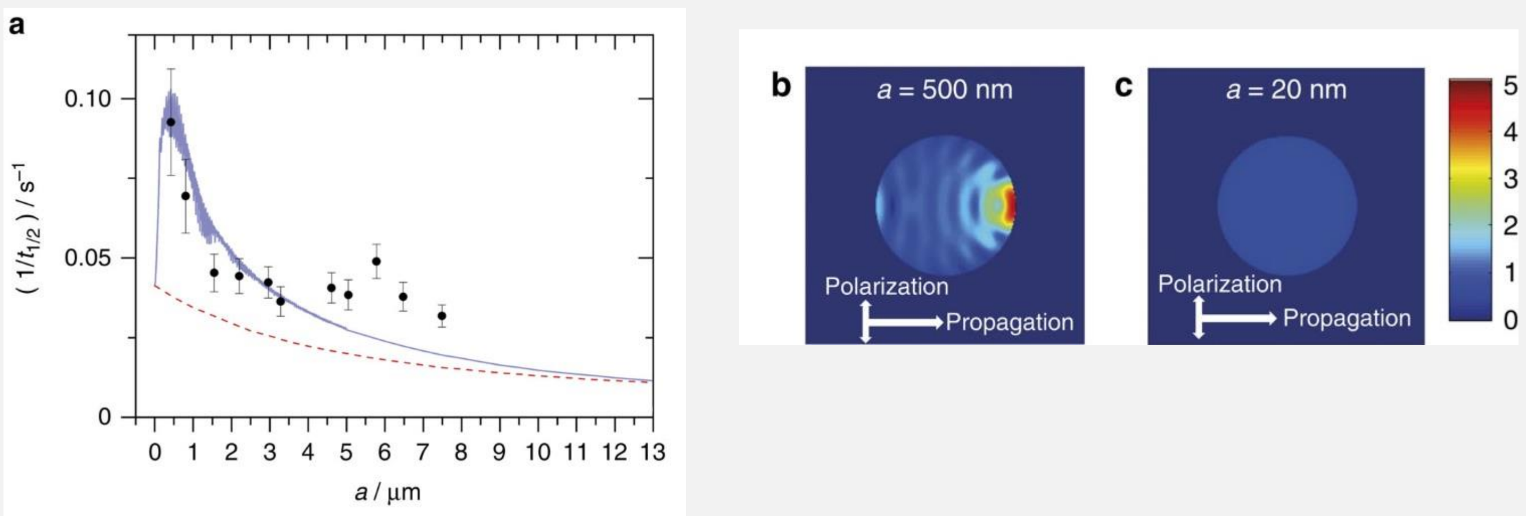
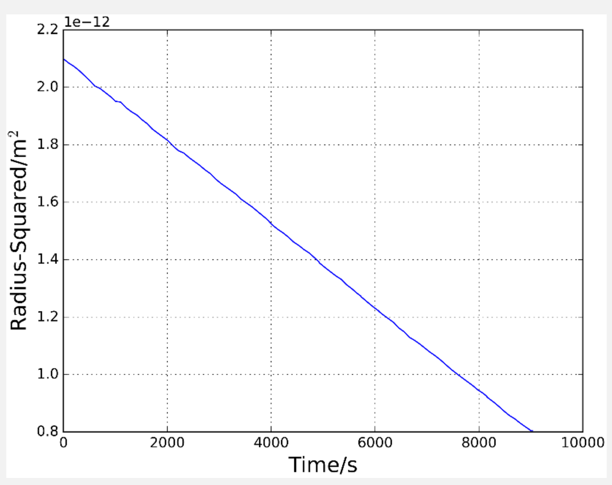


Figure 1 - (a) Inverse first half-lives as a function of the droplet radius for a laser power of 1 mW. Distribution of the light intensity inside droplets at t=0 s for (b) a 0.5 µm droplet and (c) a 20 nm droplet. The colour scheme is relative to an incident light intensity of 1. Figure is adapted from Ref.1

Droplets vapour pressure:

- Droplet vapour pressures, p, can be obtained by fitting the Maxwell equation to the time-dependent radius data.



$$\frac{da^2}{dt} = -\frac{2D_{ij}M_i p}{R\rho T}$$

D_{ij} = the gas diffusion coefficient of species i in the surrounding phase j

a = particle radius

M_i = molecular weight

ρ = density

T = temperature at droplet surface

Figure 2 – Time dependent radius change.

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) .

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

L = length of optical cavity

w = beam waist at the cavity center

c = speed of light

t = ring down time

t_0 = ring down time for empty cavity

Methodology

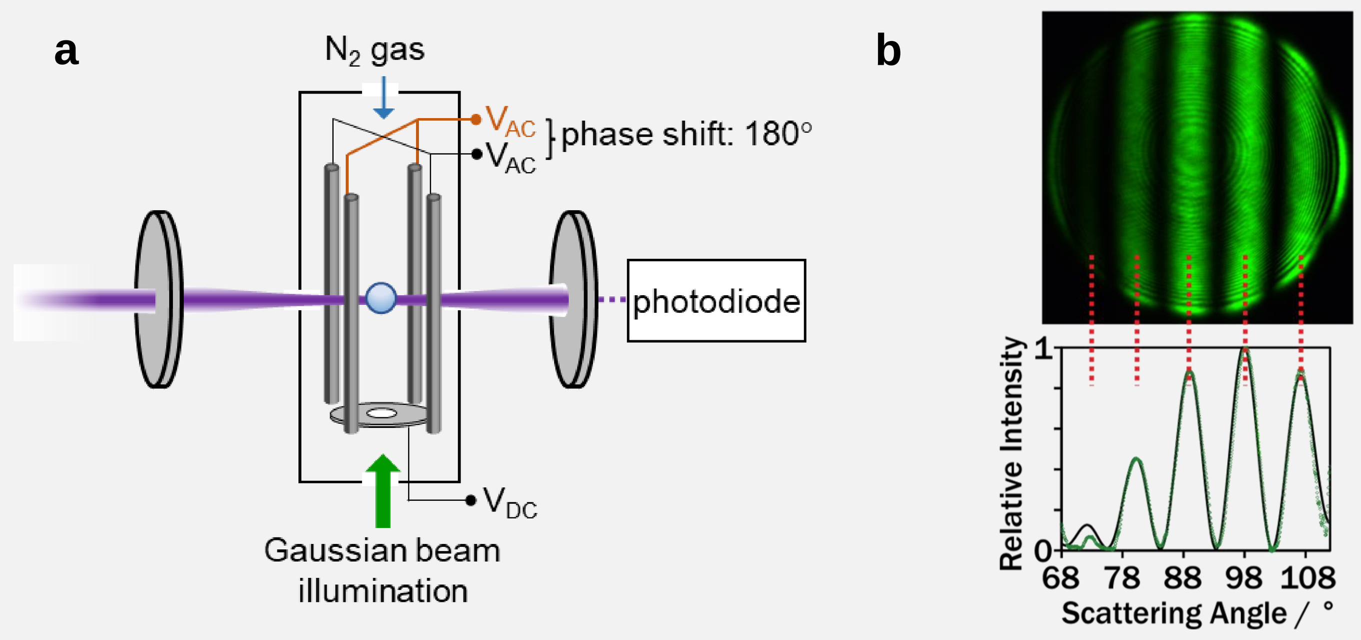
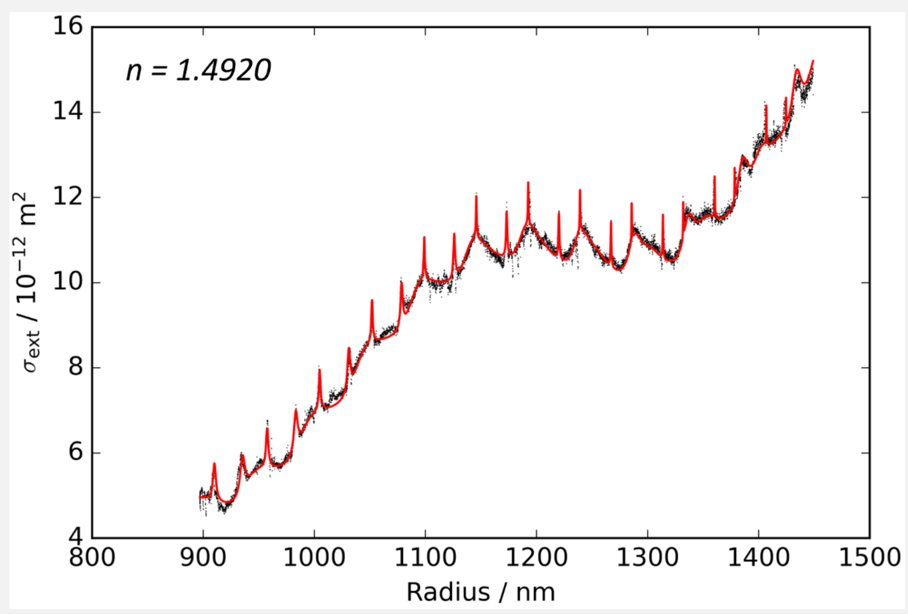


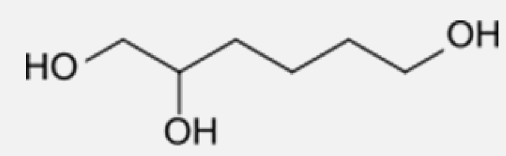
Figure 3 – (a) Schematic of CRDS and quadrupole electrodynamic trap. (b) Phase function of a single particle. Figure is adapted from Ref.2

- CRDS accurately measures the extinction cross-section of single particle, which indicates the chemical composition. And phase function measures the evolving size.

Results

Measurements on 1,2,6-hexanetriol:



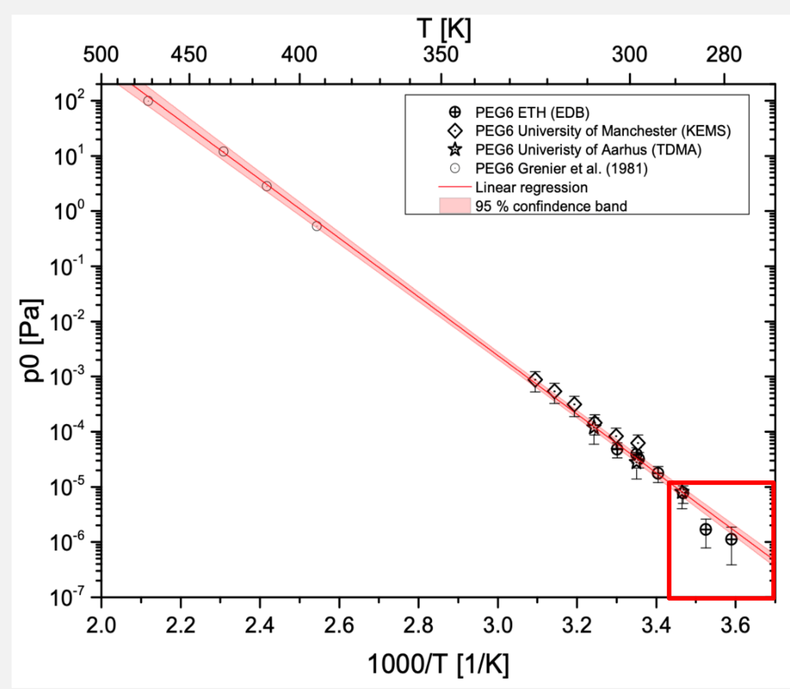


1,2,6-hexanetriol

- Non-absorbing at 405nm
- Relative low volatility

Figure 4 – Extinction cross-section measurement of 1,2,6-Hexanetriol as a function of particle radius. The red line shows the Mie theory prediction.

RI and vapour pressure of Hexaehylene glycol:



- n : 1.4796
- Vapour pressure : 1.534 E-05 Pa
- Temperature : 291K

Figure 5 – Saturation vapor pressures vs. temperature of hexaethylene glycol[3]. The red square marked the experiment point.

References

1. Cremer J W, Thaler K M, Haisch C, et al. Nature communications, 2016, 7(1): 10941.
2. Cotterell, M. I.; Knight, J. W.; Reid, J. P.; Orr-Ewing, A. J. The Journal of Physical Chemistry A 2022, 126 (17), 2619-2631.
3. . Krieger U K, Siegrist F, Marcolli C, et al. Atmospheric Measurement Techniques, 2018, 11(1): 49-63.