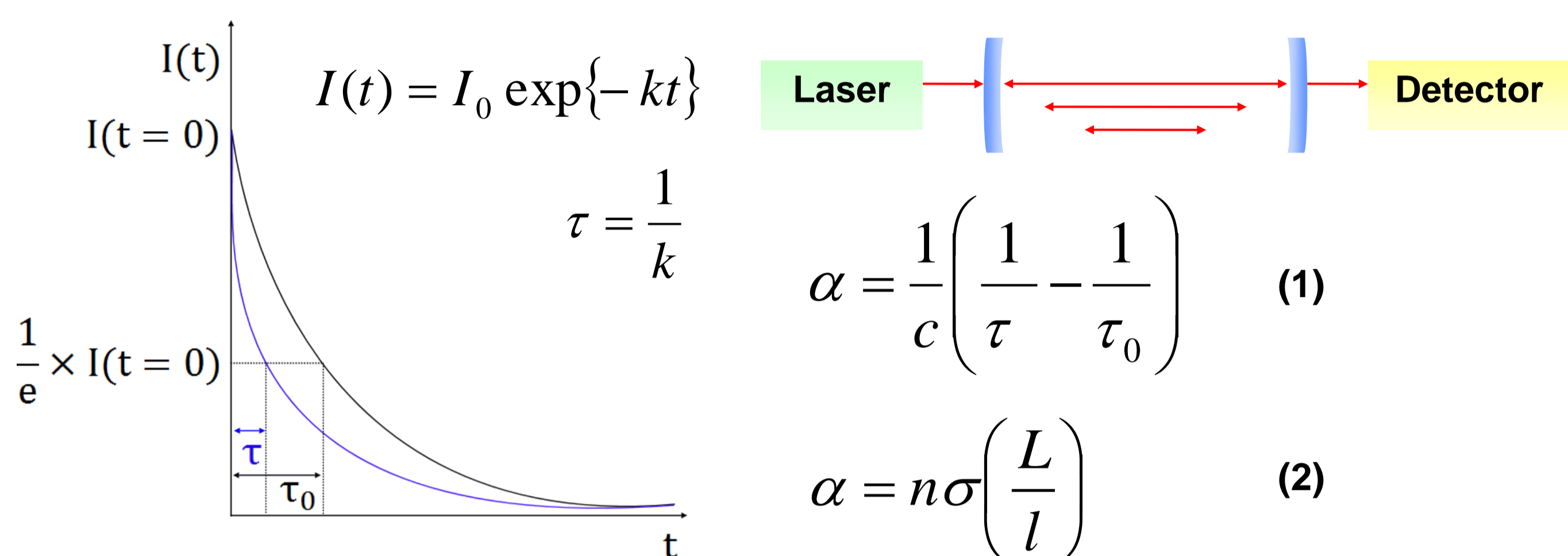


# CRDS Measurements of Extinction by Aerosol Particles

## Abstract

Cavity ringdown spectroscopy was used to measure extinction cross sections of polystyrene spheres,  $(\text{NH}_4)_2\text{SO}_4$  and NaCl aerosols at various wavelengths. From the measured extinction cross sections, refractive indices of the aerosols were retrieved by using Mie theory. The retrieved refractive indices closely match the literature values.

## Cavity Ringdown Spectroscopy



- Measure background ringdown time ( $\tau_0$ ) and ringdown time of a cavity filled with sample ( $\tau$ )
- Calculate extinction coefficient ( $\alpha$ ) from eq. (1)
- Based on  $\alpha$ , calculate extinction cross section ( $\sigma$ ) from eq. (2) where  $L$  = cavity length (distance between the mirrors),  $l$  = sample length and  $n$  = particle concentration

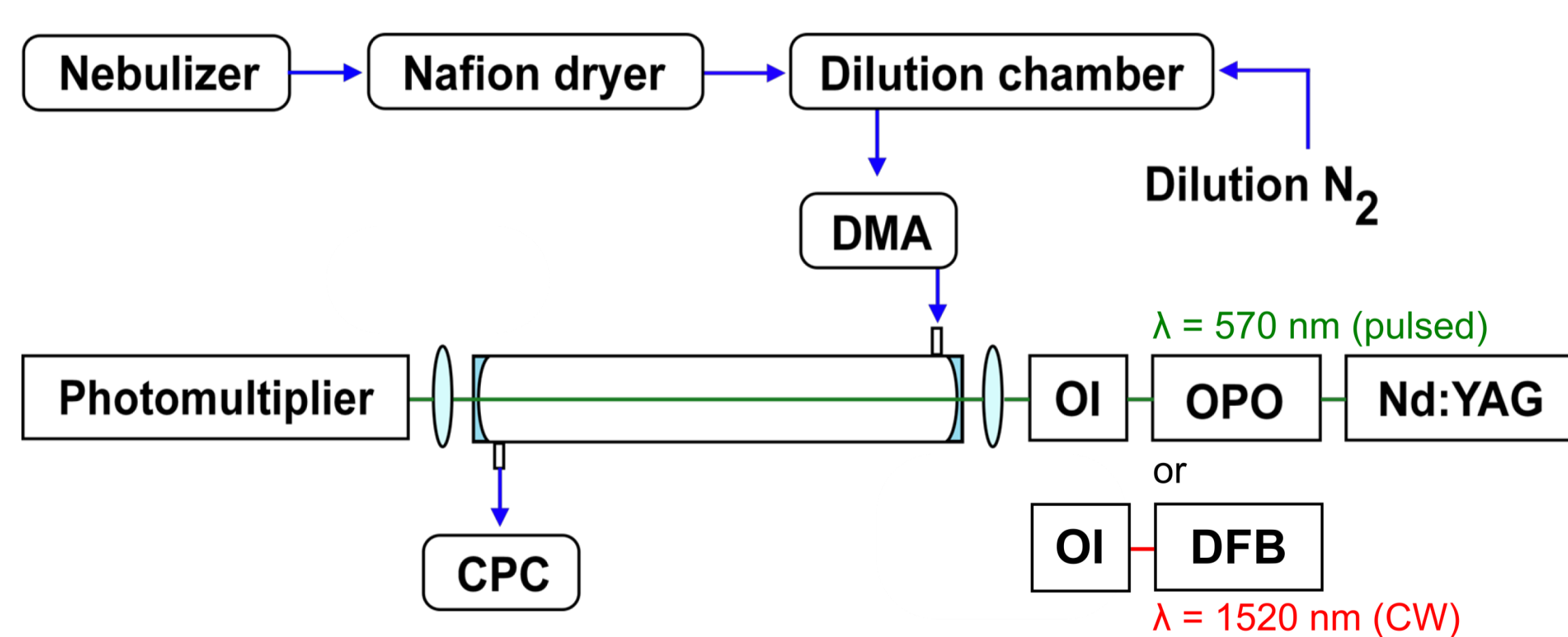
## Statistical Model

- Factors causing fluctuations in measured  $\alpha$ 
  - Particle size distribution (negligible for manufactured aerosols or when a differential mobility analyzer is used to select particle size)
  - Number and position of particles in the beam (can be modelled by Poisson statistics)
  - Inherent noise in the setup (related to minimum detectable extinction coefficient  $\alpha_{\min}$ )
- Taking the last two factors into account, the relationship between  $\alpha$  and its variance,  $\text{Var}(\alpha)$ , can be written as in eq. (3), where  $V$  is the intracavity laser beam volume

$$\text{var}(\alpha) = \frac{\sigma}{V} \alpha + \alpha_{\min}^2 \quad (3)$$

Butler *et al.*, *J. Phys. Chem. A*, **113**, 3963 (2009)

## Experimental Setup

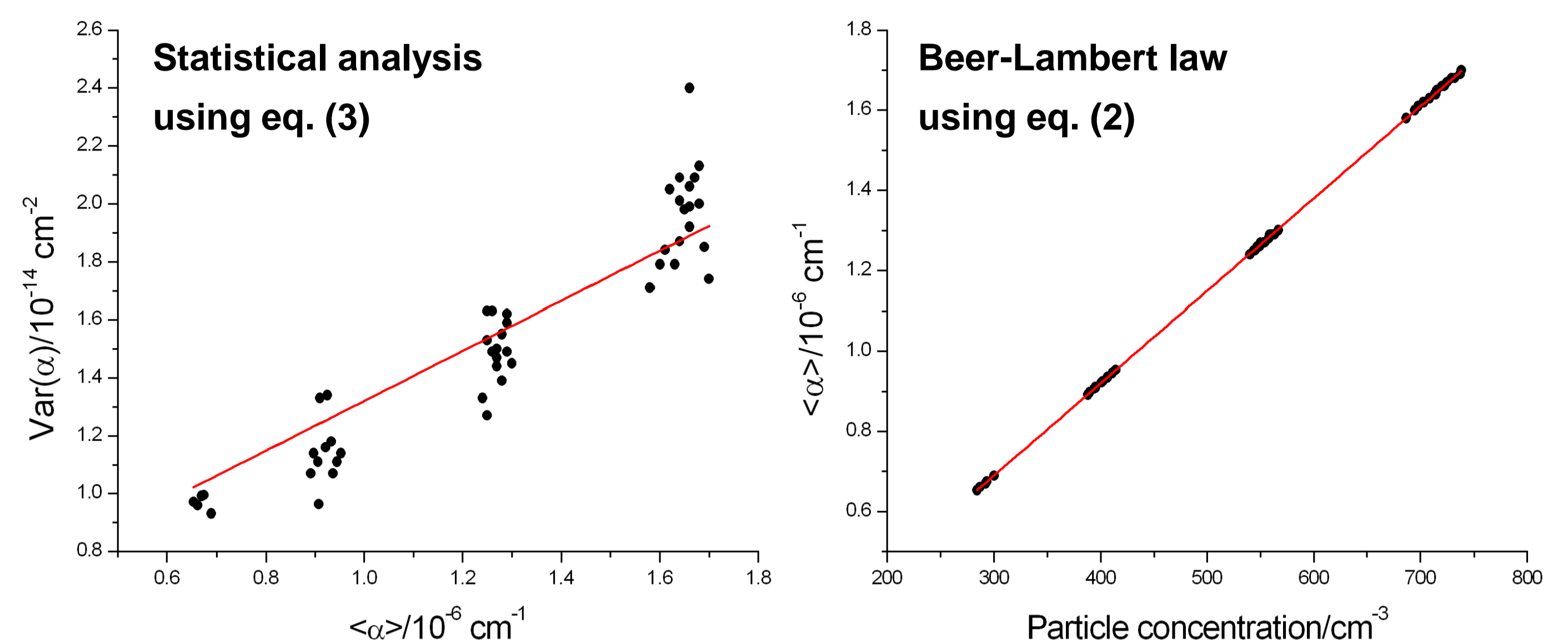


OPO: optical parametric oscillator, OI: optical isolator, DFB: distributed feedback laser, DMA: differential mobility analyzer, CPC: condensation particle counter

- Dilute solution of polystyrene spheres,  $(\text{NH}_4)_2\text{SO}_4$  and NaCl in distilled water nebulised and dried
- Particles size selected by a DMA and drawn into the cavity
- $\alpha$  and corresponding  $\text{Var}(\alpha)$  measured at various particle concentrations while a CPC simultaneously recorded the particle concentration
- Particle concentration changed by altering  $\text{N}_2$  dilution flow

## Extinction Cross Section Retrieval

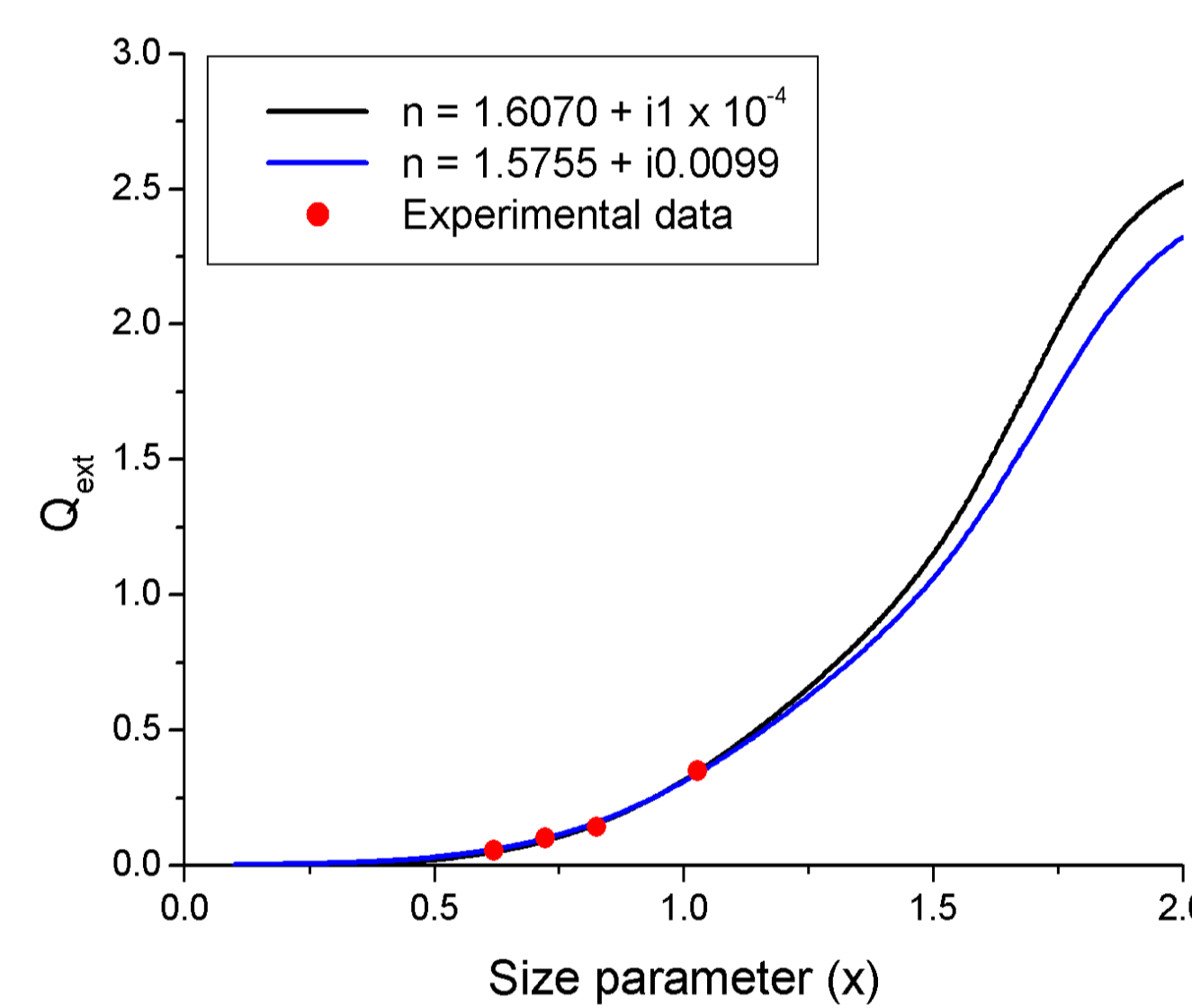
### 350 nm polystyrene spheres at $\lambda = 570$ nm



	$\sigma/10^{-9} \text{ cm}^2$
Mie theory calculation	2.21
Statistical analysis	$2.79 \pm 0.52$
Beer-Lambert law	2.02

- Experimentally retrieved values of  $\sigma$  using both methods are in good agreement with that predicted by Mie theory

## Refractive Index Retrieval

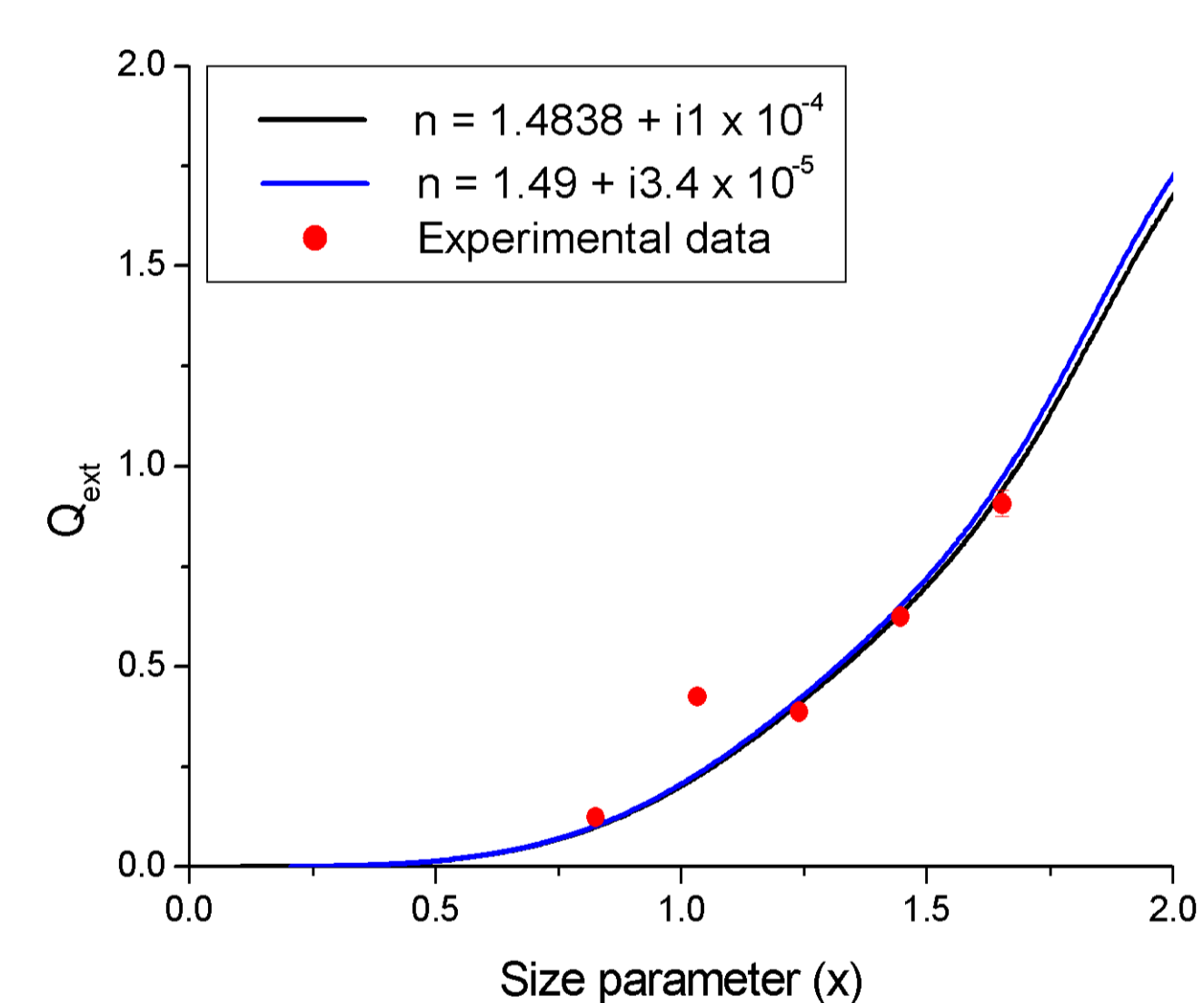


### Polystyrene spheres, $\lambda = 1520$ nm

Size/nm	$\sigma_{\text{exp}}/10^{-10} \text{ cm}^2$	$\sigma_{\text{theo}}/10^{-10} \text{ cm}^2$
$300 \pm 6$	$0.38 \pm 0.09$	0.42
$350 \pm 7$	$0.97 \pm 0.09$	0.96
$400 \pm 4$	$1.77 \pm 0.17$	2.01
$498 \pm 5$	$6.79 \pm 0.23$	6.79

Experimental  $n = 1.6070 + i1 \times 10^{-4}$   
 Ma *et al.* (2003)  $n = 1.5755 + i0.0099$

X. Ma *et al.*, *Phys. Med. Biol.*, **48**, 4165 (2003)

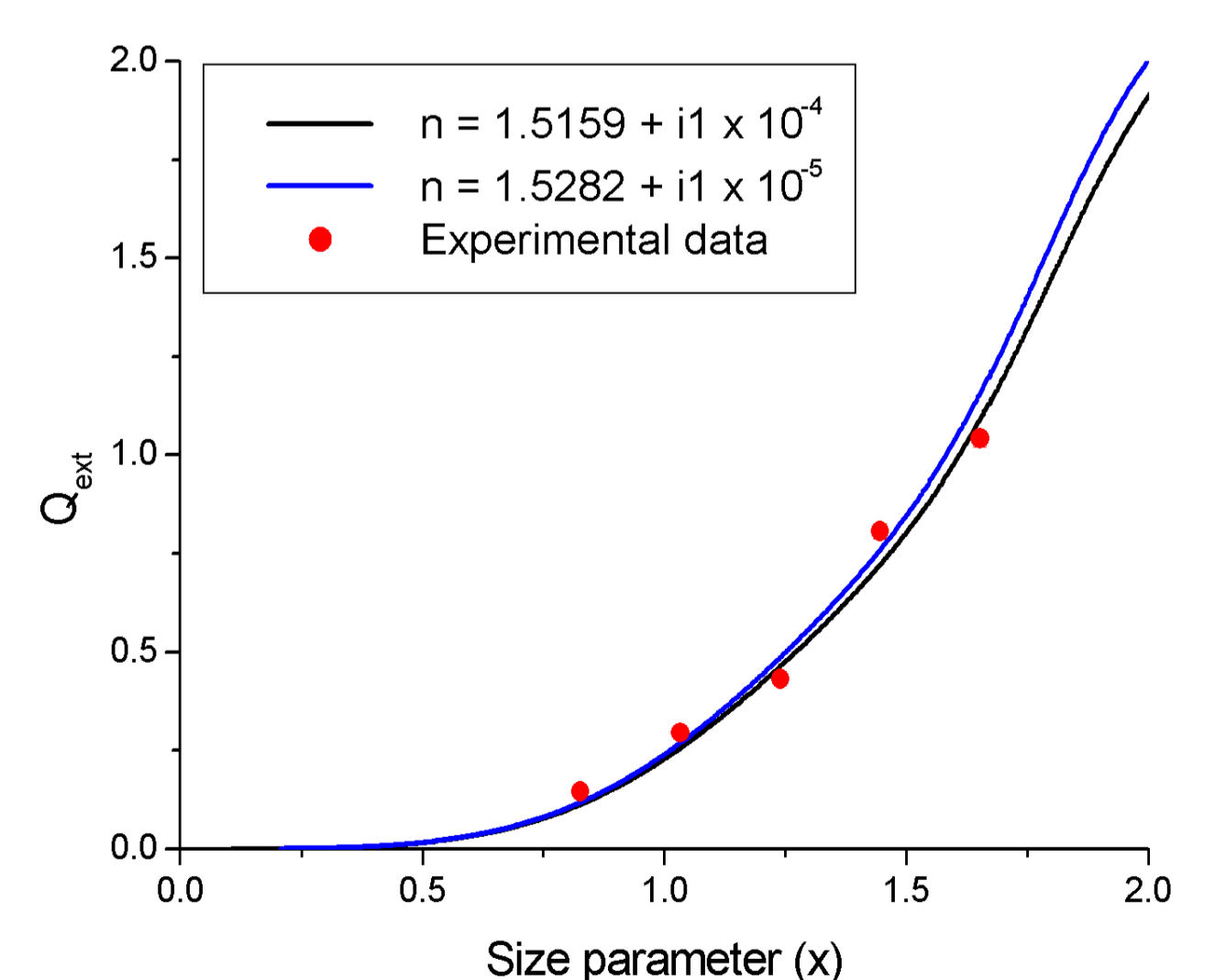


### $(\text{NH}_4)_2\text{SO}_4$ , $\lambda = 1520$ nm

Size/nm	$\sigma_{\text{exp}}/10^{-9} \text{ cm}^2$	$\sigma_{\text{theo}}/10^{-9} \text{ cm}^2$
400	$0.156 \pm 0.009$	0.130
500	$0.836 \pm 0.021$	0.456
600	$1.095 \pm 0.034$	1.184
700	$2.406 \pm 0.041$	2.505
800	$4.562 \pm 0.154$	4.873

Experimental  $n = 1.4838 + i1 \times 10^{-4}$   
 Toon *et al.* (1976)  $n = 1.49 + i3.4 \times 10^{-5}$

O. B. Toon *et al.*, *J. Geophys. Res.*, **81**, 5733 (1976)



### NaCl, $\lambda = 1520$ nm

Size/nm	$\sigma_{\text{exp}}/10^{-9} \text{ cm}^2$	$\sigma_{\text{theo}}/10^{-9} \text{ cm}^2$
400	$0.183 \pm 0.008$	0.148
500	$0.579 \pm 0.014$	0.528
600	$1.222 \pm 0.025$	1.377
700	$3.109 \pm 0.073$	2.929
800	$5.230 \pm 0.105$	5.816

Experimental  $n = 1.5159 + i1 \times 10^{-4}$   
 Li (1976)  $n = 1.5282 + i1 \times 10^{-5}$

H. H. Li, *J. Phys. Chem. Ref. Data*, **5**, 329 (1976)

\* Uncertainties in  $\sigma_{\text{exp}}$  are derived from the linear fits to  $\text{Var}(\alpha)$  vs.  $\langle \alpha \rangle$ .

## Acknowledgements

- EPSRC (grant EP/E018297) and NERC (DIAC grant NER/S/R/2004/13085) for financial support
- Dr. J. L. Miller for contributions to the early stage of this work
- Dr. J. P. Reid, Dr. S. Rudic' and R.E.H. Miles (University of Bristol) for helpful discussions