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Cavity Ringdown Spectroscopy Measurements of Extinction by Aerosol Particles

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Atmospheric aerosols play an important role in determining the Earth's radiation balance but the extent of their effect on the global climate is poorly determined and needs to be studied further. Cavity ringdown spectroscopy (CRDS) is gaining in popularity as a sensitive technique to measure optical properties of aerosols. So far, in most of the CRDS measurements of aerosols such as that by Pettersson *et al.* (2004), the aerosol extinction cross section (σ) was extracted by using Beer-Lambert law and relied on the use of a condensation particle counter to measure the particle concentration.

Recently, we proposed a statistical model based on the random fluctuations of particle numbers, which allows determination of σ without prior knowledge of particle concentration (Butler *et al.*, 2009). The model is based on the linear relationship between the extinction coefficient (α) and its variance ($Var(\alpha)$):

$$Var(\alpha) = \frac{\sigma}{V} < \alpha > + \alpha_{\min}^2$$

where V is the intracavity laser volume and α_{min} is the minimum detectable extinction coefficient, determined by the inherent noise in the system. For a TEM_{00} cavity mode, V can be straightforwardly calculated from Gaussian beam theory.

The statistical model was tested by measuring the extinction caused by an ensemble of monodisperse polystyrene spheres with optical feedback CRDS (OF-CRDS). α and corresponding values of $Var(\alpha)$ were measured at various particle concentrations and they were plotted against each other as shown in Figure 1. The value of σ was obtained from the gradient of the line of the best fit. The extinction cross sections of polystyrene spheres determined from the experiment were in good agreement with the predictions of Mie theory calculations as presented in Table 1.

Table 1. Comparison of experimentally determined and calculated extinction cross sections for the samples of polystyrene spheres.

Nominal particle diameter/nm	$\sigma_{exp}/10^{-9}$ cm^2	$\sigma_{calc}/10^{-9}$ cm^2
700	2.63 ± 0.05	2.97 ± 0.18
500	0.45 ± 0.12	0.485 ± 0.036
400	0.15 ± 0.07	0.146 ± 0.013

The relationship between α and $Var(\alpha)$ deviated from linearity at high particle concentration. An additional variance coming from the ringdown fitting method could partly account for this deviation.

Monte Carlo simulations incorporating the Brownian motion and gravitational settling of particles showed that extinction cross sections can be underestimated if the measurements are made too rapidly and consecutive measurements become correlated. The reason for using an OF-CRDS apparatus was to exploit its fast acquisition rate (1.25 kHz) but if such fast acquisition is not needed or causes problem with correlation in measurements, a normal CRDS apparatus with slower acquisition rate (~10 Hz) can be used. The use of conventional CRDS setups using either pulsed or continuous wave lasers is underway.

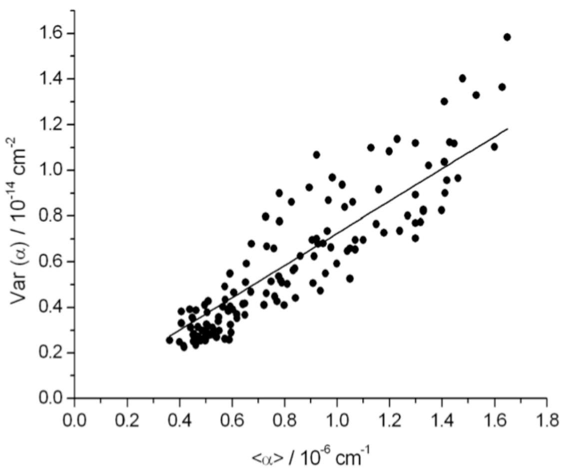

Figure 1. Plot of $Var(\alpha)$ against $<\alpha>$ for polystyrene spheres 700 nm in diameter.

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