A study of the optical properties of secondary organic aerosol using broadband cavity spectroscopy

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Introduction
Near-ultraviolet optical properties of anthropogenic and biogenic secondary organic aerosol (SOA) are poorly characterised but could significantly influence local atmospheric photochemistry and the earth’s radiative balance. This work describes a novel and sensitive spectrometer based on incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) and its application to investigate the optical properties of SOA.

Experimental setup
The simulation chamber comprised a cylindrically-shaped fluorine-ethylene-propene (FEP) bag. It was surrounded by 36 UV-visible fluorescence lamps (Philips TUV and TLD) for photochemical experiments. The chamber was 4.1 m long with a diameter of 1.1 m, giving a volume of approximately 3.91 m³. The chamber surface-to-volume ratio was ca. 0.24 m⁻¹. It was operated at atmospheric pressure and ambient laboratory temperature (ca. 21 °C). Between experiments the chamber was flushed by dry clean air at 200 L min⁻¹ for 3 to 12 hours.

The IBBCEAS instrument attached to the simulation chamber is shown schematically in Fig.1. Two highly reflective mirrors (Layertec) with maximum reflectivity of 99.6% and 5 m radius of curvature were separated across the length of the chamber. Light from a 75 W arc Xe lamp was focussed into the centre of the optical cavity formed by the two high reflectivity mirrors. After passing the cavity, light was focussed into a Czerny-Turner spectrophotograph.

The extinction (or absorption) spectrum of a sample in the cavity is given by:

\[ \epsilon(\lambda) = \sum \sigma_i(\lambda) \cdot n_i / V = \frac{1}{d} \left( \frac{I_f(\lambda)}{I_0(\lambda)} - 1 \right) (1 - R(\lambda)) \]

where I₀ and Iₐ are respectively the intensities transmitted through the optical cavity in the presence and absence of an absorber, d is the distance between the cavity mirrors, R is the mirror reflectivity, and σₐ (cm² molecule⁻¹) and nᵢ (molecules) are the absolute absorption cross section and molecules of species i. V (cm³) is the volume of the chamber.

Instrument Calibration
Because the FEP bag was flexible and subject to significant pressure fluctuations during purging, the chamber volume was slightly variable from experiment to experiment. Furthermore, the path length through the actual sample was affected by the slow purge of the cavity mirror. Therefore, instead of directly calibrating the reflectivity R(λ), the overall system response to a given number of absorbing molecules in the chamber was calibrated (Fig.2).

SOA optical properties
In previous studies, the retrieval of the aerosol extinction was based on a known absorption, such as the B-band of O₃ or the O₄ dimer (Varma et al., 2009; Thalman and Volkamer, 2010). It is also possible to calculate the aerosol extinction directly by subtracting the gaseous species absorption from the total extinction.

Conclusions and future work
The application of the technique to aerosols has also attracted recent attention but has been restricted to visible wavelengths. As the UV optical properties of aerosols are not well known and are important in radiative forcing, the near-UV IBBCEAS instrument could provide valuable insight into these climatically important atmospheric constituents.

References

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Fig.1 Schematic diagram of the IBBCEAS in-situ chamber setup.