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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-ethene-propene (FEP) bag. It was surrounded by 36 UV-visible fluorescence lamps (Philips TUV and TL05) 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 spectrograph.

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

$$\varepsilon(\lambda) = \sum_i \sigma_i(\lambda) \cdot n_i / V = \frac{1}{d} \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) (1 - R(\lambda))$$

where I and I_0 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 σ_i (cm² molecule⁻¹) and n_i (molecules) are the absolute absorption cross section and molecules of species i . V (cm⁻³) is the volume of the chamber.

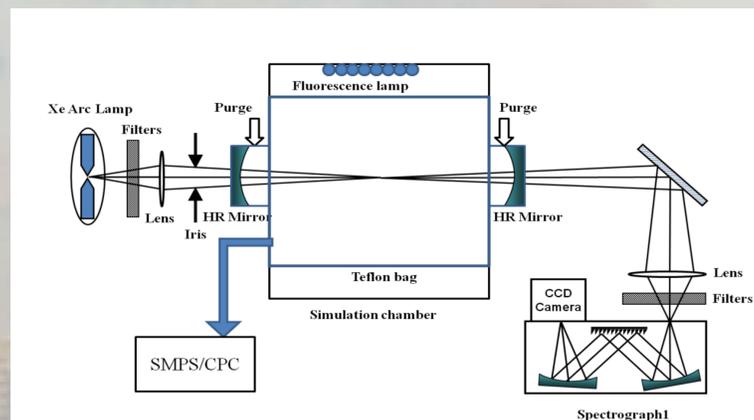


Fig.1. Schematic diagram of the IBBCEAS in-situ chamber setup.

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 $R(\lambda)$, the overall system response to a given number of absorbing molecules in the chamber was calibrated (Fig.2).

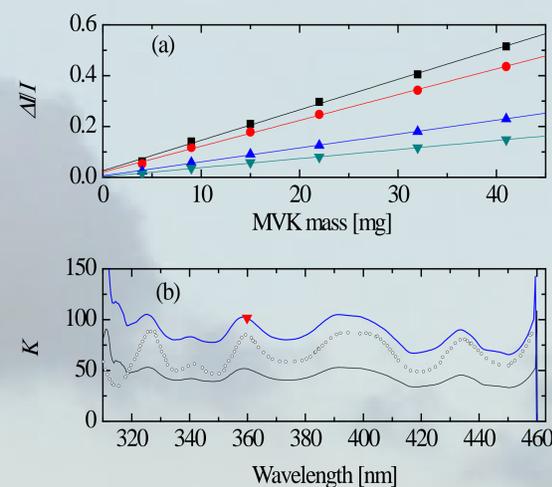
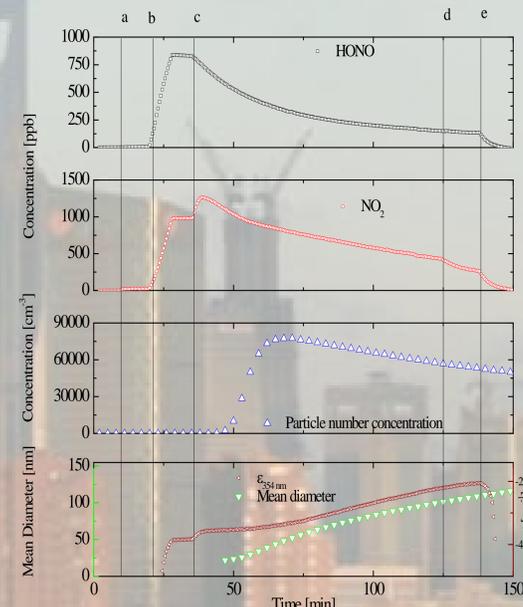


Fig.2. Calibration of the IBBCEAS simulation chamber instrument (a) Fractional absorption of MVK at 340 nm (black squares), 350 nm (red dots), 360 nm (blue triangles) and 370 nm (cyan triangles); linear regressions are also shown ($R^2_{340\text{nm}} = 0.9976$, $R^2_{350\text{nm}} = 0.9982$, $R^2_{360\text{nm}} = 0.9988$, $R^2_{370\text{nm}} = 0.9989$; y-intercepts are 0.026 at 340 nm, 0.020 at 350 nm, 0.006 at 360 nm and 0.003 at 370 nm). (b) The relative calibration from 320 to 450 nm using NO₂ (black line), and the absolute calibration at 360 nm after scaling to the reflectivity obtained from MVK (red triangle). The final scaled calibration is shown (blue line) along with the scaled transmission from the manufacturer's data (black dots)

Isoprene photooxidation:

In a preliminary study, the ability of the IBBCEAS approach to measure the optical properties of SOA formed by early stage photochemical oxidation of isoprene by OH under high NO_x conditions was investigated. HONO and NO₂ were simultaneously measured by the IBBCEAS instrument, while a SMPS monitored the particle size distribution during the experiment (Fig.3).

Fig.3. Temporal dependence of the concentrations of HONO, NO₂, and total particle number concentration as well as the mean aerosol aerodynamic diameter and the aerosol extinction at 354 nm. Points (a) – (d) indicate changes in either the input concentrations or photolysis rate: (a) Addition of isoprene, (b) Introduction of HONO/NO/NO₂, (c) Lamps switched on d) Lamps switched off, e) Flushing of chamber started.



SOA optical properties

In previous studies, the retrieval of the aerosol extinction was based on a known absorption, such as the B-band of O₂ 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

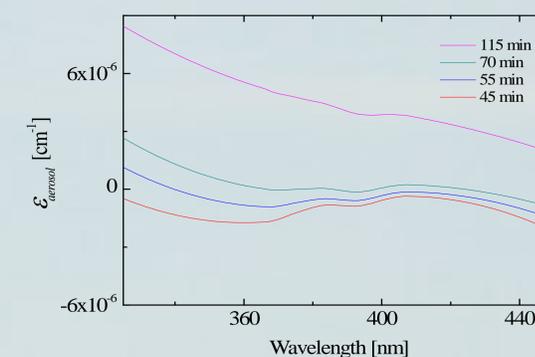


Fig.4. Wavelength-dependence of the aerosol extinction at different times

Conclusion 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

- Varma, R. M., Venables, D. S., Ruth, A. A., Heitmann, U., Schlosser, E., and Dixneuf, S., Appl. Opt., 48, B159-B171, 2009.
- Thalman, R., and Volkamer, R, Atmos. Meas. Tech., 3, 1797-1814, 2010.

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