



In situ monitoring of NO₃ in an atmospheric simulation chamber



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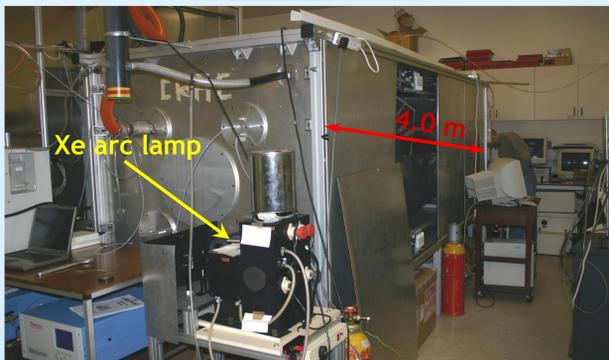


Motivation

In situ observation of radical species under typical atmospheric conditions is desirable in laboratory studies to address questions about reaction mechanisms and to determine absolute rate coefficients for atmospheric reactions. In this work, we use a method developed in our laboratory, incoherent broadband cavity-enhanced absorption spectroscopy (BBCEAS), [1] to monitor the nitrate radical, NO₃, in an atmospheric simulation chamber.

Figure 1. Photograph of the CRAC atmospheric simulation chamber with the Xe arc lamp in the foreground. The chamber length was 4 m.

Introduction



Incoherent Broad-Band CEAS

Cavity-enhanced absorption spectroscopy (CEAS) and related methods exploit the long effective pathlength of light in an optical cavity formed by two high reflectivity dielectric mirrors. Whereas most work with optical cavities has used lasers as a light source, we use an *incoherent* broadband light source (a Xe arc lamp) to achieve high sensitivity over a broad spectral range. Here we demonstrate exceptional sensitivity to NO₃ and other species in the 600 to 700 nm spectral range.

The incoherent BBCEAS spectrometer attached to the simulation chamber is shown schematically in Fig. 2. Light from the arc lamp is filtered and focused into the optical cavity formed by two high reflectivity mirrors (M₁, M₂). Light from the cavity, gradually leaks out and is collected at a monochromator/CCD, which detects a broad spectral range simultaneously.

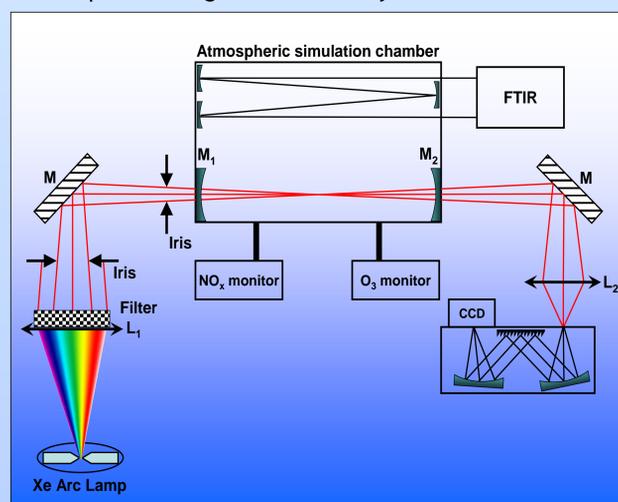


Figure 2. Schematic diagram of the experimental BBCEAS set-up, across the atmospheric simulation chamber.

Experimental

Experimental parameters

75 W Xe short-arc lamp
Monochromator resolution ≈ 0.3 nm
Mirrors: maximum reflectivity ≈ 99.78% at 665 nm
Typical measurement time of 57 s
Effective pathlength ~ 2 Km

$$\alpha(\lambda) = n \times \sigma(\lambda) = \frac{1}{L} [1 - R(\lambda)] \cdot \left(\frac{I_0}{I} - 1 \right)^{-1}$$

where:
 $\alpha(\lambda)$ is the gas absorption coefficient
 $\sigma(\lambda)$ is the gas absorption cross section
 $R(\lambda)$ is the mirror reflectivity
 n is the gas concentration
 L is the cavity length
 I_0 is the light intensity transmitted through the empty cavity
 I is the light intensity transmitted through the gas filled cavity.

Calibration of mirror reflectivities

Mirror reflectivities must be accurately known to quantify the concentration of trace gases. We calibrated the reflectivities by using known amounts of O₃ and NO₂ in the chamber.

Both gases absorb in this spectral region and their absorption cross-sections are well known. Their concentrations were determined from the IR absorption spectrum (O₃) and with a NO_x monitor (NO₂). The mirror reflectivity curve was obtained from a polynomial fit to the data (see Fig. 3).

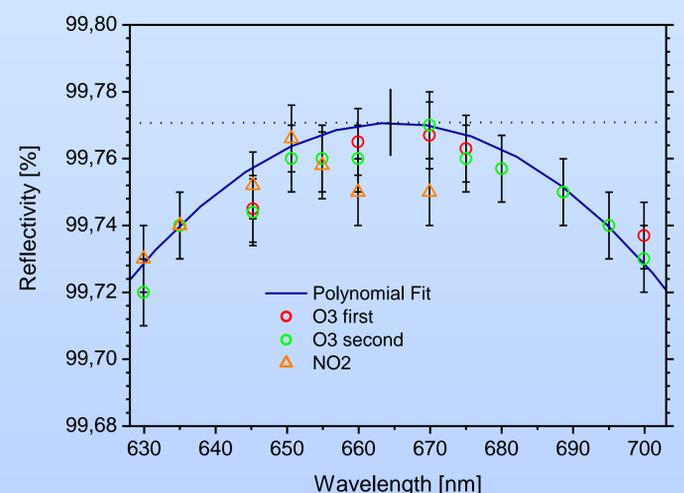


Figure 3. Mirror reflectivities determined from measured concentrations of O₃ (circles) and NO₂ (triangles). The blue line is a second-order polynomial fit to the measured points.

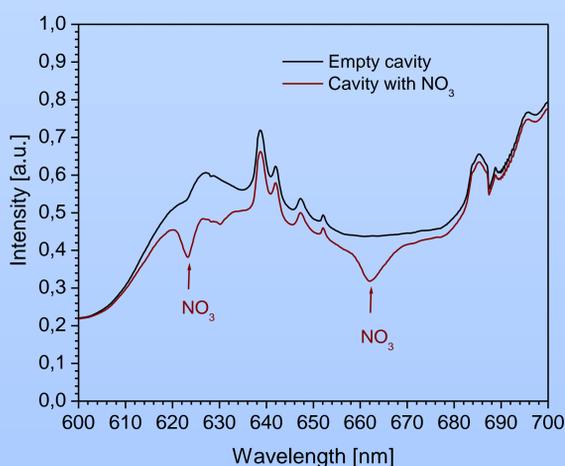


Figure 4. Transmitted intensity through the optical cavity when the chamber contained clean air (I₀-black line) and with NO₃ (I-red line). NO₃ absorption peaks are visible at 623 nm, and 662 nm.

Results

NO₃ was formed in the simulation chamber by reacting NO₂ in a large excess of O₃. NO₃ absorbs strongly around 662 nm and between 620 and 630 nm. The light intensity transmitted through the empty cavity (I₀), and that with NO₃ (I), is shown in Fig. 4, where the absorption arising from NO₃ is readily apparent in the spectrum. Also, the γ - and B bands of molecular oxygen are visible around 628 nm and 688 nm, respectively.

The sensitivity of the spectrometer was investigated by diluting the NO₃ in the chamber by flushing the system with purified air for 30 minutes. The absorption spectrum of NO₃ around 662 nm after flushing the chamber is shown in Fig. 5. For comparison, the magnitude of the absorption matches that of a literature spectrum scaled to 3.7 pptV. [2]

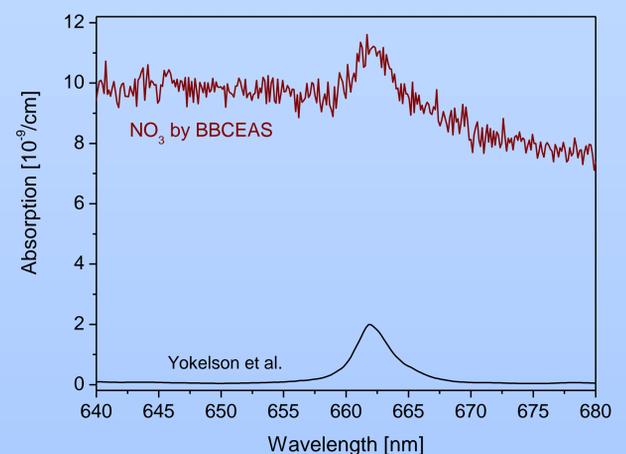


Figure 5. Comparison of the absorption spectrum recorded by incoherent BBCEAS (red) compared with a literature spectrum of NO₃ [2], scaled to 3.7 pptV (black).

Parts-per-trillion levels of NO₃ are clearly detectable within a measurement time of about 1 minute. Sampling for 10 minutes would certainly put the detection limit for NO₃ below 1 pptV. The system is therefore exceptionally sensitive and its sensitivity compares well with other approaches.

Incoherent BBCEAS has several advantages. Compared with long-path DOAS, the system is relatively small and is capable of providing high spatial resolution measurements. This is particularly important for short-lived species such as NO₃ or those with significant point sources like NO₂.

Discussion

In comparison with laser-based approaches such as cavity ring-down spectroscopy (CRDS) or cavity enhanced (CEAS), the system is robust, modestly priced, and provides broad spectral coverage, allowing multiple species to be determined simultaneously.

The IBBCEAS approach therefore has tremendous potential in both laboratory studies and field measurements.

Acknowledgements

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References

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- [2] Yokelson *et al.*, *J. Phys. Chem.*, **98** (1994) 13144.

