In situ monitoring of NO₃ in an atmospheric simulation chamber

Dean S. Venables,¹ Titus Gherman,² Johannes Orphal,²,³ John C. Wenger,¹ and Albert A. Ruth²

¹Department of Chemistry and ²Department of Physics, University College Cork, Cork, Ireland
³Laboratoire Interuniversitaire des Systèmes Atmosphériques, Créteil, France

Introduction

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 reaction chamber.

Experimental

The arrangement of the BBCEAS spectrometer attached to the CRAC simulation chamber is shown in Fig. 2. Light from the arc lamp is filtered and focused into the optical cavity formed by the high reflectivity mirrors. Light in the cavity is reflected backwards and forwards between the mirrors, making many passes and traveling a long distance through the sample. Light in the cavity gradually leaks out and is collected at a monochromator/CCD, which detects a broad spectral range simultaneously.

Experimental parameters:

- 75 W Xe arc lamp
- Monochromator resolution: 0.3 nm
- Mirrors: maximum reflectivity > 99.85% at 662 nm
- Typical measurement time of 57 s
- Fig. 3 shows a spectrum of the light transmitted through the cavity. The intensity minimum near 660 nm corresponds to the maximum in the mirror reflectivity. The γ and δ bands of molecular oxygen are visible around 628 nm and 688 nm, respectively. Also shown is the reduced intensity through the cavity after adding 0.17 ppm of O₃ to the simulation chamber.

Results

NO₃ was formed in the simulation chamber by reacting NO₂ in a large excess of O₃. NO₂ absorbs strongly around 662 nm and between 620 and 630 nm. The light intensity transmitted through the empty cavity, and that with NO₂, is shown below in Fig. 5, where the absorption arising from NO₂ is readily apparent in these spectra.

The sensitivity of the spectrometer was investigated by diluting the NO₂ in the chamber by flushing the system with purified air for 30 minutes. The absorption spectrum of NO₂ around 662 nm after flushing the chamber is shown in Fig. 6. For comparison, the mirror reflectivity was determined from a second-order polynomial fit to the measured points.

Discussion

Parts-per-trillion levels of NO₃ are clearly visible 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.

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

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

Acknowledgements

This work was supported by the European Union under contract WTKO-CT-2004-014404 “Transfer of Expertise in Atmospheric Monitoring of Urban Pollutants” (TEAM-UP) and by the Irish Research Council for Science, Engineering and Technology (SC/2002/160).

References