In situ monitoring of NO₃ using incoherent broadband cavity-enhanced absorption spectroscopy

A kinetic study of the I/O₃/NO₃ system

Titus C. Gherman, Johannes Orphal, Dean S. Venables, John C. Wenger, and Albert A. Ruth

(1) Department of Physics and (2) Department of Chemistry, University College Cork, Cork, Ireland
(3) Laboratoire Inter-Universitaire des Systemes Atmosphériques, Créteil, France

We present two application of IBBCAES (incoherent broadband cavity-enhanced absorption spectroscopy), first for the in situ monitoring of the nitrate radical, NO₃, in an atmospheric simulation chamber [1] and second for a kinetic study of the I/O₃/NO₃ system.

As we know iodine is important in tropospheric ozone and marine aerosol formation [2]. Sources of iodine are not very well understood till present and recent studies [Plane et al.] show high levels of I₂ even at night as well as I₂ and NO₃ [2]. A possible source is the reaction of NO₂ with I₂, investigated in the present work.

Results

NO₃ was formed in the simulation chamber by reacting NO₂ in a large excess of O₃ (ca. 9 ppmv). Intensity transmitted by the optical cavity, (integration time 57 sec. corresponding to an average of 3000 single readouts of the CCD array with individual exposure time), is shown in Fig. 3. Also, the γ and β bands of molecular oxygen are visible around 628 nm and 662 nm, respectively. The structure between 635 nm and 655 nm in (A) and (B) is due to insufficient suppression of emission from the Xe lamp leading into the detector via the second order of the spectograph.

The sensitivity of the spectrometer was investigated by diluting the NO₃ in the chamber (flushing the system with purified air for 30 minutes). Detection of trace amounts of NO₃ in the atmospheric simulation chamber are shown in Fig. 4. The absorption coefficient is calculated using the above equation. The minimum detectable concentration of NO₃ with 57 sec. integration time is estimated to be better than 1 ppv. The offset between the two spectra is due to the noise absorption in the atmospheric simulation chamber.

Discussion

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

The IBBCAES approach therefore has considerable potential for field measurements and for kinetic and mechanistic studies of NO₃ reactions at typical atmospheric concentrations.

Acknowledgments

This work was supported by the European Marie Curie Training scheme funded by Framework 6 (HTK-T/CT-2004-014406) "Transfer of Expertise in Atmospheric Monitoring of Urban Pollutants" and by the Irish Research Council for Science, Engineering and Technology (SC/2002/166).

References