



STRIVE Report Series No. 15

Air Pollution – Trace Radical Absorption through Cavity-Enhanced Spectroscopy (TRACES)

STRIVE

Environmental Protection Agency Programme

2007-2013





Comhshaol, Oidhreacht agus Rialtas Áitiúil Environment, Heritage and Local Government

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Air Pollution – Trace Radical Absorption through Cavity-Enhanced Spectroscopy (TRACES)

(2005-ET-MS-28-M3)

Final Report

Prepared for the Environmental Protection Agency

by

University College Cork

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ACKNOWLEDGEMENTS

This report is published as part of the Science, Technology, Research and Innovation for the Environment (STRIVE) Programme 2007–2013. The programme is financed by the Irish government under the National Development Plan 2007–2013. It is administered on behalf of the Department of the Environment, Heritage and Local Government by the Environmental Protection Agency which has the statutory function of coordinating and promoting environmental research.

We are enormously grateful to the Environmental Protection Agency (Project: TRACES 2005-ET-MS-28-M3) not only for funding this project, but also for allowing changes to the original project plan in order for us to pursue exciting research questions that arose during the course of the project. In particular, neither our participation in the Jülich intercomparison nor in the COBRA campaign (impact of combined iodine and bromine release on the Arctic atmosphere) would have been possible without the Environmental Protection Agency's support.

The NO₃/N₂O₅ intercomparison in the SAPHIR atmosphere simulation chamber at the Forschungszentrum Jülich was particularly profitable for advancing the goals of the project. We are tremendously indebted to the SAPHIR personnel, particularly Theo Brauers and Hans-Peter Dorn for organising the intercomparison and for their professional help throughout the campaign. We also thank Eric Schlosser, Rolf Häseler and Franz Rohrer for sharing their data with us. It was a privilege to work with both relatively new and well-established atmospheric groups at the SAPHIR experiment, and we appreciate the constructive and cooperative spirit in which the campaign was conducted. The 2007 INNOx (NO₃/N₂O₅ intercomparison) campaign was funded by the European Commission under the Sixth Framework Programme Integrated Infrastructure Initiative: EUROCHAMP and Global Change and Ecosystems: ACCENT (contract number: RII3-CT-2004-505968), for which we express our thanks.

We would like to thank Johannes Orphal, who contributed to the convolution of reference spectra and the development of analysis procedures. John Lucey, Joe Sheehan and Christie Roche at University College Cork (UCC) served the project enormously through their excellent technical support, which is gratefully acknowledged. The measurements made at Roches Point (Ireland) were facilitated by Met Éireann, John Wenger (UCC) and Ian O'Connor (UCC), to whom we are grateful. We thank the organisers of the COBRA campaign, particularly Lucy Carpenter (University of York) and John Plane (University of Leeds) for welcoming us in the COBRA campaign, and the other campaign participants for their support and encouragement during the field measurements. Finally, we thank Stewart Vaughan and Jun Chen, who braved -40° C temperatures at Hudson Bay to pursue exciting scientific objectives with the IBBCEAS system.

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The EPA STRIVE Programme addresses the need for research in Ireland to inform policy makers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA STRIVE PROGRAMME 2007–2013

Published by the Environmental Protection Agency

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Executive Summary

This project has developed an incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) system for the detection of the important nocturnal oxidant NO₃. The IBBCEAS system has been deployed and demonstrated in both atmosphere simulation chambers and in the field. An extensive suite of spectral analysis software was developed and tested on the system. It has been shown that very long optical cavities are feasible and robust: the 20 m cavity demonstrated at the SAPHIR (simulation of atmospheric photochemistry in a large reaction) simulation chamber is longer than typical cavity ring-down and cavity-enhanced absorption systems by over an order of magnitude. Such long cavities are particularly suited to broadband measurements and the detection of multiple atmospheric trace gases because they allow lower reflectivity mirrors to be used while retaining high absorption sensitivity. Lower reflectivity mirrors are suited to broadband measurements because broadband light sources have much lower spectral power densities than lasers; in addition, the high reflectivity region is broader for lower reflectivity mirrors, allowing several species to be detected simultaneously.

The systems in this project have used an open-path configuration which has particular advantages for highly reactive species such as radicals, since there are no surfaces in the system on which the gases can react and bias the measurements. The long cavities allow the atmosphere to be probed with a much higher spatial resolution than other broadband systems, most notably long-path differential optical absorption spectroscopy (DOAS), an established field technique.

The system was tested in an international intercomparison of major atmospheric groups targeting NO_3 and N_2O_5 in the field. This intercomparison was the best possible way of testing and validating the performance of the IBBCEAS system against a variety of other techniques. Preliminary results of the intercomparison are that the IBBCEAS measurements show excellent correlation with other NO₃ measurements; the overall agreement in retrieved concentrations is also very good. The detection limit of the IBBCEAS system was 2 pptv¹ in a 5 s acquisition time. The intercomparison also demonstrated the power of the method to simultaneously retrieve the concentrations of other trace gases. Most notable among these is NO₂ owing to its close relationship to NO₃ in the atmosphere; the retrieval of both species is a significant strength of any measurement system aiming to probe nitrogen oxide chemistry. A detection limit of 2 ppbv was found for NO₂, again with a 5 s acquisition time. It has also been demonstrated that sensitive retrieval of aerosol extinction data is possible under atmospherically typical loadings of inorganic aerosol; preliminary results also show excellent agreement with the retrieved aerosol extinction from a broadband cavity ring-down spectrometer (BBCRDS) during a secondary organic aerosol experiment. A comparison of the retrieved aerosol extinction between several systems at the chamber will also be the subject of future work.

Following the chamber experiments, the IBBCEAS system has been deployed in two very different environments: at Roches Point (Ireland) for NO₃ measurements, and at Kuujjuarapik (Hudson Bay, Canada) for BrO measurements. The Roches Point measurements coincided with a period of high winds and precipitation, greatly reducing the sensitivity of the open-path system. Nevertheless, the campaign clearly demonstrated that long open-path configurations are not only possible for field observations, but that the system functioning and cavity alignment were remarkably robust even under highly turbulent conditions. The Hudson Bay measurements, as part of the COBRA campaign, provided an exciting

A pptv is a measure of the number density of a gas in atmospheric air, so 1 pptv is equivalent to 1 molecule of the trace species for every trillion molecules of air in a given volume.

opportunity for high spatial resolution measurements of the BrO radical. Although the system was set up and aligned, the failure of a generator damaged the xenon arc lamp and prematurely terminated the campaign. Nevertheless, the system developed for Hudson Bay was the first such cavity-enhanced system for BrO detection, and demonstrated the use of IBBCEAS in the near ultraviolet. The project has therefore demonstrated that IBBCEAS is a robust, sensitive approach to the detection of trace atmospheric species. The approach has good spatial resolution and allows the detection of multiple trace gases in a single measurement. The system is particularly suited to high spatial resolution monitoring and has been thoroughly validated against other techniques.

1. Introduction

1.1 Tropospheric Chemistry of the Nitrate Radical NO₃

Free radicals are the driving force behind the chemistry of the natural and polluted atmosphere. They are highly reactive species that play a central role in the oxidising capacity of the atmosphere and are hence pivotal in understanding the temporal and spatial composition and development of the atmosphere. Owing to their high reactivity, they occur at trace concentrations (typically sub-ppb to sub-ppt) in the troposphere. However, the catalytic behaviour of some free radicals allows even minute concentrations to affect significantly the direction and evolution of atmospheric chemical processes. This catalytic behaviour is dramatically illustrated in the events such as halogen radical destruction of polar stratospheric ozone. During the day, the oxidation of organic and inorganic gases in the atmosphere occurs largely via reactions with hydroxyl (OH) radicals, which are produced from the photolysis of ozone in the presence of water. At night, when the OH radical concentration is low, the nitrate radical (NO₃) contributes to tropospheric oxidation processes.

 NO_3 plays an important role in a number of tropospheric reaction mechanisms. First, it reacts with biogenic and anthropogenic volatile organic compounds (VOCs) and is therefore responsible for the chemical transformation and eventual removal of many species from the troposphere. Secondly, many of the reactions of NO_3 produce nitric acid and thus contribute to acid deposition in the environment. Thirdly, the reaction of NO_3 with VOCs is also believed to be a night-time source of OH radicals. Furthermore, Gong *et al.* (2005) have recently demonstrated how the reaction of NO_3 with linear alkenes may lead to secondary organic aerosol (SOA) formation. For these reasons, a detailed understanding of the distribution and chemistry of nitrate radicals is currently one of the major goals in atmospheric chemistry. There have been several measurement campaigns in recent years in which recorded NO_3 levels have been high enough to suggest that the molecule plays an important role in determining the overall oxidising capacity of the troposphere. Aliwell and Jones (1998) have measured very high levels of NO_3 (average mixing ratio 89 pptv,² but reaching 470 pptv) during the night-time in the residual boundary layer, an observation supported by the modelling studies of Fish *et al.* (1999).

 NO_3 radicals are produced from the oxidation of NO_2 by ozone:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

NO₃ is photolysed rapidly during the daytime to yield NO and NO₂ – an important precursor for atmospheric pollutants such as ozone and peroxyacetyl nitrates (PANs) – although Kurtenback *et al.* (2002) concluded from observed *para*-cresol/toluene and *ortho*-cresol/ toluene ratios that NO₃ radical reactions were still important in urban air during daylight hours. However, at night the nitrate radical is sufficiently long lived to undergo a number of important chemical reactions. For instance, an atmospheric sink for NO₃ is nitric acid, HNO₃, which is produced by abstraction of a hydrogen atom from a hydrocarbon:

$$NO_3 + RH \rightarrow HNO_3 + R$$

The organic radical, R, produced in that reaction can react with O_2 to generate peroxy radicals, RO_2 , at night. NO_3 is an electrophilic radical, so it will also add to unsaturated VOCs in the atmosphere to produce nitroxy-alkylperoxy species:

 $NO_3 + R^1 R^2 C = CR^3 R^4 + O_2 \rightarrow R^1 R^2 C (ONO_2) - C(O_2) R^3 R^4$

² A pptv is a measure of the number density of a gas in atmospheric air, so that 1 pptv is equivalent to one molecule of the trace species for every trillion molecules of air in a given volume.

which can react with NO in the atmosphere to form a nitroxy-alkoxy radical, $R^1R^2C(ONO_2)-C(O)R^3R^4$ and NO_2 . These nitroxy-alkoxy radicals can further degrade to form more NO₂ and other important atmospheric species, such as aldehydes and ketones. NO₃ can also react with open-shell radicals such as RO₂:

$$NO_3 + RO_2 \rightarrow NO_2 + RO + O_2$$

Thus, understanding the extent of the interaction between NO_3 and traces gases in the night-time troposphere is crucial for determining the relative importance of the various sources and sinks of atmospheric pollutants like ozone, NO_2 , PANs and HNO₃ through the use of computer models. Hence, it is essential to have accurate, absolute concentrations of NO_3 , which is typically present in the night-time atmosphere at levels of only a few 10s of pptv, and that objective is the focus of this project.

1.2 Previous Techniques for the Determination of Atmospheric NO₃ Concentrations

Ultra-sensitive spectroscopic absorption methods based on high-finesse optical cavities are among the most promising approaches for detecting atmospheric trace species with high spatial and temporal resolution (Clemitshaw, 2004; Brown, 2003a; Paldus, 2005). A variety of atmospheric trace constituents have been successfully detected in the field using laser-based cavity ring-down (CRD) spectroscopy (Brown, 2002a; Brown, 2002b; Awtry, 2002; Ayers, 2005). CRD methods are in principle very powerful in terms of their sensitivity close to the shot-noise level. Most CRD field instruments extract atmospheric samples (Brown, 2005; Dube, 2006; Kassi, 2006; Brown, 2007) and only a few have employed an open-path configuration (Bitter, 2005; Wada, 2007). For instruments using a gas extraction inlet, losses of the target species need to be established in independent measurements. Moreover, CRD methods are generally based on the absorption detection at a single wavelength, which makes retrieving the concentrations of target species impossible without an experimentally independent method to establish the contribution of the target species to the total extinction,

for instance, through concentration variation by titration or filtering (Brown, 2003b; Brown, 2003c). Therefore single-wavelength CRD methods are not usually suited to monitoring multiple species, except where additional chemical or thermal conversion of species provides additional information to retrieve concentrations of more than one target species.

In this context, broadband methods (e.g. conventional multi-pass set-ups employing differential optical absorption spectroscopy (DOAS) (Platt, 1999)) have the advantage that atmospheric trace species can be identified by their spectral absorption signature; additional loss processes can be accounted for in the spectral analysis. The multiplex features of broadband methods enable several target species to be detected simultaneously. Broadband CRD methods have been known for several years (Scherer, 1998; Crosson, 1999; Czyżewski, 2001; Ball, 2001; Ball, 2003; Scherer, 2001; Hamers, 2002; Gherman, 2002; Thorpe, 2006) and have already been applied to atmospheric trace sensing (Bitter, 2005; Langridge, 2006). However, the drawback of these pulsed broadband CRD systems is that they require tunable laser sources along with unconventional light-detection electronics and data sampling. The complexity of the instruments has hindered their widespread adoption for field observations so far.

An alternative approach is based on dispersing and detecting the light from an incoherent broadband light source after it is transmitted by an optical cavity, so-called incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) (Fiedler, 2003). In IBBCEAS, light from an incoherent broadband light source is coupled into an optically stable cavity formed by two mirrors of high reflectivity (R). The transmission spectrum of the cavity is measured without (I_0) and with (I) a target gas mixture present in the cavity over a certain path length (d), which is not necessarily equal to the separation of the cavity mirrors. The extinction of the gas mixture (ε) as a function of wavelength (λ) is given by (Fiedler, (2003); Triki, (2008)):

$$\mathcal{E}(\lambda) = \sum_{i} \sigma_{i}(\lambda) \int_{0}^{d} n_{i}(x) dx = \frac{1}{d} \left(\frac{I_{0}}{I} - 1 \right) (1 - R) \quad (\text{Eq. 1})$$

where σ_i is the wavelength-dependent absorption cross section (cm² molecule⁻¹) of the *i*th species and n_i its number density (molecule cm⁻³).

This continuous wave approach has been successfully applied in a number of laboratory and in-situ chamber experiments (Venables, 2006; Gherman, 2008; Vaughan, 2008) and is characterised by several advantageous features that are useful for field deployment: IBBCEAS combines high detection sensitivity with experimental simplicity. Based on design, instruments are very robust with good long-term mechanical and optical stability. Moreover, depending on the emission spectrum of the light source used (e.g. xenon arc lamps (Fiedler, 2003; Venables, 2006), inexpensive light-emitting diodes (Ball, 2004; Gherman, 2008; Triki, 2008), or novel supercontinuum light sources (Langridge, 2008)), IBBCEAS set-ups also possess high spectroscopic flexibility in terms of different wavelength regimes being easily accessible. The technique also offers all the advantages of a broadband method outlined above.

There are, however, three limitations of this approach which will be addressed in this report. First, despite the high brightness of some incoherent light sources, unfavourable imaging conditions cause the transmission of light through a high-finesse optical cavity to be generally lower than for laser sources (excepting supercontinuum sources, Langridge et al. (2008)). Therefore long optical cavities with modest reflectivity mirrors ($R \approx 0.99$ to 0.999) are of particular relevance for non-directional incoherent light sources (e.g. arc lamps), since they improve the signal-tonoise ratio without loss of sensitivity. The spatial resolution of long cavities (10s of metres) is still significantly better than that of conventional long-path DOAS set-ups, and localised sources of atmospheric trace constituents can still be identified with this method. Moreover, long cavities also enable air-quality studies of medium-sized (anthropogenic pollution) sources (e.g. industrial plants, airfields or roundabouts).

Secondly, all absorption methods based on optically stable cavities (CRD and CEA spectroscopy) are limited to a certain spectral range in which the cavity mirrors exhibit maximum reflectivity. Generally, the width of the high reflectivity wavelength range of the mirrors scales with the mirror reflectivity. In other words, the higher the mirror reflectivity, the narrower the range of its high reflectivity performance and thus the spectral region of the set-up's ultimate sensitivity. This condition puts a principal restriction on the broadness of cavity-enhanced absorption spectra taken with one set of mirrors. On the one hand, a wide spectral range is the key for successful detection of multiple trace constituents under the same experimental conditions. On the other hand, truly broad spectral ranges can only be achieved by using mirrors with modest reflectivity (e.g. $R \approx 0.99$ or 0.999). The corresponding decrease of sensitivity can only be compensated for by increasing the length of the cavity. For example, the sensitivity of an absorption cavity of length L formed by mirrors with R = 0.999 is the same as that of a cavity formed by mirrors with R = 0.99 and a length of 10L. Hence long optical cavities are the key to highly sensitive, true broadband absorption measurements, provided the spectral reflectivity range of the mirrors can be fully covered by the light source employed.

Thirdly, for absolute concentrations to be retrievable with IBBCEAS the mirror reflectivity must be known. Hence, independent reflectivity calibration measurements are essential. In the case of enclosed cavities, mirror reflectivities can be measured using a known amount of a calibration gas (Venables, 2006; Ball, 2004; Gherman, 2008; Vaughan, 2008). This approach is not practical for open-path configurations. This paper will outline a straightforward way of establishing the mirror reflectivity with acceptable uncertainty using an anti-reflection coated optic of known loss.

This report demonstrates that very long optically stable cavities (*ca.* 20 m length) can be constructed in an open-path configuration for monitoring atmospheric trace constituents and aerosol extinction. The main target species were NO_3 and NO_2 . The optical design of the IBBCEAS instrument, its mechanical stability and issues concerning the cavity alignment will be addressed. The performance of the instrument in an international intercomparison will be described.

1.3 Original Objectives of the TRACES Project

(A) The core objective of the project was the development of a highly sensitive spectroscopic instrument for the detection of the NO_3 radical. The target specifications were to enable its employment in atmospheric simulation chamber studies or in field campaigns. The tasks in achieving this objective were:

- Choosing, testing and optimising appropriate light sources for the instrument (xenon arc lamp versus LEDs).
- Designing and optimising an appropriate optical system of high spatial resolution that can be adapted for field use.
- Development of software to run the instrument and to analyse the spectroscopic data for quantifying NO₃ concentrations with good time resolution.
- Development of calibration approaches that can be applied in the field. Tests to determine the instruments sensitivity.

(B) The second objective was the employment of the instrument across an atmospheric simulation chamber and deployment in the field. Specific targets were:

 To demonstrate the utility of the system for directly monitoring the NO₃ radical in an atmospheric simulation chamber by studying the kinetics of the formation of NO₃ from NO₂ and O₃.

- To study the kinetics of the reaction of NO₃ with selected VOCs in an atmospheric simulation chamber.
- To deploy the system at the Cork City Council's air quality monitoring site and demonstrate the sensitivity and functionality of the system in the field.

(C) The objectives concerning the management of the project, the research outputs, and the teaching as well as outreach aspects entailed:

- Recruiting capable and qualified personnel, maintaining a focused, smoothly functioning research team, establishing clear goals for each researcher and holding regular meetings.
- Training students during the project.
- Delivering experimental results for publication. (It was envisaged that two reports would be produced, describing: (i) the instrument performance and sensitivity, particularly for atmospheric simulation chamber studies; (ii) kinetics experiments of the reaction of NO₃ with suitable VOCs, demonstrating the direct use of NO₃ concentrations in kinetics studies; and (iii) field trials of the IBBCEAS system and evaluating short time variability in the NO₃ concentration in the urban environment.
- Presenting material at conferences and workshops.
- Documenting the project progress in interim and final reports to the EPA.

Research outputs can be found in Appendix D.

2. The Instrument

2.1 General Overview

The UCC IBBCEAS NO3 monitoring instrument was built between January and May 2007. The instrument described here was designed to quantify NO3 concentrations based on its strong B←X absorption band with a maximum at 662 nm; however, the set-up is readily adapted to other wavelength regions in the visible and near ultraviolet. The instrument consists of a transmitter unit and a receiver unit, each housing one of the cavity mirrors. The two units can be separated by any arbitrary distance in an open-path configuration depending on the mirrors' radii of curvature. Schematics of the optical components of the transmitter and receiver units of the instrument are shown in Figure 2.1. The IBBCEAS instrument consists of two components - a transmitter unit that houses a light source, filter, collimating optics and the first cavity mirror, and a receiver unit that houses the second cavity mirror, a monochromator and a charge-coupled device (CCD) array as detector.

One of the important considerations for designing the IBBCEAS field instrument was the light source. In order to use high reflecting cavity mirrors (for example, $R \sim 0.9998$), a light source with high radiance is desirable. Since the length of the optical resonator is determined by the field requirements, the ability of the telescope to image the light source into the cavity is also important. Another desirable property for the light source is to have good radiance over a broad wavelength range so that different trace species can be monitored by simply choosing the appropriate wavelength range, cavity mirrors and filters. These considerations ruled out the use of light-emitting diodes (LED) and conventional xenon arc lamps for possible use with the system described in this section. Instead, a special arc lamp provided on loan from ISAS, Berlin, was used for the duration of this project. This light source is described in the following section.



Figure 2.1. The schematic of IBBCEAS NO_3 field instrument. M_1 and M_2 are the cavity mirrors. The different optical outputs of a lamp in diffuse and hot-spot modes are also displayed.



Figure 2.2. Xenon short-arc lamp operating in hot-spot mode (GLE, Berlin, Germany); photos of the complete lamp (left) and a typical profile of the discharge (right).

2.2 The Lamp

The applied xenon short-arc lamp has a novel design and was recently developed at ISAS in close cooperation with the lamp manufacturer GLE (Berlin, Germany); it is described by Welz *et al.* (2005). The new lamp is based on a conventional xenon short-arc lamp design (see the left-hand image in Figure 2.2), as used, for example, in stadium illumination, but has been optimised to operate in a so-called 'hot-spot' mode, i.e. the discharge of the lamp is characterised by the formation of a small plasma spot close to the surface of the lamp cathode, as shown in the right photograph of Figure 2.2.

The contraction of the plasma is mainly achieved by a reduced distance between the electrodes (typically less than 1 mm), an increased gas pressure of about 16 bar (cold condition), and a special temperature regime induced by optimised electrode geometries. Under normal operating conditions the inner pressure of the lamp increases to about 50 bar, and a hot spot, with a diameter of approximately 0.2 mm and a plasma temperature of about 10 000 K, develops. The lamp is operated with a nominal power of 300 W (typically 20 V and 15 A) using a DC power supply. An additional circuit produces a short

high-voltage pulse of about 30 kV to ignite the lamp. To maintain a tolerable operating temperature, the lamp is mounted in a water-cooled housing, which is integrated in a closed water loop with air cooling. The wavelength-dependent spectral radiance of the hot-spot xenon lamp is depicted in Figure 2.3 for different distances from the cathode in relation to the prominent emission lines of some hollow cathode lamps. In addition, a comparison of its spectral radiance to a commercial xenon lamp operating in diffuse mode as well as a conventional D_2 -lamp is shown in Figure 2.4.

The formation of the hot-spot results in a spectral radiance, particularly in the far ultraviolet, up to two orders of magnitude higher than that of conventional xenon arc lamps operating in diffuse mode, and about three orders of magnitude higher than that of deuterium arc lamps. The hot-spot xenon short-arc lamp provides roughly the same spectral radiance over the whole wavelength range between 190 nm and 900 nm, which is an advantage for broadband detection of several atmospheric trace species using IBBCEAS. Since the hot spot is small and is effectively a point source, imaging the spot into the optical resonator is greatly simplified.



Figure 2.3. Wavelength-dependent spectral radiance (mW cm⁻² sr⁻¹ nm⁻¹) of the xenon short-arc lamp measured in the hot-spot and at different distances from the cathode, in comparison to some selected emission lines of hollow cathode lamps.



Figure 2.4. Comparison of the wavelength-dependent spectral radiance (mW cm⁻² sr⁻¹ nm⁻¹) of (a) the xenon short-arc lamp operating in hot-spot mode (XBO 301, 300 W, GLE Berlin, Germany); (b) a commercial xenon lamp operating in diffuse mode (L 2479, 300 W, Hamamatsu, Japan); (c) a conventional D₂-lamp (MDO 620, 30 W, Heraeus, Germany).

One disadvantage of the hot-spot design of the lamp is the fact that the position of the spot is not totally stable, i.e. sporadic movements or small hops on the cathode surface are possible. Without any compensation, this would lead to large intensity fluctuations in the system. Hence, a fast, active control loop with millisecond response times was developed to compensate for variations of the hot-spot image position with respect to the centre of the first cavity mirror. For this purpose, part of the beam was coupled out of the optical path by means of a thin quartz plate and focused onto a quadrant detector. The generated signals were subsequently processed using the SpotFix program and the output was used to tilt a lightweight, plane folding mirror in front of the xenon lamp housing via piezoelectric actuators. The spot-stabilisation unit runs independently of the rest of the IBBCEAS spectrometer. A schematic of the optical set-up of the spot-stabilisation technique is shown in Figure 2.5 and a screenshot of the SpotFix program is displayed in Figure 2.6.







Figure 2.6. Screenshot of the SpotFix program used to stabilise the direction of the light beam.

2.3 The Transmitter and Receiver Units

The transmitter unit houses the short-arc xenon lamp running in the hot-spot mode described previously. The light from the lamp is imaged onto an iris using two off-axis parabolic mirrors as shown in Figure 2.7. The wavelength range is selected by placing an interference filter (Andover 650FS80-50) between the two parabolic mirrors to prevent light from the lamp outside the range of interest entering the cavity (*ca.* 610 nm to 720 nm). A fraction of the light is focused onto a quadrant detector while an image of



Figure 2.7. The transmitter unit (a). 1: short-arc xenon lamp; 2: piezo-mounted plane mirror; 3, 4: off-axis parabolic mirrors; 5: interference filter; 6: quadrant detector and control electronics; 7: telescope; 8: highly reflective cavity mirror; 9: low-loss optic assembly on translation stage; 10, 11: stainless steel pipes for broadband beam and He-Ne laser beam, respectively.



Figure 2.8. The receiver unit (b). 12, 13: stainless steel pipes for broadband beam and He-Ne laser beam, respectively; 14: highly reflective cavity mirror; 15: Teflon[®] film joint; 16: movable mirror to couple the He-Ne laser beam into the cavity; 17: colour filter (RG630); 18: focusing lens; 19: short-pass filter (cut-off ~700 nm); 20: fibre-bundle holder; 21: fibre bundle; 22: monochromator and CCD detector.

the main beam is formed in the plane of the iris. The stabilisation of the image of the hot spot (compensating for arc wandering of the lamp) is done with a feedback loop between the quadrant detector and a piezo-mounted plane mirror placed between the lamp and the first parabolic mirror (see Figure 2.7), as explained above. A telescope images the stabilised image of the spot at the iris into the centre of the open-path cavity, formed by a pair of mirrors (Layertec GmbH) with a diameter of 4 cm, a radius of curvature of 21 m, and a reflectivity of $R \sim 0.999$.

The receiver unit (see Figure 2.8) houses the second cavity mirror. Light transmitted by the cavity is filtered further with a long-pass cut-off filter (RG630 coloured glass) and a 700 nm short-pass interference filter (Thorlabs, FES0700) to ensure that light outside the mirror reflectivity range of the cavity mirror is eliminated. The light is focused into a fibre bundle (1 mm diameter) connected to the 100 μ m entrance slit of a monochromator (holographic grating (1200 lines/mm)) and imaged onto a CCD detector (Andor DV401-BV, pixel size 26 µm). The spectral resolution of the detection system was ~0.6 nm. The spectrometer wavelength scale, which was calibrated daily using a Ne pen lamp and a He-Ne laser, was accurate to about 0.001 nm. A He-Ne laser housed in the transmitter unit served as an important tool for aligning the cavity. An acquisition time of 5 s was used for all measurements.

2.4 Calibration of Mirror Reflectivity

An important experimental aspect of the open-path IBBCEA approach is the calibration of the reflectivities of the cavity mirrors so that one can retrieve absolute number densities of absorbing species (see Equation (1)). In the case of an enclosed cavity, the mirror reflectivity, *R*, can be determined from transmission spectra with and without a known amount of a calibration gas, the absorption cross section of which is known as a function of wavelength (Venables, 2006; Langridge, 2006; Gherman, 2008). With a long open-path set-up, such an approach is impractical. Instead, an anti-reflectioncoated optical substrate (L < 0.001, Layertec) of known optical loss is used to calibrate the mirror reflectivity for 630 nm < λ < 690 nm. In the open-path instrument, the low-loss optic was placed on a translation stage that was sealed in a Teflon[®] foil assembly between a cavity mirror and the steel pipe (see Figure 2.7). The optical loss of this substrate is determined in the laboratory using a tunable dye laser covering the wavelength range of interest and measuring the ring-down times of a 2 m resonator in the absence and presence of the substrate. The set-up for calibrating the low-loss optics is shown in Figure 2.9.

A mixture of two dyes in DCM (dichloromethane) and pyridine was used to get a wavelength range between



Figure 2.9. Cavity ring-down set-up for measuring the loss of a calibration substrate (not shown) placed in the optical cavity.



Figure 2.10. Cavity ring-down transients in the absence (left-hand plot) and presence (right-hand plot) of the low-loss substrate.



Figure 2.11. Linear fits (red lines) to the experimental data (blue dots) in the absence (left-hand plot) and presence (right-hand plot) of the low-loss substrate (for the pulses shown in Figure 2.10).

620 nm and 690 nm. An intensity amplifying unit is removed from the dye laser to minimise amplified spontaneous emission in the laser pulses. The pulses from the dye laser are cleaned using a spatial filter (lens-pinhole-lens system) and focused into the centre of the resonator. A photomultiplier tube (PMT) and an oscilloscope are used to collect the light exiting the cavity through the second mirror. The automated data collection and analysis are performed using a Labview[®] program. Measurements of ring-down times are recorded without the low-loss substrate in the cavity at intervals of 2 nm for the wavelength range of 624 nm to 690 nm. Then the experiment is repeated with the calibration optic placed approximately in the middle of the cavity. Figure 2.10 shows typical ring-down transients for the resonator in the absence and presence of the low-loss substrate.

Each transient curve is fitted with an exponential decay after carefully selecting the decay region between the peak and the baseline noise. The natural logarithm of the amplitude of the cavity output is linearly fitted as a function of time. Figure 2.11 displays the fits for the transients shown in Figure 2.10; the experimental data are shown as blue points and the fit is shown as a red line for each plot. Those measurements were made at 640 nm and the ringdown times were 5.38 µs (without substrate) and 1.19 µs (with substrate). If $\tau_1(\lambda)$ and $\tau_2(\lambda)$ are the ring-down times measured with and without the substrate in the laboratory resonator of length ℓ (2 m in this case), then the loss per pass (*L*) due to the substrate can be calculated from

$$L(\lambda) = \frac{\ell}{c} \left(\frac{1}{\tau_2(\lambda)} - \frac{1}{\tau_1(\lambda)} \right)$$
 (Eq. 2)



Figure 2.12. Loss spectrum of the substrate measured in the laboratory using the cavity ring-down technique (February 2008, after cleaning the substrate). Error bars are from the standard deviations of seven measurements.



Figure 2.13. Typical cavity spectra measured with (red line) and without (green line) the low-loss substrate present in the cavity. Each intensity spectrum shown in this figure is averaged over twelve 1 s spectra (1 m cavity, $R(662 \text{ nm}) \sim 0.9985$).

where c is the speed of light in air. The loss of the optical substrate measured in the laboratory is shown in Figure 2.12; the error bars represent the standard deviations of seven measurements.

Typical cavity transmissions with (red line) and without (green line) the low-loss substrate in the resonator are shown in Figure 2.13.

The mirror reflectivity, $R(\lambda)$, is then calculated using

$$R(\lambda) = 1 - \left[\frac{I_1(\lambda)}{I_0(\lambda) - I_1(\lambda)} L(\lambda) \right]$$
 (Eq. 3)

where I_0 and I_1 are the averaged spectra acquired with and without the low-loss substrate in the cavity, respectively. An example of the laboratory-measured reflectivity curve (corresponding to the transmission spectra displayed in Figure 2.13) is shown in Figure 2.14 (blue diamonds); the red line is a second-order polynomial fit to the measured values of *R*.

There are uncertainties associated with the outlined calibration of *R*, some of which are difficult to quantify: first, the CRD loss measurement of $L(\lambda)$ is performed with a short cavity. Even though the measured loss should, to a first approximation, be independent of the cavity length, possible systematic errors cannot be easily estimated without CRD measurements using a long cavity. Secondly, the loss of the calibration optic is measured using a beam travelling along the optical axis of the cavity. The broadband application, however, uses the full diameter

of the cavity mirrors and integrates over all off-axis modes of the resonator. The inherently different average residence time of photons propagating off axis in the cavity causes R in Equation (1) to represent an effective (empirical) reflectivity (Triki, 2008), which is generally slightly lower for broadband applications than for on-axis CRD. The on-axis loss calibration of the substrate and its subsequent application in a cavity, where the full area of the optic is utilised, leads to systematic errors which are again difficult to quantify without additional information on mode-dependent loss mechanisms in the cavity. The discrepancy between the true broadband effective R and the reflectivity found by the calibration procedure outlined here is expected to be small (a few percent).

It can be noted that the retrieved reflectivity was not critically dependent on the orientation of the low-loss substrate. Deliberately misaligning the substrate by up to $\pm 2.5^{\circ}$ between the substrate's normal and the cavity axis resulted in errors that are small in comparison to the uncertainty in $L(\lambda)$. Hence, the accuracy with which *R* can be determined is not compromised by small misalignments. This insensitivity with respect to misalignment is a result of the broad anti-reflection coating of the substrate.



Figure 2.14. Experimentally-derived reflectivity curve for the cavity mirrors.

2.5 Data Acquisition and Analysis

A data-acquisition and analysis program was created using Matlab[®] algorithms in a Labview[®] environment. Data are acquired from the CCD and saved in ASCII file format using this software. A screenshot of the program interface is shown in Figure 2.15. This software has a user interface where the experimental parameters can be provided prior to data collection and saved in the header of the subsequent ASCII file. The CCD-acquisition parameters can also be controlled using this interface.

Spectral windows of 10 nm to 15 nm were used to quantify the absorption of NO_3 and NO_2 . These wavelength ranges were selected to include appropriate absorption features of the target molecule while avoiding significant absorption structures from other species. The absorption of NO₃ was analysed between 658 nm and 668 nm, and the NO₃ concentrations were quantified using absorption cross sections from Yokelson *et al.* (1994). Those cross sections, valid for 298 K, were scaled to the recorded temperature using the temperature dependence of the NO₃ absorption reported by Orphal *et al.* (2002). The analysis of NO₂ was carried out in the 630 nm to 645 nm window to minimise water vapour interference. Reference NO₂ absorption cross sections from Burrows *et al.* (1998) were used. All reference spectra were convoluted with the instrument function of approximately 0.6 nm. For spectral fitting, the extinction coefficient, $\varepsilon(\lambda)$, is described by:

$$\mathcal{E}(\lambda) = a_0 + a_1 \lambda + a_2 \lambda^2 + a_3 \sigma_{H_2O}(\lambda) + a_4 \sigma_{NO_3}(\lambda) + a_5 \sigma_{NO_3}(\lambda)$$
(Eq. 4)



Figure 2.15. Screenshot of the data-acquisition and analysis software.

where σ_i is the reference absorption cross section (cm² molecule⁻¹) of species *i*, and the coefficients a_3 to a_5 are the number densities of these species. The term $a_0 + a_1\lambda + a_2\lambda + a_3\lambda + a_4\lambda + a_$ $a_2\lambda^2$ describes an unspecified background signal such as that resulting from the aerosol. A linear algebraic method known as singular value decomposition (SVD) was used to determine the parameters a_i from the extinction spectra obtained with Equation (1). The spectral range covered for each measurement would comprise over 100 extinction values as a function of wavelength, constituting 100 equations of the type of Equation (4). With only six unknown parameters the set of equations is greatly overdetermined. In SVD, an $n \times p$ matrix A is constructed from Equation (4), where *n* is the length of λ and *p* is the number of components to be retrieved (p is 6 in the present case):

$$A = \begin{bmatrix} 1 & \lambda_{1} & \lambda_{1}^{2} & \sigma_{H_{20}}(\lambda_{1}) & \sigma_{NO_{3}}(\lambda_{1}) & \sigma_{NO_{2}}(\lambda_{1}) \\ 1 & \lambda_{2} & \lambda_{2}^{2} & \sigma_{H_{20}}(\lambda_{2}) & \sigma_{NO_{3}}(\lambda_{2}) & \sigma_{NO_{2}}(\lambda_{2}) \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ \vdots & \ddots & \vdots & \ddots & \vdots & \vdots \\ 1 & \lambda_{n} & \lambda_{n}^{2} & \sigma_{H_{20}}(\lambda_{n}) & \sigma_{NO_{3}}(\lambda_{n}) & \sigma_{NO_{2}}(\lambda_{n}) \end{bmatrix}$$
(Eq. 5)

Singular value decomposition uses this rectangular matrix of *A* to calculate a set of three matrices as follows. $A_{n \times p} = US_{n \times p}V^{T}{}_{p \times p}$, where the columns of *U* are the left singular vectors, *S* has 'singular' values and is diagonal (it has the same dimension as *A*) and *V*^T has rows that are the right singular vectors. Also, $U^{T}U = I_{n\times n}$ and $V^{T}V = I_{p\times p}$ (i.e. *U* and *V* are orthogonal matrices). Calculating the SVD consists of finding the eigenvalues and eigenvectors of *AA*^T and *A*^T*A*. The eigenvectors of *A*^T*A* make up the columns of *V*; the eigenvectors of *AA*^T make up the columns of *U*. The singular values in *S* are square roots of eigenvalues from *AA*^T or *A*^T*A*. The singular values are the diagonal entries of the *S* matrix and are arranged in descending order. If the matrix *A* is a real matrix, then *U* and *V* are also real.

A Matlab[®] routine for SVD returns *U*, *S*, and *V*. A matrix *W* is calculated using W = (1/S), which is a diagonal matrix. Then the coefficients are calculated as $a_i = V * W * (U^T * \varepsilon)$; where * denotes the matrix product. The covariance matrix needed to derive the error of the unknown parameters is given by $V * W^2 * V^T$ and can be readily calculated. Note that *a* is a column vector of length *p*, and α is a column vector of length *n*. Coefficients a_4 and a_5 correspond to the number densities of NO₃ and NO₂. The uncertainties of the coefficients were calculated as

$$\Delta_a = S \sum \left[\frac{(A * a - \varepsilon)^2}{n - p} \right] * \operatorname{diag} \left(V * W^2 * V^T \right) \quad (\text{Eq. 6})$$

3. The NO₃ Intercomparison Campaign

3.1 Introduction

From June 9 to June 21 2007, the newly built instrument participated in an NO₃/N₂O₅ intercomparison in the SAPHIR (simulation of atmospheric photochemistry in a large reaction) chamber (Figure 3.1) at the Forschungszentrum Jülich in Germany. This intercomparison, which included established research groups in atmospheric science, was a unique and outstanding opportunity to test and validate the University College Cork system in a controlled environment against other techniques. The objective of the intercomparison was to improve the quality of atmospheric measurements of the NO3 radicals and N₂O₅ in accordance with the key objective of the ACCENT quality assurance scheme. The participants and the instruments at the campaign are summarised in Table 3.1 (See Appendix A). A variety of experiments were carried out in the chamber to test the response of the different systems to potential interferences, particularly NO₂, H₂O, and aerosols. In addition, several oxidation experiments of biogenic VOCs were carried out. A summary of the 10 experiments performed during the intercomparison is given in Table 3.2.



Figure 3.1. Photograph of the SAPHIR chamber at the Forschungszentrum Jülich (Germany).

Principal investigator	Institution	Country	Technique
Theo Brauers Hans-Peter Dorn	Forschungszentrum Jülich	Germany	Multi-pass DOAS
Steven Brown	NOAA	USA	CRDS
John Crowley	MPI Mainz	Germany	CRDS
Steven Ball	University of Leicester	UK	BBCRDS
Ronald Cohen	University of California, Berkley	USA	Laser induced fluorescence (LIF)
William Simpson	University of Alaska, Fairbanks	USA	CRDS
Ulrich Platt	Institut für Umwelt Physik	Germany	CE-DOAS
Albert Ruth Dean Venables	University College Cork	Ireland	IBBCEAS

Table 3.1. Summary of the groups and techniques measuring NO₃ at the SAPHIR intercomparison.

Date	Experiment no.	Description
9 June 07	1	NO ₂ interference and preliminary tests; chamber dry
10 June 07	2	Influence of water on retrieval of NO ₃ concentrations
11 June 07	3	Ambient air with added NO_2 and O_3
12 June 07	4	Clean air and photolysis experiment (opening chamber roof)
13 June 07	4c	Photolysis experiment continued (higher NO ₃ levels)
14 June 07	5	Reaction of butanal and NO ₃
15 June 07	6	Influence of inorganic aerosol $(NH_4)_2SO_4$
16 June 07	7	Limonene oxidation
18 June 07	8	Isoprene oxidation with seed aerosol
20 June 07	9	<i>B</i> -Pinene oxidation (dry)
21 June 07	10	B-Pinene oxidation (humid)

Table 3.2. Summary of the experiments during the intercomparison. NO_3 was formed in all the experiments by adding NO_2 and O_3 to the chamber.

Because the intercomparison involves the data from several different groups, a full presentation of the results will not be possible until the full intercomparison papers have been published (Dorn, 2008; Fuchs, 2008), although a preliminary view of the data is shown in the poster in Appendix A. However, a preliminary summary of the performance of the IBBCEAS retrieval of NO₃ and NO₂ concentrations is presented here. This section is followed with a detailed description of the installation and calibration of the IBBCEAS system, as well as the analysis of the IBBCEAS spectra, following which the results of one of the days of the campaign (15 June 2007) are presented in which the chamber atmosphere was reasonably representative of the lower troposphere.

The results of the IBBCEAS NO_3 correlation against one of the established techniques are presented in Table 3.3 (See Appendix B). The correlation between the two systems is clearly very good over a very large number of observations.

In general, the IBBCEAS measurements tended to record a slightly higher value than this and other techniques, giving an average 11% higher value than the other system compared in Table 3.3. It is also not clear if the higher IBBCEAS measurements result from a calibration issue of the IBBCEAS system, NO3 concentration gradients in the chamber (the IBBCEAS system probed the centre of the chamber, whereas most other techniques extracted chamber samples from the bottom of the chamber), or if losses occurred on the inlet systems of the other techniques. In the photolysis experiments, the roof of the SAPHIR chamber was opened to allow in daylight, resulting in the very rapid loss of NO₃ inside the chamber. These conditions present an excellent test of the time response of the different instruments and the retrieved NO₃ concentrations under conditions of zero NO₃. For these measurements, the IBBCEAS system retrieved an average value of -0.5 pptv, with a precision of 1.1 pptv.

Date	Slope	Intercept	R	N
09 June	1.08 ± 0.01	0.0 ± 0.2	0.99	357
10 June	1.33 ± 0.01	4.1 ± 0.4	0.99	298
11 June	1.24 ± 0.01	1.1 ± 0.2	0.99	363
12 June	1.05 ± 0.01	-0.6 ± 0.3	0.99	479
13 June	1.25 ± 0.01	1.8 ± 0.7	0.99	233
14 June	0.91 ± 0.01	-0.6 ± 0.1	0.99	476
15 June	1.20 ± 0.01	-1.7 ± 0.2	0.99	460
16 June	1.06 ± 0.01	2.0 ± 0.1	0.99	1728
18 June	1.03 ± 0.01	0.2 ± 0.1	0.99	854
20 June	1.20 ± 0.01	-6.3 ± 0.7	0.99	523
21 June	1.07 ± 0.01	-0.4 ± 0.1	0.98	521
ALL	1.11 ± 0.01	0.5 ± 0.1	0.99	6292

Table 3.3. Summary of the correlation of the IBBCEAS measurements of NO_3 against one of the established NO_3 systems. *R* is the regression coefficient and *N* is the number of observations.

Table 3.4. Summary of the groups and techniques monitoring NO₂ at the SAPHIR intercomparison.

Principal investigator	Institution	Country	Technique
Theo Brauers Hans-Peter Dorn	Forschungszentrum Jülich	Germany	Chemiluminescence Multi-pass DOAS
Steven Brown	NOAA	USA	CRDS
Steven Ball	University of Leicester	UK	BBCRDS
Ronald Cohen	University of California, Berkley	USA	LIF
Albert Ruth Dean Venables	University College Cork	Ireland	IBBCEAS

Since NO_2 absorbs throughout the visible part of the spectrum, it is also possible to retrieve concentrations of NO_2 and NO_3 simultaneously. Table 3.4 summarises the groups that retrieved NO_2 concentrations during the intercomparison. The correlation between the IBBCEAS results and the measurements of the SAPHIR chemiluminescence detector is shown in Table 3.5. The

IBBCEAS system retrieved slightly higher values of NO₂ than the chemiluminescence detector; with the exception of a few days, notably 10 June, the correlation between the two systems is very good. When NO₂ was not present in the chamber, the IBBCEAS system recorded an average concentration of -0.2 ppbv with a precision of 0.5 ppbv.

Date	Slope	Intercept	R	N
09 June	1.19 ± 0.08	-0.93 ± 0.18	0.95	169
10 June	0.95 ± 0.12	0.10 ± 0.22	0.42	119
11 June	0.86 ± 0.02	1.11 ± 0.15	0.99	150
12 June	1.00 ± 0.01	-0.03 ± 0.02	0.97	305
13 June	1.51 ± 0.01	0.40 ± 0.04	0.99	428
14 June	1.12 ± 0.08	-0.14 ± 0.05	0.98	188
15 June	0.66 ± 0.02	-0.74 ± 0.05	0.91	190
16 June	1.04 ± 0.00	0.42 ± 0.05	0.90	331
18 June	1.08 ± 0.00	-1.28 ± 0.09	0.99	307
20 June	1.33 ± 0.00	-0.28 ± 0.10	0.99	185
21 June	1.22 ± 0.00	-0.73 ± 0.08	0.98	182
ALL	1.17 ± 0.00	-0.32 ± 0.02	0.99	2992

Table 3.5. Summary of the correlation of the IBBCEAS measurements of NO_2 against the SAPHIR chemiluminescence detector. *R* is the regression coefficient and *N* is the number of observations.

3.2 Installation of the IBBCEAS Instrument

Figure 3.2 shows the inside of the transmitter and receiver units before installation. The transmitter and receiver units were each equipped with a 1 m stainless steel pipe (diameter 57 mm) pointing from the cavity mirrors along the optical axis of the cavity. Each pipe was mounted to the unit's chassis to support its weight (see Figure 3.2). A seal was made between the pipes and the adjustable mirror mounts of the cavity mirrors using flexible Teflon[®] foil in each unit. The pipes served three purposes: first, they allowed the mirrors to be purged with an inert gas to keep the mirrors clean. The purge gas in the present case was N₂ at a flow rate of *ca.* 10 dm³ min⁻¹. Purging the mirrors reduced the effective cavity length *L* to 18.27 \pm 0.20 m. Secondly, on the receiver side of the set-up the pipe reduced stray light entering the detection system. Thirdly, the pipes were necessary to attach the instrument to the SAPHIR chamber and to make a seal with its Teflon[®] wall. Apart from the pipes for the broadband light beam, two smaller pipes (diameter 25 mm) were also used to form openings for the He-Ne laser beam. The small pipes were sealed on one side with a simple optical window.



Figure 3.2. Inside the transmitter unit (right-hand photograph) and receiver unit (left-hand photograph) before installation in the SAPHIR chamber. M is the high reflectivity dielectric mirror.



Figure 3.3. Positions of the transmitter unit (left-hand photograph) and receiver unit (right-hand photograph) on top of the Jülich DOAS system inside the SAPHIR chamber.

The cavity was aligned using a He-Ne laser beam passing through two pinholes in each of the units to define a secondary axis parallel to the cavity axis. For coarse alignment, the cavity mirror on the receiver side was removed. The He-Ne laser beam was sent along the secondary axis from the transmitter unit to the receiver unit, where it was directed onto the cavity axis and to the centre of the high reflectivity mirror in the transmitter unit. The cavity mirror in the transmitter unit was adjusted to reflect the laser beam back onto itself. All optics inside the chassis of the receiver unit rested on a home-made x, y, ztranslational stage which could also be rotated about the azimuthal and polar angles, enabling all relevant degrees of freedom to be adjusted in order to align the receiver unit with respect to the transmitter unit. The second cavity mirror was then put back into place in the receiver unit and the He-Ne laser beam was reflected back onto itself again. By removing the interference filter in the transmitter unit, spectrally broad light from the arc lamp was allowed into the cavity and the telescope was adjusted to focus the image of the hot spot in the centre of the SAPHIR chamber. The optical filters were then put into place and the cavity mirrors were fine-tuned to optimise the intensity of the cavity transmission once an initial transmission was observed. At optimum alignment it was even necessary to attenuate the light to avoid saturating the CCD detector (which indicates that even higher reflectivity mirrors could be used with this set-up to further improve the sensitivity). The transmitter and receiver units were mounted to a rigid frame on top of a permanently installed ultraviolet multi-pass DOAS system, which itself rested on a very heavy concrete block that was largely decoupled from the SAPHIR chamber. The mechanical stability of the set-up was excellent – the IBBCEAS system ran without any substantial realignment of the cavity over the 12 days of the campaign. Figure 3.3 shows the positions of the transmitter and receiver units inside the SAPHIR chamber.

3.3 Calibration of the Mirror Reflectivity

The calibration of mirror reflectivity during the NO_3/N_2O_5 intercomparison campaign was performed in the morning of each day. The average of 100 intensity spectra at 5 s integration times was recorded. The low-loss substrate was then introduced into the cavity by moving the translation stage and the average of another 100 spectra was recorded. Figure 3.4(a) shows the intensities (units: 10^6 counts) of the cavity transmission spectra with (red line) and without (black line) the optical substrate in the cavity.



Figure 3.4. (a) Typical transmission spectra of the cavity (unit: 10^6 counts) containing clean air only (l_0 – the black line), and with a low-loss substrate in the cavity (l_1 – the red line). The spectra are the average of 100 spectra each with a 5 s acquisition time. The γ - and B-band of O₂ at around 624 nm and 687 nm are the only absorption features in this spectrum. (b) The spectrum of the loss, $L(\lambda)$, of the anti-reflection coated substrate measured with pulsed CRDS in a 2 m cavity. The error bars correspond to the 1σ standard deviation of seven measurements of *L*. (c) The average mirror reflectivity, $\langle R \rangle$, of 11 individual reflectivity measurements taken on each day of the campaign. The error bars represent the corresponding 1σ standard deviation.

The loss of the substrate, $L(\lambda)$, was determined as described in Section 2.4 and the measured loss as a function of wavelength is shown in Figure 3.4(b). The error bars in the figure are based on the reproducibility of seven loss measurements, where the cavity was realigned each time. Reflectivity calibration measurements were performed daily during the campaign and the average of 11 of these reflectivity measurements, $\langle R \rangle$, is shown in Figure 3.4(c).

3.4 Other Instruments in SAPHIR Used for Analysis and Comparison

3.4.1 LP-DOAS

NO₃ was measured by a long path differential optical absorption spectroscopy (LP-DOAS) with a multiple reflection set-up (Bossmeyer, 2006). Light from a xenon arc lamp (OSRAM, XBO 75W/2) was directed into a multi-reflection cell of 20 m base length, which was set up along the axis of the cylindrical SAPHIR chamber. After 48 passes, equalling an optical path length of 960 m, the light was dispersed by a Czerny-Turner spectrograph with a blazed holographic grating (Jobin Yvon, HR 460). Absorption spectra were recorded with a resolution of 0.4 nm in the range between 617 nm and 670 nm using a photodiode array (Hamamatsu, S3904, 1024 pixels). The detector array was connected to a computer via a controller (Hoffmann Messtechnik). Mixing ratios of NO₃ derived from the DOAS analysis procedure are based on the reference data of Yokelson et al. (1994).

3.4.2 Chemiluminescence Analyser

NO, NO₂, and O₃ mixing ratios were measured with an Eco Physics, CLD 780TR chemiluminescence analyser (Rohrer, 1998). NO was detected after reaction with an excess of O₃, and the sum of NO and NO₂ was detected after photolytic conversion of NO₂ (Eco Physics PLC760). O₃ was detected after reaction with an excess of NO. The analyser's detection limits were 5 pptv and 10 pptv with accuracies of 5% and 10% for NO and NO₂, respectively, and for an acquisition time of 90 s.

3.4.3 Hygrometer

The chamber's water vapour content was measured with a dew point hygrometer (General Eastern, 1311DR) with a detection limit of 50 ppmv in a sampling time of three minutes.

3.5 Analysis of the Spectra

Spectral data were analysed as described above using the singular value decomposition of Equation (4). The fitting routine allows a small shift, $\Delta \lambda$, in the wavelength of the reference spectra ($\lambda' = \lambda + \Delta \lambda$). The second-order polynomial term in Equation (4) accounts for the baseline offset of the extinction spectrum, which could arise from the scattering from aerosols, fluctuations in the lamp intensity, and other unspecified loss processes. The linear component, $a_1\lambda$, of the polynomial function largely accounts for the absorption of the Chappuis band of O₃, whose broad, unstructured absorption covers the spectral region of interest. Explicitly including the O_3 absorption with an additional term $a_6 s_{O_3}$ in Equation (4) did not significantly improve the fit to the measured extinction nor did the values of a6 represent meaningful number densities of O3. Thus, O3 concentrations cannot be easily determined with the analysis procedure outlined here. The results from the SVD approach did not differ appreciably from those obtained with a non-linear Levenberg-Marquardt routine. Although SVD analysis depends on the size of the fit range, there is no start parameter selection that may influence the fit results, and the inherent degree of correlation of the parameters in Equation (4) is not affected by the analytical approach. Moreover, the SVD analysis was much faster than iterative methods, an important practical consideration for the large data sets generated.

Standard uncertainty propagation was used to estimate the uncertainty of the retrieved number densities. The uncertainty in the measured sample extinction, $\Delta \varepsilon$, is given by

$$\Delta \varepsilon^2 = \left| \frac{\mathrm{d}n_i}{\mathrm{d}(1-R)} \right|^2 \Delta (1-R)^2 + \left| \frac{\mathrm{d}n_i}{\mathrm{d}L} \right|^2 \Delta L^2 + \left| \frac{\mathrm{d}n_i}{\mathrm{d}I_0} \right|^2 \Delta I_0^2 \quad (\text{Eq. 6})$$

where the fractional uncertainties of the parameters are estimated to be 8% for (1 - R), 1% for the effective cavity length *L* and 5% for I_0 . The uncertainty in the measured extinction is therefore *ca.* 10%. Furthermore, spectral analysis using Equation (4) contributes additional uncertainties to the retrieved concentrations of absorbing species. These uncertainties arise through the dependence of the fit on the spectral window (3%) and the uncertainties of the reference absorption cross sections, which are ca. 10% for the NO3 absorption cross section (Yokelson, 1994) and ca. 3% for the NO2 absorption cross section (Burrows, 1998). Assuming that the uncertainty of the reference spectra lies in their magnitude across the spectral window, contributions from species apart from those of interest can be ignored in the fit, since the fitting parameter yielding the associated number density of the species should scale accordingly. Cross-sensitivities in the fit between different species only become important close to the detection limit of the target species, where the precision dominates the error in the number density retrieval. The overall uncertainty in the retrieved number density of species *i*, $n_{i,fit}$, is then given by Equation (7).

$$\Delta n_{i,\text{fit}}^{2} = \Delta (\text{range})^{2} + \left| \frac{\mathrm{d}n_{i}}{\mathrm{d}\varepsilon} \right|^{2} \Delta \varepsilon^{2} + \left| \frac{\mathrm{d}n_{i}}{\mathrm{d}\sigma_{i}} \right|^{2} \Delta \sigma_{i}^{2} \quad (\text{Eq. 7})$$

The overall uncertainty in NO_3 concentrations is 18%, while NO_2 concentrations have a 14% uncertainty.

Fluctuations in the light intensity degraded the precision of the retrieved concentrations on the timescale of the measurements. Independently monitoring the lamp output as a basis for normalising cavity spectra should improve measurement precision, but was not implemented in the intercomparison experiment. In the absence of direct measurements of lamp intensity, the effect of such fluctuations was substantially reduced by normalising cavity spectra based on the intensity transmitted through the cavity at 684 nm, a region with insignificant molecular absorption. For each data set of approximately 5500 spectra, the time series of the intensity at 684 nm was smoothed by fitting a cubic spline to the plot (see Figure 3.5(d)), in effect discarding short-term lamp intensity fluctuations. The ratio of the intensity at 684 nm for each individual spectrum to that of the smoothed value was then used to scale the overall intensity spectrum, I, before the extinction coefficient was calculated. This procedure corrected short-term fluctuations, while longer term drifts in the transmitted intensity (by introduction



Figure 3.5: (a) Time series of mixing ratios of NO₃ measured by IBBCEAS (black data) and LP-DOAS (red data). (b) Time series of mixing ratios of NO₂ measured by IBBCEAS (black data) and the chemiluminescence analyser (red data). (c) Time series of number densities of H₂O measured with a dew point hygrometer. (d) Cavity transmission (unit: 10^6 counts) at 685 nm (black line) and the cubic spline through the data (blue line). The SAPHIR chamber event sequence on 15 June 2008 was: 6:11 - fan on; 6:15 - 180 ppbv of O₃ added; 6:22 - 1.5 ppbv of NO₂ added; 8:33 - fan off (1); 8:52 - fan on (2); 8:55 - flushing of chamber with clean humid air started (2); 9:52 - flushing of chamber ended (3); 9:53 - 80 ppbv of O₃ and 2 ppbv of NO₂ added (3); 9:56 - 9 ppbv of NO₂ added (3); 10:45 - addition of (NH₄)₂SO₄ aerosol started (4); 11:25 - addition of aerosol ended ($5 \mu g m^{-3}$) (5); 12:12 - 9 ppbv of NO₂ added (6); 12:30 addition of (NH₄)₂SO₄ aerosol started (7); 14:30 - addition of aerosol ended ($12 \mu g m^{-3}$) (8); 17:00 - fan off. The numbers in parentheses describe the numbered times indicated by vertical gridlines.

of aerosols, for instance) did not erroneously scale the spectra and the corresponding retrieved concentrations. In the instrument that was later deployed in the field, modifications were made to record the lamp intensity directly using the quadrant detector in order to normalise the intensity spectra.

Figure 3.5 presents detailed results for the experiment performed on 15 June 2007. The SAPHIR chamber event sequence on 15 June 2008 was:

- 6:11 fan on 6:15 – 180 ppbv of O_3 added 6:22 – 1.5 ppbv of NO_2 added 8:33 – fan off (1) 8:52 – fan on (2) 8:55 – flushing of chamber with clean humid air started (2) 9:52 – flushing of chamber ended (3) 9:53 – 80 ppbv of O_3 and 2 ppbv of NO_2 added (3) 9:56 – 9 ppbv of NO_2 added (3) 10:45 – addition of $(NH_4)_2SO_4$ aerosol started (4)
- 11:25 addition of aerosol ended (5 μ g m⁻³) (5)

12:12 – 9 ppbv of NO₂ added (6) 12:30 – addition of $(NH_4)_2SO_4$ aerosol started (7) 14:30 – addition of aerosol ended (12 µg m⁻³) (8) 17:00 – fan off.

The numbers in parentheses describe the numbered times indicated by vertical gridlines in Figure 3.5. This day was chosen because of the range of NO_3 concentrations produced in the chamber, the presence of water vapour interference and the presence of $(NH_4)_2SO_4$ aerosol. The NO_3 and O_3 concentrations were maintained between 100 ppbv and 200 ppbv except during periods when the chamber was being purged. This experiment thus serves as a suitable proxy for the real atmosphere where multiple extinction processes occur (Dorn, 2008; Fuchs, 2008).

The retrieval of NO₃ and NO₂ concentrations is complicated by a water absorption band that overlaps the strong NO₃ absorption at 662 nm and, to a lesser extent, the 630 nm to 645 nm window used to quantify NO₂ concentrations. Apparent deviations from the Beer–Lambert law arise because the water lines are much narrower than the resolution of the monochromator. A procedure to account for the multi-exponential ring-down decay of the unresolved absorption of water vapour was reported by Bitter and co-workers for the BBCRDS technique (Bitter, 2005). In the following, the approach for treating this effect in the IBBCEAS spectra is described.

To properly describe the absorption of water vapour, a concentration-corrected absorption cross section, $\sigma'_{H_{0}0}$, was calculated for each spectrum (that is, for each water concentration that occurred in the chamber). Starting with an arbitrary synthetic spectrum, $I_0(\lambda)$, at a wavelength interval of 0.001 nm, Equation (1) was used to calculate the high-resolution cavity transmission spectrum, $I(\lambda)$, using the water absorption data from the HITRAN database (Rothman, 2005), the water vapour concentration in the chamber and the calibrated mirror reflectivity spectrum. $I(\lambda)$ was then convoluted with the 0.6 nm resolution of our monochromator and Equation (1) was applied a second time to retrieve the concentration-corrected absorption cross section, $\sigma'_{\rm H,O}$, for water vapour at that concentration. A different $\sigma'_{\rm H,O}$ was thus calculated for each spectrum and the entire process was automated. The effect of non-Beer-Lambert behaviour on the water vapour absorption cross section is illustrated in Figure 3.6, together with the results obtained by directly convoluting the water cross sections from HITRAN (corresponding to the low concentration limit). As expected, apparent



Figure 3.6: Black line – absorption spectrum of water vapour calculated by convoluting HITRAN cross sections (Rothman, 2005) with the spectrometer's resolution of 0.6 nm. Red line – spectrum of the effective H_2O cross sections calculated with Equation (1) as outlined in the text using the parameters: number density of water = 2.72×10^{17} molecule cm⁻³, cavity length = 18.27 m, spectrometer resolution = 0.6 nm, reflectivity spectrum as measured on 15 June 2007.

deviations from Beer–Lambert behaviour are greatest for large absorption features. In principle, the same procedure should be applied to the structured NO_2 absorption cross sections, but the small absorption of NO_2 in this region made this unnecessary in practice.

The correction procedure depends on independently measuring the water vapour concentrations. It should also be possible to retrieve the water vapour concentrations directly, using, for example, a lookup table correlating water concentrations with the magnitude of prominent absorption features. This procedure would not only eliminate the need for an independent water vapour measurement, but also provide the water vapour concentration as a routine result. Nevertheless, such a procedure is not trivial as it would have to account for both the concentration dependence of the water absorption and the effect of other extinction processes.

Cavity transmission spectra are shown in Figure 3.7(a) of clean synthetic air in the chamber (black line, taken at 4:09 a.m.), and of a simulated high nitrogen oxide atmosphere in the chamber (red line, taken at 9:58 a.m.). The extinction spectrum for the NO₃ window derived



Figure 3.7. (a) Typical cavity transmission spectra (unit: 10^6 counts) in the absence (black line) and presence (red line) of water vapour and NO₃ taken with 5 s acquisition time at 9:58 a.m. on 15 June 2007. (b) Corresponding extinction (solid circles) in the region between 658 nm and 668 nm; the red and blue lines in this panel represent SVD fits of Equation (4) to the experimental data with and without using corrected H₂O cross sections, respectively (compare Figure 3.6). The two lower panels show the corresponding fit residuals $\Delta \varepsilon$. (c) Extinction (solid circles) shown in panel (b) without the water vapour contribution and the corresponding fit (green line). The mixing ratio of NO₃ was determined to be ~20.7 pptv. The lower panel shows the corresponding fit residuals, $\Delta \varepsilon$.

from the intensity measurements in Figure 3.7(a) is shown in Figure 3.7(b). The number density of water was 4×10^{17} molecule cm⁻³ (60% relative humidity). Equation (4) was fitted to the extinction data with the concentration-corrected water cross sections (red line) and the uncorrected (low concentration limit) cross sections (blue line). The quality of the fit to the measured spectrum improves markedly when using the corrected water absorption cross section: the 1σ rms of the fit residual obtained using the corrected water absorption cross section is about 0.55 \times 10⁻⁹ cm⁻¹, compared to 2.03×10^{-9} cm⁻¹ from the uncorrected water cross section. Properly accounting for the water absorption is particularly important at low NO3 concentrations because typical atmospheric concentrations of water vapour mask the NO₃ absorption. After subtracting the fitted water absorption from the measured spectrum, the NO₃ absorption peak is readily distinguished from the background extinction (Figure 3.7(c)). The NO3 concentration obtained in this example was 20.7 \pm 1.0 pptv and that of NO₂ was 5 ± 1 ppbv.

The time dependence of the concentrations of NO₃ and NO₂ during the chamber experiment on 15 June 2007 is shown in Figures 3.5(a) and (b). The atmosphere in the chamber was initially dry (-58°C dew point) and free of aerosol. NO3 was formed at moderately high concentrations by adding 1.5 ppbv of NO₂ in the presence of approximately 180 ppbv of O_3 (see caption of Figure 3.5). The precision of temporally close measurements is around 1.3 pptv when the concentration of NO₃ was around 100 pptv, while the precision for NO₂ is about 2 ppbv when the concentration was 5 ppbv, which is worse than that of typical chemiluminescent NO_x detectors, although the 5 s sampling time is also an order of magnitude smaller (about 1 minute for the Forschungszentrum Jülich chemiluminescence analyser). The chamber was purged with synthetic air at 60% relative humidity between 8:55 a.m. and 9:52 a.m., resulting in a sharp decrease in the concentrations of both NO3 and NO2 and rapid humidification of the chamber atmosphere (Figure 3.5(c)). NO₃ was essentially absent from the chamber between 9:30 a.m. and 9:52 a.m., when an average concentration

of 0.4 pptv was found with a precision of 0.9 pptv. During the same time, slightly negative NO_2 concentrations were retrieved. Although these negative values were close to the experimental uncertainty, the retrieval of concentrations of NO_2 seems to slightly depend on the water content for the fitting range used. Further loading of O_3 and the addition of 9 ppbv of NO_2 at 9:56 a.m. rapidly regenerated NO_3 .

(NH₄)₂SO₄ aerosol was injected into the chamber between 10:45 a.m. and 11:25 a.m. to a loading of 5 μ g m⁻³. A constant rate of decrease of NO3 was observed over this interval and arises from the hydrolysis on particles of N_2O_5 , with which NO_3 is in equilibrium (Brown, 2007). The rate of NO₂ loss in the humid atmosphere depended on the NO2 concentration but no effect of particle loading on NO₂ concentrations was apparent in our data. A further 9 ppbv of NO2 was injected into the chamber at 12:12 p.m. The NO3 concentration responds with a sharp initial decrease, resulting from the shifting of the equilibrium NO₂ + NO₃ \Leftrightarrow N₂O₅ to favour N₂O₅ formation. This decrease was followed by a rapid increase in the NO3 concentrations to over 100 ppbv as NO2 reacted with excess O₃ to produce more NO₃. A second loading of aerosol to 12 µg m⁻³ was added between 12:30 p.m. and 14:30 p.m. NO₃ concentrations again decreased over this period. The slower decay of NO3 in this case is attributed to the higher concentration of N2O5 acting as a source of NO₃.

The retrieved NO₃ concentrations from the IBBCEAS system can also be compared with the data from the established DOAS technique (Figure 3.5(a)). The agreement over the 10 hours of the experiment is very good both at high concentrations and at low concentrations; neither aerosols nor water vapour affected the NO₃ concentrations retrieved with either technique. The results are highly correlated (Dorn *et al.*,2008) and differ mainly in the acquisition time (5 s versus 90 s) and the precision of the measurements. Reasonable agreement in the measured NO₂ concentrations is also achieved between IBBCEAS and the chemiluminescence detector (Figure 3.5(b)). Both instruments yield similar NO₂ concentrations following the introduction of NO₂ at 9:56 a.m. and 12:12 p.m. A small discrepancy of about

1 ppbv is apparent at the start of the experiment and with the flushing of the chamber. The difference is usually within the combined uncertainty of both methods. Careful selection of the NO_2 retrieval window in the IBBCEAS experiments may be able to reduce or eliminate the crosssensitivity to water vapour (or O_3) absorption, but this is beyond the scope of this study.

3.6 Extinction by Aerosol

As indicated by the polynomial $(a_0 + a_1\lambda + a_2\lambda^2)$ in Equation (4), it is necessary to account for the sample's background losses and their temporal changes. Background losses can be assigned to aerosol extinction as long as other contributions from molecular absorbers and instrumental artefacts have been accounted for. Aerosol extinction based on Equation (4) is very sensitive to the value of I_0 . While the normalisation procedure described above accounts for rapid fluctuations in the intensity, and hence in I_0 , long-term changes in the lamp intensity are difficult to distinguish from aerosol extinction in the chamber. An alternative approach to retrieving the aerosol extinction is based on using the change in the fractional absorption of a known absorption feature. The fractional absorption changes because aerosol and other extinction processes shorten the effective path length in the cavity - this effect is illustrated in Figure 3.4(a) where the O₂ absorption at 687 nm is proportionally smaller in I_1 (which has greater losses per pass) than in I_0 . The O₂ B-band with an observed maximum around 687.3 nm is particularly appropriate for this purpose because O₂ is present at a constant concentration and thus the absorption coefficient at the maximum of the B-band is constant in the real atmosphere. Furthermore, the absorption falls within the spectral window of the spectrometer, and other molecular absorptions are small in this region.

For an atmospheric sample whose total extinction, $\varepsilon_{\rm T} = \varepsilon_{\rm B} + \alpha'$, is the sum of a contribution from background extinction, $\varepsilon_{\rm B}$, and sample absorption, α' , three intensities transmitted through the cavity can be defined: (i) I_0 , the intensity in the absence of any extinction ($\varepsilon_{\rm T} = 0$); (ii) $I_{\rm B}$, the intensity when only background extinction is present ($\varepsilon_{\rm T} = \varepsilon_{\rm B}$); and (iii) *I*, the intensity in the general case of $\varepsilon_{\rm T} = \varepsilon_{\rm B} + \alpha'$. It is clear that $I < I_{\rm B} < I_0$ and only one intensity can be measured at any given time. With $\Delta I_{\rm A} \equiv I_{\rm B} - I$, Equation (1) can be manipulated to give

$$\alpha' = \left(\frac{\Delta I_{\rm A}}{I}\right) \left(\frac{1-R}{L}\right) \left(1 + \frac{\varepsilon_{\rm B}L}{1-R}\right)$$
(Eq. 7)

This equation implies that the effective path length, $L_{\rm eff} = d / (1-R)$ in Equation (1) is shortened in the presence of additional extinction processes to $L' = L_{\rm eff} / (1+\epsilon_{\rm B}L_{\rm eff})$. Equation (7) can be rearranged to give

$$\varepsilon_B = \alpha' \left(\frac{I}{\Delta I_A} \right) - \left(\frac{1-R}{d} \right)$$
 (Eq. 8)

Note that Equation (8) is insensitive to fluctuations in the intensity of the lamp since both *I* and ΔI_A scale proportionately to changes in I_0 .

Equation (8) was applied to determine ε_B at 687.3 nm by using the change in the fraction absorption of the O₂ B-band with aerosol loading in the chamber. As with water vapour absorption, apparent deviations from the Beer-Lambert law must be taken into account with the O_2 absorption lines. An empirical value of α'_{O_2} at our instrument resolution was obtained in clean chamber air by interpolating the baseline under the O₂ B-band and using Equation (1). During the experiment, the value of I_B at the centre of the B-band was estimated from the intensity at 683.9 nm (outside the O₂ absorption). A scaling factor was calculated from the transmission spectrum in a clean chamber by interpolating a baseline under the B-band and taking the ratio of the interpolated intensity at 687.3 nm to the intensity at 683.9 nm. For each spectrum, the measured intensity at 683.9 nm was first increased to compensate for H₂O and O₃ absorption; the new reference intensity was then multiplied by the scaling factor to estimate the intensity at 687.3 nm in the absence of H₂O and O_3 absorption. I_B was then calculated by removing the absorption of H₂O and O₃ at 687.3 nm and used in Equation (8) to retrieve the aerosol extinction.



Figure 3.8. Background extinction on 15 June 2007 retrieved by the procedure outlined in the text. 1: Addition of $(NH_4)_2SO_4$ aerosol started (10:45); 2: addition of aerosol ended (5 µg m⁻³) (11:25); 3: addition of $(NH_4)_2SO_4$ aerosol started (12:30); 4: addition of aerosol ended (12 µg m⁻³) (14:30).

The background extinction on 15 June retrieved using Equation (8) is shown in Figure 3.8. The precision of the measurements, estimated at the start of the experiment, is about 0.5×10^{-8} cm⁻¹. Aerosol extinction is the major contributor to the background extinction. Figure 3.8 shows two time periods with significant changes in the background extinction. The background extinction increases from 0×10^{-8} cm⁻¹ to 1×10^{-8} cm⁻¹ over the period of the first aerosol addition (10:45 a.m. to 11:25 a.m.), which corresponded to an aerosol loading of 5 µg m⁻³. The second, larger increase in ε_B coincides with the addition of aerosol from 12:30 to 14:30 and reaches a maximum of about 5.5 $\times 10^{-8}$ cm⁻¹ when the aerosol concentration is

about 12 μ g m⁻³. In both cases, the extinction decreases steadily when aerosol loading is stopped and particles deposit on the chamber walls. Other increases in the background extinction are observed around the time when humidified air was introduced into the chamber, and may indicate that the effect of water or O₃ absorption was not been completely removed in the analysis procedure. Although the above procedure provides a method for retrieving the aerosol extinction based on two intensities, a more comprehensive analysis should use spectral fitting to use more of the O₂ absorption profile. Such work is currently being pursued by the group.

4. Field Observations

4.1 Roches Point, Ireland

In addition to the chamber experiments, field measurements were taken with a slightly modified instrument at Roches Point, Ireland (51.795N, 08.252W) between 29 November and 11 December 2007. Roches Point is the shipping entrance to Cork harbour and is approximately 20 km south-east of Cork City. The transmitter and receiver units were installed on the roof (*ca.* 43 m above mean sea level) of the Met Éireann weather station (see Figure 4.1); electric power, lamp cooling water, and N₂ purge gas were supplied from inside the building. Each unit was mounted on four lead blocks for stability; windbreaker netting tied to the roof railing shielded the units from high winds and PVC sheet covers protected them from rain. The cavity mirrors (10 m radius of curvature and R = 0.9998 at 662 nm) were separated by 8.6 m and the base path length through the open atmosphere was 6.7 m. Spectra were collected with an acquisition time of 1 minute. In order to measure l_0 transmission spectra, the transmitter and receiver units were connected along the optical axis with a PVC pipe of 10 cm diameter along the optical axis, which was purged with N₂ at a high flow rate. After the initial alignment of the cavity, the pipe for the He-Ne beam was removed and the openings sealed with opaque material to prevent stray light or water from entering the units.

Field observations coincided with a period of high winds and heavy rain which were unfavourable for open-path measurements. Nevertheless, intermittent spells of calmer weather allowed a few measurements to be made with good sensitivity. The instrument was remarkably stable despite



Figure 4.1. Photograph of the open-path IBBCEA set-up on the roof of the Met Éireann weather station at Roches Point (Ireland). The transmitter and receiver units are also shown as insets. The effective cavity length was 6.7 m. The field trial lasted from 29 November to 11 December 2007.



Figure 4.2. Typical cavity transmission spectra measured at Roches Point (Ireland), 10 December 2007. Red line: Open-path measurement. Black line: l_0 measurement with a long PVC tube between transmitter and receiver unit that was continuously purged with dry N₂.

the high winds experienced. Figure 4.2 shows typical transmission spectra $I_0(\lambda)$ (black line) and $I(\lambda)$ (red line). The transmission spectrum through the open atmosphere clearly shows the absorption features of O2 and H2O in that region. The large decrease in the background is caused by the scattering and absorption of aerosols in the beam path, which often exceeded 10^{-6} cm⁻¹. Such high aerosol extinction, which is not surprising given the proximity of the site to the coastline, can have a marked impact on the sensitivity of the instrument. The effective path length of the instrument is <33.5 km at 665 nm in an aerosol-free atmosphere, but decreases to <7.7 km when extinction from aerosols corresponds to 10^{-6} cm⁻¹. Assuming an aerosol extinction of 10^{-6} cm⁻¹, an NO₃ detection limit of ca. 1 pptv for a 1 minute integration time was estimated, based on the chamber performance. However, NO3 was not observed above this detection limit during the few night-time periods without rain or mist when meaningful measurements were possible. Such low concentrations of NO₃ have been observed in the coastal environment by other workers (Sommariva, 2007), who also proposed that NO emissions over land could deplete NO₃ concentrations.

4.2 COBRA Campaign at Kuujjuarapik, Canada

Every spring, ozone depletion events (ODEs) occur with regularity in the coastal regions of the Arctic and Antarctic. These episodes have been linked to the exchange of halogen species between snowpack and sea ice and the overlying atmosphere; specifically, the catalytic reaction of bromine atoms (Br) with ozone to produce bromine oxide (BrO) is believed to be the primary loss for ozone in this region. Since tropospheric ozone is not only an important greenhouse gas, but it also has significant consequences for the oxidative capacity at a regional scale, it is imperative to develop the quantitative understanding of relevant chemical interactions so that the future states of the Arctic and Antarctic atmosphere can be better predicted. For that purpose, a major international campaign - COBRA (combined impact of bromine and iodine on the Arctic atmosphere) - with collaboration between University College Cork (UCC), several UK research institutions (the universities of York, Leeds, Manchester, East Anglia, Cambridge and Leicester, and the British Antarctic Survey), and international bodies (the universities of Bremen, Montreal and Battelle, and Environment Canada)



Figure 4.3. Jun Chen (left) and Stewart Vaughan (right) working on the IBBCEA instrument at Hudson Bay, Canada.

took place at Hudson Bay, Canada in spring 2008 as part of the 2007–2008 International Polar Year (IPY).

The accurate determination of the concentration of BrO during polar ODEs will allow the reliable prediction of the chemical behaviour in this region from models of atmospheric interactions. Current data have been obtained using methods - for instance, long-path differential absorption spectroscopy (LP-DOAS) - that rely on performing measurements across several kilometres and thus have unavoidably been limited in their ability to follow the spatial variation in the concentration of BrO. Hence, questions still remain as to the nature of the source of the BrO-precursors Br₂ and BrCI: Do these species evolve from frost flowers (crystalline structures that form on new sea ice), open leads in the ice, or from the ice or snow itself; are they released steadily with time or in 'bromine explosions'?; What is the temporal and spatial variation of BrO relative to the source?; and Is there recycling of BrO on the snowpack/ice? A compact field instrument based on the IBBCEAS field instrument would allow the sensitive monitoring of BrO over just a few metres, thus providing excellent spatial and temporal versatility. Also, there has been great interest in the possibility that iodine-related species could play a significant role in Arctic chemistry following the recent observations of iodine oxides in the Antarctic atmosphere; the IBBCEAS instrument would allow the monitoring of BrO, I_2 , IO and OIO (See Appendix C).

An IBBCEA spectrometer, based on the design of the instrument used in Jülich and adapted specifically for cold climates, was developed and installed by Dr Stewart Vaughan (Marie Curie Fellow, Department of Physics, UCC) and Jun Chen (second-year PhD student, Department of Chemistry, UCC) at a research site at Kuujjuarapik on Hudson Bay (55°16′48.32′′N, 77°45'16.40"W) from 7 February 2008 to 7 March 2008; Figures 4.3 and 4.4 show photographs of the measurement site. Research groups from the universities of Leeds, York and Manchester, the British Antarctic Survey and Environment Canada were also present at the site. In spring, the sea in this region is covered with about 1 m of ice, with open leads and frost-flower formation in some areas near the research site. Hence, ODEs and subsequent generation of BrO was expected during the campaign. The objective was to install the UCC instrument at various sites near frost flowers and open leads to investigate the evolution



Figure 4.4. Installation of the UCC instrument (black boxes on tripods) at the measurement site. The spectrometer was positioned approximately 20 m from the edge of the ice-covered bay.

of BrO and iodine-containing species.

Several modifications of the instrument used in Jülich were made. For instance, the main bodies of the transmitter and receiver units used in Jülich were constructed from aluminium, and the lamp platform from stainless steel, whereas the COBRA instrument was made mainly from a plastic, Delrin[®], and the lamp platform from aluminium. These changes allowed a reduction in the weight of the instrument so that the instrument could be placed near open leads and fields of frost flowers with less risk of breaking the ice that supported it. Also, Delrin® has a lower thermal conductivity than aluminium. Daytime temperatures were regularly below -20°C, falling on occasion below -30°C at night, and the temperature could vary by as much as 30°C over a 24 hour period. Thus, constructing the bodies of the instrument from Delrin® rather than aluminium also reduced the rate of heat loss from inside the two boxes. Further insulation was provided by lining the walls with polystyrene foam. The COBRA instrument also contained heaters and thermostats to maintain the internal temperature above 0°C so that the electronic and optical components could function satisfactorily.

A water circulation system, consisting essentially of a loop circuit between the lamp and a secondary recirculating pump was required because there was no supply of flowing water for the cooling of the 'hot-spot' lamp. Also, because the outdoor temperature was consistently below the freezing point of water (0°C), it was necessary that the line was insulated and a water–antifreeze mixture, rated to remain liquid above –56°C, was used.

Unlike in the Jülich campaign, where the instrument was mounted on platforms so that the transmitter could be pointed directly at the receiver, it was unlikely that the snow/ice surface at Hudson Bay would allow the two boxes to be easily positioned for a clear passage of light without adapting the instrument to allow greater degrees of freedom. Thus, both boxes were mounted on adjustable tripods so that the heights and relative angles of the boxes relative to the ground could be set to allow the clear passage of the light beam between the transmitter and the receiver. The last critical modification was the substitution of various filters, lenses and mirrors for those complimentary for the detection of BrO in the near ultraviolet ($\lambda \sim 350$ nm), and the detector – an Andor monochromator–CCD array – for one that had a greater sensitivity in the ultraviolet.

Unfortunately, the IBBCEA spectrometer was critically impaired by the unforeseeable breakdown of the light sources, without which the instrument could not operate. First, the hot-spot lamp was severely damaged after the power generator for the site failed due to a coolant leak. The power failure lasted several hours overnight, during which the temperature (with wind chill) dropped to below -50°C; that night was the coldest during the four weeks of the campaign, with temperatures dropping below -40°C. Thus, the temperature with wind chill was cold enough for the water-antifreeze mixture to freeze during the power outage. However, the scientists operating the spectrometer were at the research station and were not made aware that there had been any problems at the research site until the following morning. Hence, the UCC scientists were not present when the power was restored and the lamp initiated without the necessary flow of coolant, leading to burn-out. Due the remoteness of the research location (Kuujjuarapik is over 1000 km from the nearest major city) and the limited timescale of the field campaign,³ the lamp could not be repaired on-site before the end of the campaign and thus could not be used for the remainder of the experiments.

A high-power LED, with strong emission in the ultraviolet, replaced the broken lamp unit. However, for unknown reasons, the LED stopped functioning on the first night that measurements were being recorded, and could not be repaired on-site. Thus, our participation in the campaign had to be aborted.

Although the campaign produced no new data to explain the behaviour of BrO and iodo species in the Arctic troposphere, there were several positive aspects of the campaign. For instance, this was the first deployment of an IBBCEA spectrometer in the field outside Ireland; it is our belief that if the light sources had not failed, then the instrument would have yielded interesting and important scientific information. The campaign has also provided the research groups of Cork, including a second-year PhD student, with valuable experience of fieldwork in extreme, difficult environments. Finally, the presence of this international scientific community allowed the significant transfer of knowledge and expertise, as well as generating important contacts between University College Cork and researchers who are leading experts in their field, so future collaborations in the field may be possible.

³ It is worth noting that the campaign was brought to an end for all the field scientists one week before the planned cessation date when the same power generator exploded.

5. Outlook

5.1 Cork City Council Urban Monitoring Site

Owing to the damage to the xenon arc lamp during the COBRA campaign, it was not possible to carry out the planned urban monitoring campaign in Cork City before the end of the project. Nevertheless, it is still intended to carry out these measurements of NO3 in an urban environment when the lamp has been repaired and returned to the group. The site chosen for the study is at the Cork City air quality monitoring station at Anglesea Street, in the centre of the city. This location is well suited to studying the chemistry of nitrogen oxides owing to the high traffic and significant domestic heating in the proximity, which should result in significantly elevated NO_x and NO₃ concentrations. Furthermore, the suite of instruments at the site includes chemiluminescence NO_x detectors and O₃ monitors, allowing the NO3 measurements to be modelled and studied in greater detail. The site will also present a different environment for open-path measurements compared to the Roches Point site (where very high aerosol extinctions were observed close to the coast) and allow an evaluation of the open-path measurements in these different environments.

5.2 Grassland Site in West Cork

A third field monitoring campaign is planned for a grassland site in west Cork, in conjunction with the greenhouse gas flux measurements of Professor Ger Kiely's group at UCC. The meteorology and some of the chemistry of this site have been studied extensively in the past, but the formation and effects of NO₃ are not understood in this environment. Here the impact of NO₃-initiated oxidation chemistry will be closely linked to the fluxes of NO and NO₂ at the site. For conditions of high NO concentrations, NO₃ concentrations are expected to be below the detection limit of the IBBCEAS system owing to the reaction and NO₃ would play little role in the atmospheric chemistry under these conditions. On the other hand, under low NO but elevated NO₂ conditions, significant amounts of NO₃ would be expected and NO₃-initiated oxidation processes would assume a much greater importance in the atmosphere.

5.3 Aerosol Extinction Intercomparison

One of the strengths of the broadband approach is the simultaneous retrieval not only of absorbing gases, but also of the extinction arising from aerosols. Aerosol extinction has received much recent attention owing to the direct radiative forcing of aerosols and their role in climate change. The role of both the direct and indirect (via the formation of cloud condensation nuclei) radiative forcing of aerosols remains one of the greatest uncertainties in the global radiation budget. The results presented above show that broadband methods allow the simultaneous retrieval of the aerosol extinction, i.e. the sum of light losses to both scattering and absorption. Preliminary results show that the IBBCEAS extinction results compare favourably with broadband cavity ring-down measurements (Steven Ball, personal communication), and that both methods provide good temporal resolution with relatively broadband coverage of 10s of nm. Clearly, these results indicate that existing data from the SAPHIR experiments could be used as the basis for an intercomparison of the aerosol extinction. In addition, the SAPHIR chamber data also included scanning mobility particle sizer SMPS data on the particle size distribution as a function of time, allowing the aerosol scattering to be calculated on the basis of Mie theory. Thus, the scope exists for comparing the experimental and theoretical extinction of aerosols across a relatively broad spectral window, and will be the subject of future work.

$$NO + NO_3 \rightarrow 2NO_2$$

5.4 Retrieval of Water Concentrations

Although water vapour is readily measured with standard instrumentation, the ability to retrieve water vapour concentrations as a routine measurement in IBBCEAS systems would further enhance the attractiveness of the technique for field and laboratory measurements. Starting with the large data set generated in the SAPHIR chamber experiments, a routine will be developed to retrieve the water vapour concentration from the spectra. The retrieval routine will have to take deviations from Beer–Lambert behaviour into account. In order to verify the retrieved water concentrations, a comparison with the co-located measurements of water vapour of the SAPHIR hygrometer will be made.

References

- S. R. Aliwell, R. Jones, 'Measurements of tropospheric NO₃ at midlatitudes', J. GeoPhys. Res., **103 (D5)**, 5719–5727 (1998).
- A. R. Awtry and J. H. Miller, 'Development of a cw-laserbased cavity-ringdown sensor aboard a spacecraft for trace air constituents', Appl. Phys. B, **75**, 255–260 (2002).
- J. D. Ayers, R. L. Apodaca, W. R. Simpson, and D. S. Baer, 'Off–axis cavity ringdown spectroscopy: application to atmospheric nitrate radical detection', Appl. Opt., 44, 7239–7242 (2005).
- S. M. Ball, I. M. Povey, E. G. Norton, and R. L. Jones, 'Broadband cavity ringdown spectroscopy of the NO₃ radical', Chem. Phys. Lett., **342**, 113–120 (2001).
- S. M. Ball and R. L. Jones, 'Broad-band cavity ring-down spectroscopy', Chem. Rev., 103, 5239–5262 (2003).
- S. M. Ball, J. M. Langridge, and R. M. Jones, 'Broadband cavity enhanced absorption spectroscopy using light emitting diodes', Chem. Phys. Lett., **398**, 68–74 (2004).
- M. Bitter, S. M. Ball, I. M. Povey, and R. L. Jones, 'A broadband cavity ringdown spectrometer for in situ measurements of atmospheric trace gases', Atmos. Chem. Phys. 5, 2547–2560 (2005).
- J. Bossmeyer, T. Brauers, C. Richter, F. Rohrer, R. Wegener, and A. Wahner, 'Simulation chamber studies on the NO₃ chemistry of atmospheric aldehydes', Geophys. Res. Lett., **33**, L18810 (2006) doi:10.1029/2006GL026778.
- S. S. Brown, 'Absorption spectroscopy in high-finesse cavities for atmospheric studies', Chem. Rev., **103**, 5219–5238 (2003a).
- S. S. Brown, H. Stark, and A. R. Ravishankara, 'Cavity ring-down spectroscopy for atmospheric trace gas detection: application to the nitrate radical (NO₃)', Appl. Phys. B, **75**, 175–182 (2002a).
- S. S. Brown, H. Stark, and A. R. Ravishankara, 'Applicability of the steady state approximation to the interpretation of atmospheric observations of NO₃ and N_2O_5 ', J. Geophys. Res. D, **108**, Art. No. 4539 (2003).

- S. S. Brown, H. Stark, S. J. Ciciora, R. J. McLaughlin, and A. Ravishankara, 'Simultaneous in situ detection of atmospheric NO_3 and N_2O_5 via cavity ring-down spectroscopy', Rev. Sci. Instrum., **3**, 3291–3301 (2002b).
- S. S. Brown, W. P. Dubé, H. D. Osthoff, D. E. Wolfe, W. M. Angevine, and A. R. Ravishankara, 'High resolution vertical distributions of NO₃ and N₂O₅ through the nocturnal boundary layer', Atmos. Chem. Phys., **7**, 139–149 (2007).
- S. S. Brown, H. Stark, T. B. Ryerson, E. J. Williams, D. K. Nicks, M. Trainer, F. C. Fehsenfeld, and A. R. Ravishankara, 'Nitrogen oxides in the nocturnal boundary layer: Simultaneous in situ measurements of NO₃, N₂O₅, NO₂, NO, and O₃', J. Geophys. Res. D, **108**, Art. No. 4299 (2003).
- S. S. Brown, H. D. Osthoff, H. Stark, W. P. Dube, T. B. Ryerson, C. Warneke, J. A. DeGouw, A. G. Wollny, D. D. Parrish, F. C. Fehsenfeld, and A. R. Ravishankara, 'Aircraft observations of daytime NO_3 and N_2O_5 and their implications for tropospheric chemistry', J. Photochem. Photobiol. A, **176**, 270–278 (2005).
- J. P. Burrows, A. Dehn, B. Deters, S. Himmelmann, A. Richter, S. Voigt, and J. Orphal, 'Atmospheric remote-sensing reference data from GOME: 1. Temperature-dependent absorption cross-sections of NO₂ in the 231–794 nm range', J. Quant. Spectrosc. Rad. Trans., **60**, 1025–1031 (1998).
- K. C. Clemitshaw, 'A review of instrumentation and measurement techniques for ground-based and airborne field studies of gas-phase tropospheric chemistry', Critic. Rev. Environ. Sci. Technol., 34, 1–108 (2004).
- E. R. Crosson, P. Haar, G. A. Marcus, H. A. Schwettman, B. A. Paldus, T. G. Spence, and R. N. Zare, 'Pulsestacked cavity ring-down spectroscopy', Rev. Sci. Instrum., **70**, 4–10 (1999).
- A. Czyżewski, S. Chudzyński, K. Ernst, G. Karasiński, Ł. Kilianek, A. Pietruczuk, W. Skubiszak, T. Stacewicz, K. Stelmaszczyk, B. Koch, and P. Rairoux, 'Cavity ring-down spectrography', Opt. Comm., **191**, 271–275 (2001).

- H.-P. Dorn, R. L. Apodaca, S. M. Ball, T. Brauers, S. S. Brown, R. C. Cohen, J. Crowley, W. P. Dube, J. Fry, H. Fuchs, R. Häseler, U. Heitmann, S. Kato, Y. Kajii, I. Labazan, J. Langridge, J. Matsumoto, J. Meinen, S. Nishida, U. Platt, D. Rollins, A. A. Ruth, E. Schlosser, G. Schuster, A. Shillings, W. Simpson, J. Thieser, R. Varma, D. Venables, A. Wahner, and P. Wooldridge, 'Intercomparison of NO₃ radical detection techniques in the atmosphere simulation chamber SAPHIR', Atmos. Chem. Phys. Disc. (2008), in preparation.
- W. P. Dubé, S. S. Brown, H. D. Osthoff, M. R. Nunley, S. J. Ciciora, M. W. Paris, R. J. McLaughlin, and A. R. Ravishankara, 'Aircraft instrument for simultaneous, in situ measurement of NO₃ and N₂O₅ via pulsed cavity ring-down spectroscopy', Rev. Sci. Instrum., **77**, 034101 (2006).
- S. E. Fiedler, A. Hese, and A. A. Ruth, 'Incoherent broadband cavity-enhanced absorption spectroscopy', Chem. Phys. Lett., **371**, 284–294 (2003).
- D. J. Fish, D. E. Shallcross, R. L. Jones, 'The vertical distribution of NO₃ in the atmospheric boundary layer', Atmos. Environ., **33**, 687–691 (1999).
- H. Fuchs, R. L. Apodaca, S. M. Ball, T. Brauers, S. S. Brown, R C. Cohen, J. Crowley, H.-P. Dorn, W. P. Dube, J. Fry, R. Haseler, U. Heitmann, S. Kato, Y. Kajii, A. Kiendler-Scharr, I. Labazan, J. Matsumoto, J. Meinen, S. Nishida, U. Platt, F. Rohrer, A A. Ruth, E. Schlosser, G. Schuster, A. Shillings, W. Simpson, J. Thieser, R. Tillmann, R. M. Varma, D. Venables, R. Wegener, and P. Wooldridge (2007). 'Intercomparison of different NO₂ measurement techniques at the simulation chamber SAPHIR'. In preparation for *Atmospheric Chemistry and Physics Discussions* (2008).
- T. Gherman and D. Romanini, 'Mode-locked cavityenhanced absorption spectroscopy', Optics Express, 10, 1033–1042 (2002).
- T. Gherman, D. S. Venables, S. Vaughan, J. Orphal, and A. A. Ruth, 'Incoherent broadband cavity enhanced absorption spectroscopy in the near-ultaviolet: application to HONO and NO₂', Environ. Sci. Technol., 42, 890–895 (2008).
- H. Gong, A. Matsunaga, and P.J. Ziemann, 'Products and mechanism of secondary organic aerosol formation from reactions of linear alkenes with NO₃ radicals', J. Phys. Chem. A, **109**, 4312–4324 (2005).
- E. Hamers, D. Schram, and R. Engeln, 'Fourier transform phase shift cavity ring down spectroscopy', Chem. Phys. Lett., **365**, 237–243 (2002).

- S. Kassi, M. Chenevier, L. Gianfrani, A. Salhi, Y. Rouillard, A. Ouvrard, and D. Romanini, 'Looking into the volcano with a mid-IR DFB diode laser and cavity enhanced absorption spectroscopy', Opt. Express, **14**, 11442– 11452 (2006).
- R. Kurtenbach, R. Ackermann, K. H. Becker, A. Geyer, J. A. G. Gomes, J. C. Lörzer, U. Platt, P. Wiesen, 'Verification of the contribution of vehicular traffic to the total NMVOC emissions in Germany and the importance of the NO₃ chemistry in the city air', J. Atmos. Chem., **42**, 395–411 (2002).
- J. M. Langridge, S. M. Ball, and R. L. Jones, 'A compact broadband cavity enhanced absorption spectrometer for detection of atmospheric NO₂', Analyst, **131**, 916– 922 (2006).
- J. M. Langridge, T. Laurila, R. S. Watt, R. L. Jones, C. F. Kaminski, J. Hult, 'Cavity-enhanced absorption spectroscopy of multiple trace gas species using a supercontinuum radiation source', Opt. Express, 16, 10178–10188 (2008).
- J. Orphal, C. E. Fellows, and P. M. Flaud, 'The visible absorption spectrum of NO₃ measured by high-resolution Fourier transform spectroscopy', J. Geophys. Res. D, **108**, 4077–4087 (2003b).
- B. A. Paldus and A. A. Kachanov, 'An historical overview of cavity-enhanced methods', Can. J. Phys., 83, 975– 999 (2005).
- U. Platt, 'Modern methods of the measurement of atmospheric trace gases', Phys. Chem. Chem. Phys., 1, 5409–5415 (1999).
- F. Rohrer, D. Brüning, E. S. Grobler, M. Weber, D. H. Ehhalt, R. Neubert, W. Schübler, and L. Levin, 'Mixing ratios and photostationary state of NO and NO₂ observed during the POPCORN field campaign at a rural site in Germany', J. Atmos. Chem., **31**, 119–137 (1998).
- L. S. Rothman, D. Jacquemart, A. Barbe, D. C. Benner, M. Birk, L. R. Brown, M. R. Carleer, C. Chackerian Jr., K. V. Chance, V. Dana, V. M. Devi, J.-M. Flaud, R. R. Gamache, A. Goldman, J.-M. Hartmann, K. W. Jucks, A. G. Maki, J.-Y. Mandin, S. Massie, J. Orphal, A. Perrin, C. P. Rinsland, M. A. H. Smith, R. A. Toth, J. Vander Auwera, P. Varanasi, and G. Wagner, 'The HITRAN 2004 molecular spectroscopic database', J. Quant. Spectrosc. Rad. Transf. **96**, 139– 204 (2005).
- J. J. Scherer, 'Ringdown spectral photography', Chem. Phys. Lett., **292**, 143–153 (1998).

- J. J. Scherer, J. B. Paul, H. Jiao, and A. O'Keefe, 'Broadband ringdown spectral photography', Appl. Opt., **40**, 6725–6732 (2001).
- M. J. Thorpe, K. D. Moll, R. J. Jones, B. Safdi, and J. Ye, 'Broadband cavity ringdown spectroscopy for sensitive and rapid molecular detection', Science, **311**, 1595– 1599 (2006).
- M. Triki, P. Cermak, G. Méjean, and D. Romanini, 'Cavityenhanced absorption spectroscopy with a red LED source for NO_X trace analysis', Appl. Phys. B, **91**, 195–201 (2008).
- S. Vaughan, T. Gherman, A.A. Ruth, and J. Orphal, 'Incoherent broadband cavity-enhanced absorption spectroscopy of the marine boundary layer species I₂, IO and OIO', Phys. Chem. Chem. Phys., **10**, 4471– 4477 (2008).

- D. S. Venables, T. Gherman, J. Orphal, J. Wenger, and A. A. Ruth, 'High sensitivity in situ monitoring of NO₃ in an atmospheric simulation chamber using incoherent broadband cavity-enhanced absorption spectroscopy', Environ. Sci. Technol., **40**, 6758–6763 (2006).
- R. Wada, J. M. Beames, and A. J. Orr-Ewing, 'Measurement of IO radical concentrations in the marine boundary layer using a cavity ring-down spectrometer', J. Atmos. Chem., **58**, 69–87 (2007).
- B. Welz, H. Becker-Ross, S. Florek, and U. Heitmann, *High-resolution continuum source AAS: The better way to do atomic absorption spectrometry*, Wiley VCH, Weinheim (2005).
- R. J. Yokelson, J. B. Burkholder, R. W. Fox, R. K. Talukdar, and A. R. Ravishankara, 'Temperature dependence of the NO₃ absorption spectrum', J. Phys. Chem., **98**, 13144–13150 (1994).

Appendix A: AGU Poster

This poster was presented by H.-P. Dorn at the American Geophysical Union meeting in San Francisco (December 2007).



Appendix B: EGU Poster

This poster was presented by D. Venables at the European Geosciences Union meeting in Vienna (April 2008).



Appendix C: AICI Poster

This poster was presented by D. Venables at the Air-Ice Chemical Interface workshop in Cambridge (June 2008).



Appendix D: Research Output from the Project

Peer-Reviewed Publications

- R. M. Varma, D. S. Venables, A. A. Ruth, U. Heitmann, E. Schlosser, S. Dixneuf (2008). A long open-path cavityenhanced absorption instrument for in-situ monitoring of tropospheric trace gases. Manuscript submitted to *Applied Optics*.
- T. Brauers, R. L. Apodaca, S. M. Ball, S. S. Brown, R. C. Cohen, J. Crowley, H.-P. Dorn, W. P. Dube, J. Fry, H. Fuchs, R. Häseler, U. Heitmann, S. Kato, Y. Kajii, A. Kiendler-Scharr, I. Labazan, J. Matsumoto, J. Meinen, S. Nishida, U. Platt, F. Rohrer, A. A. Ruth, E. Schlosser, G. Schuster, A. Shillings, W. Simpson, J. Thieser, R. Tillmann, R. M. Varma, D. S. Venables, R. Wegener, and P. Wooldridge (2008). Intercomparison of nine different NO₃ measurement techniques at the simulation chamber SAPHIR. In preparation for *Atmospheric Chemistry and Physics Discussions*.
- H. Fuchs, R. L. Apodaca, S. M. Ball, T. Brauers, S. S. Brown, R. C. Cohen, J. Crowley, H.-P. Dorn, W. P. Dube, J. Fry, R. Häseler, U. Heitmann, S. Kato, Y. Kajii, A. Kiendler-Scharr, I. Labazan, J. Matsumoto, J. Meinen, S. Nishida, U. Platt, F. Rohrer, A. A. Ruth, E. Schlosser, G. Schuster, A. Shillings, W. Simpson, J. Thieser, R. Tillmann, R. M. Varma, D. Venables, R. Wegener, and P. Wooldridge (2008). Intercomparison of nine different NO₂ measurement techniques at the simulation chamber SAPHIR, In preparation for *Atmospheric Chemistry and Physics Discussions*.

Conference Contributions and Seminars

- R. M. Varma*, A. A. Ruth, D.S. Venables, U. Heitmann, H.-P. Dorn, T. Brauers, E. Schlosser: A new field instrument for NO₃ detection using incoherent broadband cavity enhanced spectroscopy, 101st Annual Conference of the Air and Waste Management Association (paper no. 809), Portland, Oregon, USA, June 24–27, 2008. (Lecture)
- J. Chen, U. Heitmann, A. A. Ruth, R. Varma, S. Vaughan, and D. S. Venables*. Novel approaches to investigating gas phase halogen chemistry in the laboratory and field, Atmosphere Ice Chemical Interactions Workshop, British Antarctic Survey, Cambridge, UK, June 16-19 2008. (Poster)
- D. S. Venables*, T. Brauers, H.-P. Dorn, U. Heitmann, A. A. Ruth, E. Schlosser, R. Varma (2008). High sensitivity in situ absorption measurements in simulation chambers: Intercomparison results and application to field and chamber studies. EGU General Assembly 2008, April 14–18, 2008, Vienna, Austria (Geophysical Research Abstracts, Vol. 10, EGU2008-A-02751, 2008). (Poster)
- T. Brauers*, H.-P. Dorn, E. Schlosser, A. A. Ruth, D. S. Venables, U. Heitmann, R. Varma, J. Thieser, U. Platt (2008). The NO₃ instrument intercomparison at SAPHIR: Results from three in-situ instruments. Fourth DOAS International Workshop For Environmental Research and Monitoring, March 30 – April 3, 2008, Hefei, China. (abstract at http://doas.aiofm.ac.cn/tables/ Workshop%20Programme.pdf, p. 35). (Lecture)

- H.-P. Dorn, R. L. Apodaca, S. M. Ball, M. Berg, T. Brauers,
 S. S. Brown, R. C. Cohen, J. Crowley, W. P. Dube,
 J. Fry, H. Fuchs, R. Häseler, U. Heitmann, S. Kato,
 Y. Kajii, A. Kiendler-Scharr, J. Kleffmann, I. Labazan,
 J. Langridge, J. Matsumoto, J. Meinen, S. Nishida,
 U. Platt, F. Rohrer, D. Rollins, A. A. Ruth, E. Schlosser,
 G. Schuster, A. Shillings, W. Simpson, G. Tapia,
 J.Thieser, R. Tillmann, R. Varma, D. Venables,
 R. Wegener, A. Wahner, and P. Wooldridge.
 Intercomparison of NO₃ and N₂O₅ measurement
 techniques at the atmosphere simulation chamber
 SAPHIR, AGU, San Francisco, December 2007.
 (Poster)
- R. M. Varma*, A. A. Ruth, D. S. Venables, U. Heitmann (2008). A new field instrument for NO₃ detection using incoherent broadband cavity enhanced spectroscopy. Optical Society of America, Laser Applications of Chemical, Security and Environmental Analysis (LACSEA) Meeting, March 16–20, 2008, St. Petersburg, Florida, USA. (Lecture)
- A. Ruth, Incoherent Broadband Cavity Enhanced absorption spectroscopy – An overview, Seminar (invited), November 2007, Physics Department, Ludwig-Maximilian University of Munich, Germany. (Lecture)
- T. Gherman, J. Orphal*, D. S. Venables, J. C. Wenger, A. A. Ruth, In situ monitoring of NO₃ using incoherent broadband cavity-enhanced absorption spectroscopy: A kinetic study of the I₂/O₃/NO_x system. September 17–19 2006, 6th Cavity Ring-Down Spectroscopy User Meeting, Cork, Ireland. (Poster)

Workshops

- U. Heitmann, A. A. Ruth, D. S. Venables*, R. Varma. 'Detection of NO₃ in an Atmospheric Simulation Chamber using Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy', Forschungszentrum Jülich (Troposphäre IGC-2), Germany (11/2006). (Lecture)
- U. Heitmann, A. A. Ruth*, D.S. Venables, R. Varma,
 'Detection of NO₃ at SAPHIR using Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy',
 Forschungszentrum Jülich (Troposphäre IGC-2),
 Germany (11/2007). (Lecture)

Advanced Undergraduate Research Projects

- Vicky O'Connor, Department of Physics (2008): 'Field measurement of NO₃ using IBBCEAS'.
- Kevin Eccles, Department of Chemistry (2007): 'Accounting for non-Beer–Lambert behaviour in the analysis of NO₃ spectra'.
- Maria Daly, Department of Chemistry (2006): 'A new approach to calibrating an IBBCEAS system'.

Articles in General Media

'Cold Science', UCC News, June 2008.

'Looking for answers in an icy place', *Irish Times*, 31 July 2008.

Acronyms

AGU	American Geophysical Union
AICI	air-ice chemical interface
CCD	charge-coupled device
CEAS	cavity enhanced absorption spectroscopy
CLD	chemoluminescence detector
CRD(S)	cavity ring down (spectroscopy)
COBRA	combined impact of bromine and iodine on the Arctic atmosphere
DCM	dichloromethane
DOAS	differential optical absorption spectroscopy
EGU	European Geophysical Union
EPA	Environmental Protection Agency
IBBCEAS	incoherent broadband cavity-enhanced absorption spectroscopy
INNOx	NO ₃ /N ₂ O ₅ intercomparison
IPY	International Polar Year
LED	light-emitting diodes
(LP-)DOAS	(long path-) differential optical absorption spectroscopy
ODE	ozone depletion event
PAN	peroxyacetyl nitrate
PMT	photomultiplier tube
SAPHIR	simulation of atmospheric photochemistry in a large reaction
SOA	secondary organic aerosol
STRIVE	Science, Technology, Research and Innovation for the Environment
SVD	singular value decomposition
TRACES	trace radical absorption through cavity-enhanced spectroscopy
UCC	University College Cork
VOC	volatile organic compound

An Ghníomhaireacht um Chaomhnú Comhshaoil

Is í an Gníomhaireacht um Chaomhnú Comhshaoil (EPA) comhlachta reachtúil a chosnaíonn an comhshaol do mhuintir na tíre go léir. Rialaímid agus déanaimid maoirsiú ar ghníomhaíochtaí a d'fhéadfadh truailliú a chruthú murach sin. Cinntímid go bhfuil eolas cruinn ann ar threochtaí comhshaoil ionas go nglactar aon chéim is gá. Is iad na príomh-nithe a bhfuilimid gníomhach leo ná comhshaol na hÉireann a chosaint agus cinntiú go bhfuil forbairt inbhuanaithe.

Is comhlacht poiblí neamhspleách í an Ghníomhaireacht um Chaomhnú Comhshaoil (EPA) a bunaíodh i mí Iúil 1993 faoin Acht fán nGníomhaireacht um Chaomhnú Comhshaoil 1992. Ó thaobh an Rialtais, is í an Roinn Comhshaoil agus Rialtais Áitiúil a dhéanann urraíocht uirthi.

ÁR bhFREAGRACHTAÍ

CEADÚNÚ

Bíonn ceadúnais á n-eisiúint againn i gcomhair na nithe seo a leanas chun a chinntiú nach mbíonn astuithe uathu ag cur sláinte an phobail ná an comhshaol i mbaol:

- áiseanna dramhaíola (m.sh., líonadh talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh., déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- diantalmhaíocht;
- úsáid faoi shrian agus scaoileadh smachtaithe Orgánach Géinathraithe (GMO);
- mór-áiseanna stórais peitreail.

FEIDHMIÚ COMHSHAOIL NÁISIÚNTA

- Stiúradh os cionn 2,000 iniúchadh agus cigireacht de áiseanna a fuair ceadúnas ón nGníomhaireacht gach bliain.
- Maoirsiú freagrachtaí cosanta comhshaoil údarás áitiúla thar sé earnáil - aer, fuaim, dramhaíl, dramhuisce agus caighdeán uisce.
- Obair le húdaráis áitiúla agus leis na Gardaí chun stop a chur le gníomhaíocht mhídhleathach dramhaíola trí comhordú a dhéanamh ar líonra forfheidhmithe náisiúnta, díriú isteach ar chiontóirí, stiúradh fiosrúcháin agus maoirsiú leigheas na bhfadhbanna.
- An dlí a chur orthu siúd a bhriseann dlí comhshaoil agus a dhéanann dochar don chomhshaol mar thoradh ar a ngníomhaíochtaí.

MONATÓIREACHT, ANAILÍS AGUS TUAIRISCIÚ AR AN GCOMHSHAOL

- Monatóireacht ar chaighdeán aeir agus caighdeáin aibhneacha, locha, uiscí taoide agus uiscí talaimh; leibhéil agus sruth aibhneacha a thomhas.
- Tuairisciú neamhspleách chun cabhrú le rialtais náisiúnta agus áitiúla cinntí a dhéanamh.

RIALÚ ASTUITHE GÁIS CEAPTHA TEASA NA HÉIREANN

- Cainníochtú astuithe gáis ceaptha teasa na hÉireann i gcomhthéacs ár dtiomantas Kyoto.
- Cur i bhfeidhm na Treorach um Thrádáil Astuithe, a bhfuil baint aige le hos cionn 100 cuideachta atá ina mór-ghineadóirí dé-ocsaíd charbóin in Éirinn.

TAIGHDE AGUS FORBAIRT COMHSHAOIL

Taighde ar shaincheisteanna comhshaoil a chomhordú (cosúil le caighdéan aeir agus uisce, athrú aeráide, bithéagsúlacht, teicneolaíochtaí comhshaoil).

MEASÚNÚ STRAITÉISEACH COMHSHAOIL

Ag déanamh measúnú ar thionchar phleananna agus chláracha ar chomhshaol na hÉireann (cosúil le pleananna bainistíochta dramhaíola agus forbartha).

PLEANÁIL, OIDEACHAS AGUS TREOIR CHOMHSHAOIL

- Treoir a thabhairt don phobal agus do thionscal ar cheisteanna comhshaoil éagsúla (m.sh., iarratais ar cheadúnais, seachaint dramhaíola agus rialacháin chomhshaoil).
- Eolas níos fearr ar an gcomhshaol a scaipeadh (trí cláracha teilifíse comhshaoil agus pacáistí acmhainne do bhunscoileanna agus do mheánscoileanna).

BAINISTÍOCHT DRAMHAÍOLA FHORGHNÍOMHACH

- Cur chun cinn seachaint agus laghdú dramhaíola trí chomhordú An Chláir Náisiúnta um Chosc Dramhaíola, lena n-áirítear cur i bhfeidhm na dTionscnamh Freagrachta Táirgeoirí.
- Cur i bhfeidhm Rialachán ar nós na treoracha maidir le Trealamh Leictreach agus Leictreonach Caite agus le Srianadh Substaintí Guaiseacha agus substaintí a dhéanann ídiú ar an gcrios ózóin.
- Plean Náisiúnta Bainistíochta um Dramhaíl Ghuaiseach a fhorbairt chun dramhaíl ghuaiseach a sheachaint agus a bhainistiú.

STRUCHTÚR NA GNÍOMHAIREACHTA

Bunaíodh an Ghníomhaireacht i 1993 chun comhshaol na hÉireann a chosaint. Tá an eagraíocht á bhainistiú ag Bord lánaimseartha, ar a bhfuil Príomhstiúrthóir agus ceithre Stiúrthóir.

Tá obair na Gníomhaireachta ar siúl trí ceithre Oifig:

- An Oifig Aeráide, Ceadúnaithe agus Úsáide Acmhainní
- An Oifig um Fhorfheidhmiúchán Comhshaoil
- An Oifig um Measúnacht Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáide

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag ball air agus tagann siad le chéile cúpla uair in aghaidh na bliana le plé a dhéanamh ar cheisteanna ar ábhar imní iad agus le comhairle a thabhairt don Bhord.



Science, Technology, Research and Innovation for the Environment (STRIVE) 2007-2013

The Science, Technology, Research and Innovation for the Environment (STRIVE) programme covers the period 2007 to 2013.

The programme comprises three key measures: Sustainable Development, Cleaner Production and Environmental Technologies, and A Healthy Environment; together with two supporting measures: EPA Environmental Research Centre (ERC) and Capacity & Capability Building. The seven principal thematic areas for the programme are Climate Change; Waste, Resource Management and Chemicals; Water Quality and the Aquatic Environment; Air Quality, Atmospheric Deposition and Noise; Impacts on Biodiversity; Soils and Land-use; and Socio-economic Considerations. In addition, other emerging issues will be addressed as the need arises.

The funding for the programme (approximately €100 million) comes from the Environmental Research Sub-Programme of the National Development Plan (NDP), the Inter-Departmental Committee for the Strategy for Science, Technology and Innovation (IDC-SSTI); and EPA core funding and co-funding by economic sectors.

The EPA has a statutory role to co-ordinate environmental research in Ireland and is organising and administering the STRIVE programme on behalf of the Department of the Environment, Heritage and Local Government.



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Comhshaol, Oidhreacht agus Rialtas Áitiúil Environment, Heritage and Local Government