

Off-axis cavity ringdown spectroscopy: application to atmospheric nitrate radical detection

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Atmospheric nitrate radicals (NO_3) are detected using off-axis cavity ringdown spectroscopy (CRDS) for the first time to our knowledge with a room-temperature continuous-wave (cw) diode laser operating near 662 nm. A prototype instrument was constructed that achieved a 1σ absorption sensitivity of $5 \times 10^{-10} \text{ cm}^{-1} \text{ Hz}^{-1/2}$, corresponding to a 1.4 part per trillion by volume 2σ detection limit in 4.6 s at 80°C. This sensitivity is a significant improvement over a recent implementation of off-axis cavity-enhanced absorption spectroscopy and comparable to that of the most advanced cw CRDS and pulsed CRDS applications for atmospheric detection of NO_3 . A comparison of measurements of ambient air in Fairbanks, Alaska, recorded with the off-axis CRDS instrument and a previously characterized conventional cw CRDS instrument showed good agreement ($R^2 = 0.97$). © 2005 Optical Society of America

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Cavity ringdown spectroscopy (CRDS) and variant techniques are promising new technologies for the measurement of atmospheric absorbers in field situations. The sensitivity of CRDS and its ability to quantify gases at low concentrations have been known since its inception.¹ This high sensitivity is achieved by increasing the sample path length with a multireflection cell and using a temporal-domain measurement that is insensitive to intensity variations of the light source. CRDS has become increasingly popular in atmospheric applications,^{2,3} both to detect products in laboratory atmospheric kinetics studies and to measure trace gas concentrations in field applications.

Nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) are two molecules recently measured with CRDS. Strong electronic absorption transitions at 662 nm ($\sigma = 2.18 \times 10^{-17} \text{ cm}^2/\text{molecule}$ at 662 nm and 298 K)⁴ permit detection of NO_3 using optical spectroscopy techniques. Thermal dissociation of N_2O_5 forms NO_3 . Therefore N_2O_5 may be measured indirectly as NO_3 in a heated detection cell. Before

CRDS-based $\text{NO}_3/\text{N}_2\text{O}_5$ sensors, atmospheric N_2O_5 was undetected. Instruments have been developed and field deployed to detect these species using both pulsed⁵ and continuous-wave (cw)⁶ CRDS techniques. Additionally, studies of NO_3 in the laboratory have been conducted using cavity-enhanced absorption spectroscopy (CEAS, also called integrated cavity output spectroscopy, or ICOS)⁷ and broadband CRDS,⁸ two new variations of the CRDS technique. Here we demonstrate the first application to our knowledge of off-axis CRDS for the detection of NO_3 and N_2O_5 in ambient air.

The most mature high-finesse cavity absorption spectroscopy for detection of atmospheric absorbers is CRDS. CRDS uses either pulsed or cw sources and requires spatial and spectral mode matching of the laser light with the optical cavity for reliable time-domain absorbance measurements. The technique is promising for use in atmospheric field work; however, it is not without disadvantages. Pulsed CRDS laser systems are typically larger and require more power than modern diode lasers. Continuous-wave CRDS systems can use small, portable diode lasers but require rigorous vibration isolation and temperature stability to operate with high sensitivity. These limitations for both techniques pose engineering challenges for field deployment. ICOS techniques^{9,10} retain the high-finesse cavity for path-length extension but instead use an intensity-domain measurement. For ICOS measurements, in general, the signal-to-noise ratio of the measured steady-state transmission is limited by excessive cavity resonances.

Off-axis alignment can be used in conjunction with

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ICOS to increase the reentrant length and produce a denser cavity-mode structure.⁹ For a laser with a sufficiently broad spectral bandwidth, a reentrant length greater than the laser coherence length can be achieved, and the interference in the cavity becomes statistical rather than coherent. The result is cavity transmission that is quasi-independent of wavelength, albeit with a substantially reduced throughput intensity. Off-axis ICOS reduces the sensitivity to vibration and temperature and can employ small, power-efficient lasers. However, instabilities in the light source intensity may decrease the signal-to-noise ratio.

In this work we report recent demonstrations of an off-axis CRDS-based instrument for N_2O_5 and NO_3 measurement. Off-axis CRDS preserves the simplicity of off-axis alignment while still retaining the sensitivity of the more traditional mode-matched CRDS techniques. This combination is ideal for field measurements because simplicity is preferred in the field, especially when it can be achieved without significant loss of sensitivity. Several specific simplifications are worth note. High data rates can be maintained because there is no need to couple light actively into a single cavity mode, as is required in CRDS. In the current work, the data repetition rate is limited only by the ringdown time of the cavity. Small, portable diode lasers and small, high-sensitivity detectors improve instrument portability. Less restrictive alignment requirements facilitate operation in a vibration-rich environment that might be encountered in field work (for example, on board aircraft).

The apparatus that we use to measure NO_3 with off-axis CRDS is depicted in Fig. 1. Light at 662 nm from a diode laser (Power Technologies) was directed into a 66 cm long optical cavity consisting of two highly reflective mirrors ($R > 0.99995$ at 662 nm, Los Gatos Research). The output of the cavity was collected by an aspheric lens ($f = 2$ cm) and directed into a photomultiplier tube (Hamamatsu). The output of the photomultiplier was digitized (at a 5 megasample s^{-1} sampling rate) using a 12-bit Gage 1250 CompuScope card mounted in a personal computer. The computer also controlled the diode laser operation through a data-acquisition and control card (NI PCI-6023E) that modulated the laser output intensity on and off repetitively at a 500 Hz rate. Baseline ringdown times were of the order of 130 μs . A straightforward alignment procedure was used.⁹

Sampling of ambient air (at 8 standard liters per minute flow rate) was accomplished through a measurement cell constructed of 1 in. (2.54 cm) steel tubing (2.39 cm inside diameter) coated with halocarbon wax (Halocarbon Corp.) as shown in Fig. 1. The cavity mirrors were mounted on the two ends of the cell. The mirrors were adjusted using O-ring mounts and three fine-pitched screws. The sample gas first flowed through a Teflon filter to remove particulate matter. New filters were installed before each night of measurement to reduce NO_3 and N_2O_5 losses

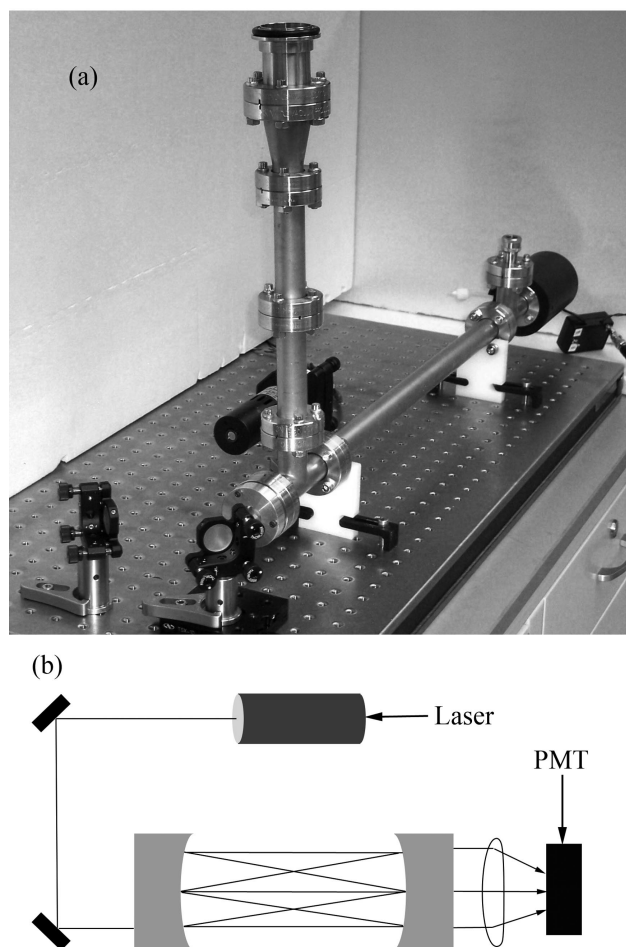


Fig. 1. (a) Photograph of the off-axis CRDS instrument. (b) Schematic of the instrument showing laser light entering the high-finesse cavity off axis. The cavity output light is focused onto a photomultiplier tube (PMT) by an aspheric lens.

through possibly dirty filters. This gas then flowed through a heated inlet (95 °C) for 30 cm, then through the optical cavity. The mirrors were purged with 200 sccm (cubic centimeters per minute at STP) house air filtered for particles with a high-efficiency particulate air filter (Gellman Sciences 12144). The main flow cell was heated to 85 °C to allow detection of N_2O_5 , which dissociates stoichiometrically to form NO_3 at this temperature. Sample gas residence time in the instrument was 4 s. Nitric oxide (NO) was added to the flow for a 40 s period out of every 160 s so that the mixing ratio of NO is 50 parts per billion by volume. Because NO reacts with NO_3 quickly to remove it from the flow, this “chemical zero” was used to provide a baseline ringdown time.

This instrument is compared with one that uses an external-cavity diode laser and cw CRDS described in detail by Simpson.⁶ In both cases heated cells were used to detect the sum of NO_3 and N_2O_5 as NO_3 in the cavity using the NO_3 absorption feature at 662 nm. The two instruments differ in several important ways. First, off-axis CRDS samples a significantly larger portion of the flow cell than cw CRDS, which

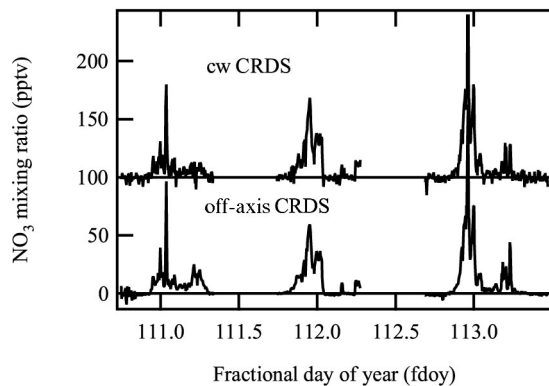


Fig. 2. Measured $\text{NO}_3 + \text{N}_2\text{O}_5$ mixing ratios as a function of time (given in fractional day of year, in which noon local time on 1 January 2005 is fday of 1.50). The top trace represents the cw CRDS implementation, while the bottom trace represents the off-axis CRDS. The top trace is offset 100 pptv with respect to the bottom trace for clarity. Excellent agreement between the three nights' data is observed.

samples only the axis of the flow cell. The sampling area can be estimated by observing the size of the light exiting the optical cavity. The cross-sectional area of light exiting the off-axis CRDS instrument is 100 mm^2 , whereas the cw CRDS instrument spot size is on the order of 1 mm^2 . Second, in an effort to simplify the assembly, the flow cell was constructed with standard tubing using Del-Seal Conflat flanges. This change unfortunately increased turbulence in the cell and thus the increased possibility of wall losses.

The two instruments sampled outdoor air for two weeks through ports at the International Arctic Research Center in Fairbanks, Alaska. NO_3 was detected on three nights. Figure 2 shows a time-series plot of these measurements. All data are averaged to a 5 min time resolution for comparison. High noise on the cw CRDS instrument was caused by temperature fluctuations in the laboratory of 4°C . The off-axis instrument was only marginally affected by these temperature variations. Agreement of measurements between the two instruments is outstanding and is illustrated in the correlation plot in Fig. 3. A correlation R^2 value of 0.97 with a slope of 1.01 ± 0.02 shows that the two instruments agree within experimental uncertainty.

The noise-equivalent optical sensitivity of our prototype instrument is estimated using²

$$\alpha_{\min} = \frac{L}{L_{\text{abs}}c} \frac{\Delta\tau_{\min}}{\tau_0^2}, \quad (1)$$

where α_{\min} is the minimum detectable absorbance, L is the cavity length, L_{abs} is the length of the cavity filled with absorber, τ_0 is the baseline ringdown time, and $\Delta\tau_{\min}$ is the smallest measurable difference between τ and τ_0 . We estimate $\Delta\tau_{\min}$ to be the 2σ uncertainty in the measure of τ_0 times $2^{1/2}$. Using this formalism, the 2σ sensitivity of the off-axis CRDS instrument is $1.0 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ (for $\Delta\tau_{\min} =$

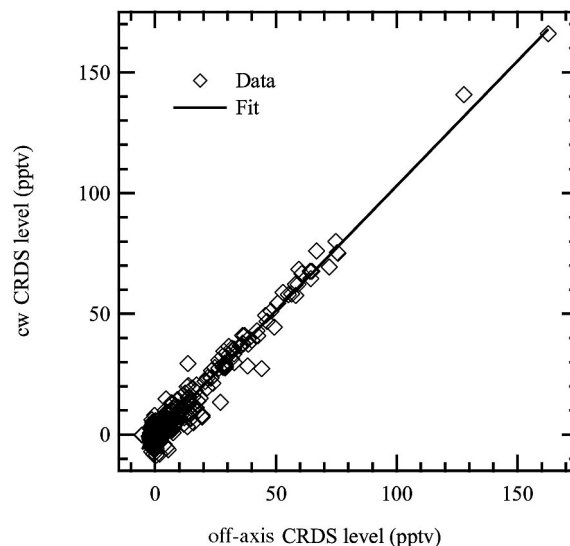


Fig. 3. Correlation between measurements made with off-axis CRDS (bottom axis) and cw CRDS (left axis). The linear regression fit gives $y = 1.01$ and $x = 0.85$ pptv, where y is the mixing ratio given by the cw CRDS instrument and x is the mixing ratio of the new off-axis CRDS instrument. The correlation coefficient $R^2 = 0.97$.

$4.95 \mu\text{s}$, $\tau_0 = 130 \mu\text{s}$, $L/L_{\text{abs}} = 1.2$, 500 Hz data rate), comparable to other instruments when traditional CRDS is used. The noise-equivalent detection limit is calculated by multiplying the minimum optical absorbance by the absorption cross section of NO_3 at the cell operation temperature. For operation at 80°C (NO_3 cross section is estimated to be $1.7 \times 10^{-17} \text{ cm}^2/\text{molecule}$), we obtain a 2σ detection limit of $2.9 \times 10^7 \text{ molecules cm}^{-3}$ [1.4 part per trillion by volume (pptv) at 1 atm, 80°C] in 4.6 s. This detection limit is more than 2 orders of magnitude lower than the reported 1σ noise-equivalent detection limit by use of off-axis CEAS in Ref. 7 ($5.5 \times 10^9 \text{ molecules cm}^{-3}$ in 3 s), highlighting the future promise of off-axis CRDS as a simple technique that can be used to detect NO_3 . Similar performance calculations for two field-deployed CRDS instruments yielded 2σ detection limits of 1.6 pptv in 25 s (cw CRDS)⁶ and 0.5 pptv in 5 s (pulsed CRDS).⁵ Although the best mode-matched CRDS instrument has a better sensitivity, off-axis CRDS is significantly simpler than pulsed CRDS and has the potential for improved sensitivity beyond the results presented here. Preliminary static cell measurements at room temperature by use of off-axis CRDS have achieved noise statistics a factor of 3 lower than reported here, although these changes have not yet been implemented or tested under field operation conditions. The simplicity of this instrument permits excellent performance without significant engineering and makes off-axis CRDS an ideal candidate for future field studies.

In conclusion, we have demonstrated that off-axis cavity ringdown spectroscopy can be used to detect ambient NO_3 and N_2O_5 with high sensitivity. The off-axis CRDS demonstration achieved sensitivity that was 2 orders of magnitude better than previous ap-

plications of off-axis cavity techniques used to measure NO_3 . We compared the performance of the new off-axis CRDS instrument to a previously characterized cw CRDS instrument and found that the two measurements agree within the instrumental uncertainty. The simplicity of the off-axis ringdown technique is promising for applications in atmospheric field studies in which simple alignment, small size, insensitivity to vibration, and low power consumption are critical features.

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