



HAL
open science

Portable cavity ring-down spectrometer for an HO₂ radical measurement: instrument's performance and potential improvement using a narrow linewidth laser

Chunhui Wang, Weixiong Zhao, Bo Fang, Nana Yang, Feihu Cheng, Xiao Hu, Yang Chen, Weijun Zhang, Christa Fittschen, Weidong Chen

► To cite this version:

Chunhui Wang, Weixiong Zhao, Bo Fang, Nana Yang, Feihu Cheng, et al.. Portable cavity ring-down spectrometer for an HO₂ radical measurement: instrument's performance and potential improvement using a narrow linewidth laser. *Optics Express*, 2022, 30 (21), pp.37446-37456. 10.1364/oe.470296 . hal-03853371

HAL Id: hal-03853371

<https://hal.science/hal-03853371>

Submitted on 15 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Portable cavity ring-down spectrometer for an HO₂ radical measurement: instrument's performance and potential improvement using a narrow linewidth laser

CHUNHUI WANG,^{1,2} WEIXIONG ZHAO,^{2,*}  BO FANG,² 
NANA YANG,^{2,3} FEIHU CHENG,² XIAO HU,^{2,3} YANG CHEN,^{2,3}
WEIJUN ZHANG,^{1,2,6} CHRISTA FITTSCHEN,⁴ AND WEIDONG CHEN⁵

¹School of Environmental Science and Optoelectronic Technology, University of Science and Technology of China, Hefei 230026, Anhui, China

²Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics and Fine Mechanics, HFIPS, Chinese Academy of Sciences, Hefei 230031, Anhui, China

³Graduate School, University of Science and Technology of China, Hefei 230026, Anhui, China

⁴Université Lille, CNRS, UMR 8522-PC2A-Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France

⁵Laboratoire de Physicochimie de l'Atmosphère, Université du Littoral Côte d'Opale, 59140 Dunkerque, France

⁶wjzhang@aiofm.ac.cn

*wxzhao@aiofm.ac.cn

Abstract: We report the development of a portable cavity ring-down spectrometer (CRDS) for direct and absolute measurement of HO₂ radical concentration using a distributed feedback (DFB) diode laser operating at 1506 nm. The spectrometer has a compact design with all optics in a 1000 × 400 × 140 mm³ box. At a pressure of 100 mbar and a ring-down time (τ_0) of 136 μ s, the detection limit of the CRDS spectrometer was $\sim 7.3 \times 10^7$ molecule/cm³ (1 σ , 10s). The corresponding detection sensitivity was 1.5×10^{-11} cm⁻¹, which was close to the state-of-the-art performance. By replacing the DFB diode laser with a narrow linewidth erbium-doped fiber (EDF) laser, the amplitude fluctuation caused by the laser phase noise was reduced and the cavity mode injection efficiency was improved. The sensitivity was improved to 3.9×10^{-12} cm⁻¹ with a short data-acquisition time of 0.2 s. Compared with the DFB laser, the improvement was nearly an order of magnitude. The use of the narrow linewidth laser is attractive. The instrument can achieve very high sensitivity without the need for a complex locking technique, ensuring simple and ease of use in future field applications.

© 2022 Optica Publishing Group under the terms of the [Optica Open Access Publishing Agreement](#)

1. Introduction

The hydroperoxyl radical (HO₂) plays key roles in atmospheric chemistry [1]. It reacts with NO to generate hydroxyl radical (OH) and nitrogen dioxide (NO₂), resulting in the HO_x (\equiv OH + HO₂) cycle that governs the atmospheric oxidation capacity and the formation of air pollution [2], and a net production of ozone that determines the troposphere ozone budget [3]. Quantitative measurement of its absolute concentration is very important. However, due to its short lifetime and low concentration (typically about 10⁸ to 10⁹ molecule/cm³ under atmospheric condition), most of the currently used methods are indirect methods that require chemical conversion; direct measurement remains very challenging [4].

The cavity ring-down spectroscopy (CRDS) technique uses high reflectivity mirrors to increase the effective absorption pathlength to tens of kilometers, enabling very high detection sensitivity;

the absolute concentration of the target absorbers can be quantitatively determined by the Beer-Lambert law, providing a powerful tool for direct measurement of free radicals [5–7]. In 2006, CRDS was successfully combined with laser photolysis to perform spectroscopic and kinetic measurement of HO₂ near 6625 cm⁻¹ by Thiébaud and Fittschen [8]. The reported detection limit was 2 × 10¹² molecule/cm³. Later, a stronger absorption line at 6638.207 cm⁻¹ (1506.43 nm, with a line strength (*S*) of 7.09 × 10⁻²¹ cm⁻¹/(molecule cm⁻²)) was selected to lower the detection limit down to 1.5 × 10¹⁰ molecule/cm³ [9,10]. Recently, a CRDS spectrometer was developed in the HIRAC (Highly Instrument Reactor for Atmospheric Chemistry) atmospheric simulation chamber by Onel et al. [4] using higher reflectivity mirrors ($\tau_0 \sim 230 \mu\text{s}$). The cavity length was 1.5 m across the chamber. The reported detection limit was 3 × 10⁸ molecule/cm³ (2 σ , 30 s data acquisition time) at 150 mbar, corresponding to a detection sensitivity of about 1.5 × 10⁻¹¹ cm⁻¹. When the pressure was increased to 1000 mbar, the detection limit decreased to 1.5 × 10⁹ molecule/cm³ due to the air-broadening of the absorption line and the reduction of the absorption cross section.

In this work, we report the development of a portable CRDS spectrometer operating at 1506 nm for the direct and absolute measurement of HO₂ radical. The effect of laser linewidth on detection sensitivity was studied by using a distributed feedback (DFB) diode laser with a linewidth of approximately 2 MHz and a narrow linewidth (< 0.1 kHz) erbium-doped fiber (EDF) laser. With a ring-down time τ_0 of 136 μs , a detection sensitivity of $\sim 1.5 \times 10^{-11} \text{ cm}^{-1}$ (1 σ , 10s) was achieved using the DFB diode laser at 100 mbar, corresponding to a HO₂ detection limit of 7.3 × 10⁷ molecule/cm³. Using the EDF laser, the sensitivity was better than 3.9 × 10⁻¹² cm⁻¹ (1 σ , 0.2 s). Compared to DFB laser, the improvement was about an order of magnitude, making it possible for ambient applications.

2. Experimental section

The experimental setup of the developed CRDS HO₂-spectrometer and the photograph of the optical layout are shown in Fig. 1. The optical layer was made of high-strength hard aluminum alloy with dimensions of 1000 × 400 × 140 mm³. The optical cavity was made of perfluoroalkoxy (PFA) tube with 9 mm inner diameter (1/2 inch outer diameter). The sample inlet and outlet of the cavity were composed of tee unions. The sample flow rate was controlled at 1.5 L/min. The pressure inside the cavity was monitored with a capacitance diaphragm gauge (Agilent, CDG-500), and maintained at 100 mbar with a butterfly vacuum valve (VAT). Two high reflectivity mirrors (Layertec, 1 m radius of curvature, 25 mm diameter), separated by a distance of ~ 49.8 cm, were installed in mirror chambers and protected with flushed pure dry zero air (50 ml/min for each mirror). One of the mirrors was mounted on the mirror mount (Thorlabs, Polaris-K1S3P) with piezoelectric adjuster (PZT) to dither the cavity length at a frequency of 250 Hz via a piezo controller.

The laser source used was a room-temperature-operated DFB diode laser (NTT, butterfly-type, 14 pin package) operating at 1506 nm with a typical output power of ~ 20 mW and a linewidth of ~ 2 MHz, which was controlled by an LDC 501 laser diode controller (Stanford Research System). Laser frequency tuning was achieved by controlling the laser injection current step-by-step with a GPIB card [11]. The fiber output of the laser was directly connected to a fiber-coupled acousto-optic modulator (AOM, Brimrose, IPM-200-25-20-1509); collimated with an adjustable fiber aspheric collimator (Thorlabs, CFC8-C), and then coupled to the high-finesse optical cavity. The effective focal length of the collimator was 7.5 mm. By rotating the outer barrel of the collimator, the distance between the fiber tip and the lens can be adjusted from 4.2 to 6.8 mm. Once the spatial mode of the laser matched the cavity mode, the adjustment was locked into place. Between the collimator and the optical cavity, an infrared free-space isolator (Thorlabs, IOT-4-1550-VLP) was placed to avoid the back reflections. A half-wave plate was placed between the collimator and isolator to control the polarization of the beam. Light exiting the cavity was

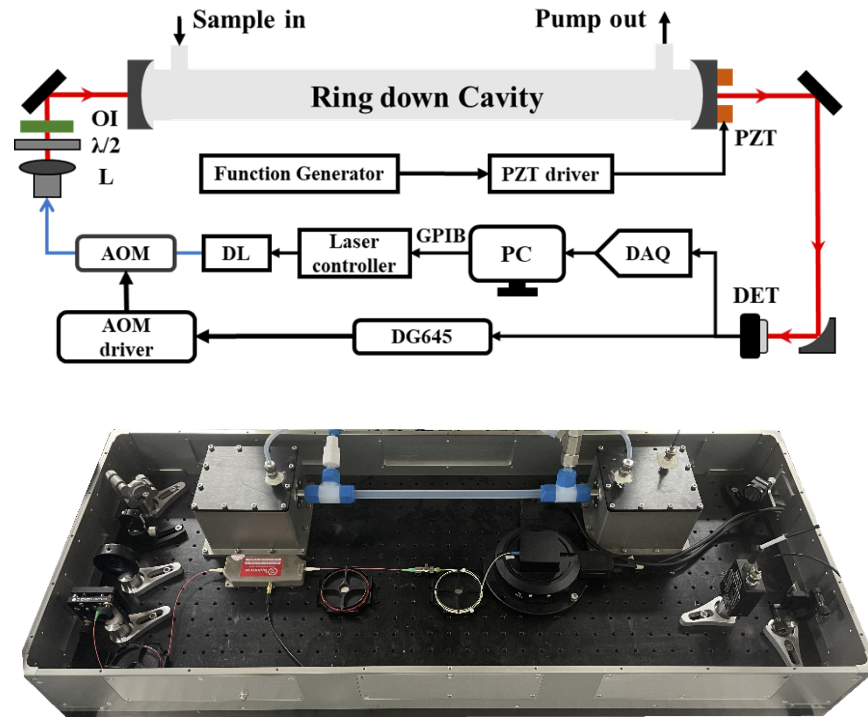


Fig. 1. Schematic diagram of the CRDS HO₂-spectrometer (upper panel) and the corresponding photograph of the optical layout (lower panel). DL, diode laser; L, collimator; OI, isolator; DET, detector; DAQ, data acquisition; PC, personal computer.

collimated by a parabolic mirror and detected by an InGaAs avalanche photodetector (Thorlabs, APD410C) with 10 MHz bandwidth. When the transmission intensity of the cavity reached the set threshold, the digital pulse generator (DG645) sent a trigger signal to the AOM and DAQ card (NI, USB 6356) to block the laser and record the ring-down signal.

A typical ring-down curve is shown in Fig. 2. The exponential decay was fitted with the linear regression of the sum (LRS) method [12] to obtain the decay time constant (τ). Compared with the commonly used nonlinear Levenberg–Marquardt algorithm, the LRS method has demonstrated the advantages of high speed and high accuracy [12,13]. For the cavity consisting of two mirrors with identical reflectivity (R), the ring-down time of the empty cavity is:

$$\tau_0 = \frac{L}{c(1-R)} \quad (1)$$

where L is the distance between the two high-reflectivity mirrors and the effective absorption pathlength (L_{eff}) is equal to $L/(1-R)$ or $c\tau_0$. The cavity mode linewidth ($\Delta\nu_{cavity}$) is given by [7]:

$$\Delta\nu_{cavity} = \nu_{FSR}/F \quad (2)$$

where $\nu_{FSR} = c/2L$ is the free-spectral-range (FSR), and $F = \pi\sqrt{R}/(1-R)$ is the finesse of the cavity.

The absorption coefficient (α) can be determined from the change of the ring-down time with (τ) and without (τ_0) sample in the cavity:

$$\alpha = \sigma n = \frac{R_L}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (3)$$

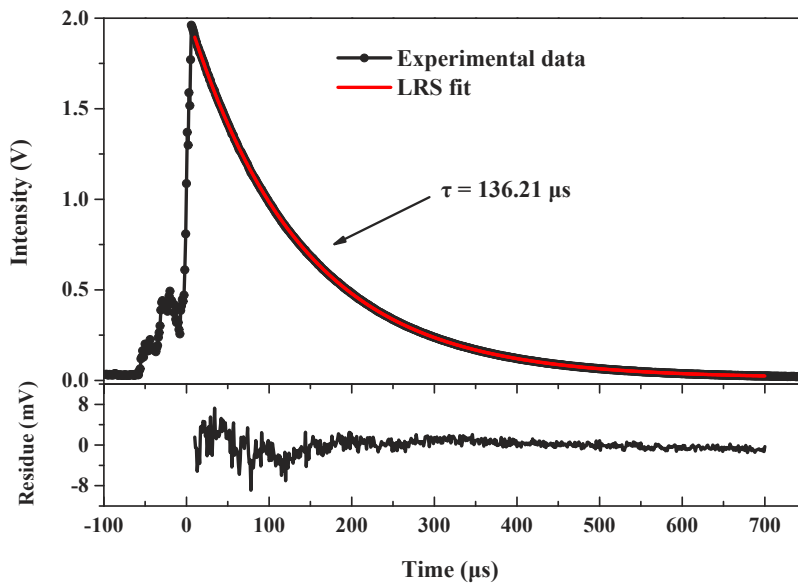


Fig. 2. An example of the recorded ring-down curve, exponential fit, and the corresponding fit residual.

where σ and n are the absorption cross-section and number density of the sample, respectively. c is the speed of the light, and R_L is the ratio between the cavity mirror distance to the cell length containing the sample.

In this work, the ring down time τ_0 was $\sim 136 \mu\text{s}$, giving a mirror reflectivity $R \sim 99.9988\%$, which corresponded to an effective absorption pathlength of $\sim 40.8 \text{ km}$. The cavity finesse and mode linewidth were about 257000 and 1.2 kHz, respectively. R_L was determined to be ~ 1.23 by measuring the absorption of different concentrations of gas with and without mirror purging [14].

3. Results

3.1. HO_2 absorption measurement

For the performance evaluation of the CRDS HO_2 -spectrometer, a custom-built photochemical reactor was used to generate HO_2 radicals by the photolysis of H_2O with UV lamps at 184.9 nm ($\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$, $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$) [15]. A schematic diagram of the photoreactor is shown in Fig. 3, which was similar to the oxidation flow reactor developed by Shah et al. [16]. The reactor was made of 300 mm long quartz tube (with 160 mm outer diameter and 3 mm wall thickness). The photolysis sources, two low-pressure Hg lamps (Analytic jena, 90-0004), were mounted inside an 18 mm inner diameter UV fused silica glass tube (with 450 mm long and 1 mm wall thickness) in the center of the photoreactor. A small stream of N_2 was used to cool the Hg lamps and prevent the formation of ozone in the glass tube to address the effects of temperature and ozone absorption on the transmission spectrum of the Hg lamp. The H_2O was produced by passing zero air flow through a water bubbler. The lamps photolyzed the humidified air in the radial direction. Different concentrations of H_2O can be obtained by changing the ratio of the bypass flow, thereby producing different concentrations HO_2 radicals.

An example of the HO_2 CRDS absorption spectra with a resolution of 0.0005 cm^{-1} at 100 mbar pressure for the DFB diode laser system is shown in Fig. 4. At each laser frequency, 600 ring-down events was averaged. The corresponding sampling time for each data point was approximately 4 s. There is a H_2O absorption line (6638.165 cm^{-1} , $S = 3.74 \times 10^{-27} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$)

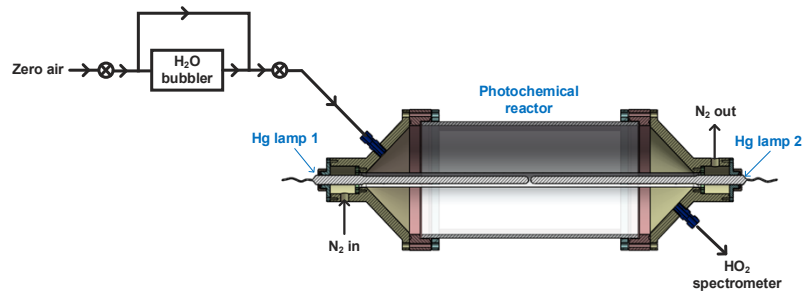


Fig. 3. Schematic of the photochemical reactor for the generation of different concentrations of HO₂ radicals.

[17] in the middle of the two HO₂ absorption lines. The concentrations of HO₂ (1.03×10^{11} molecule/cm³) and H₂O (2.3%) were obtained by fitting the spectra with Voigt line profiles. With a peak absorption coefficient of $\sim 2.1 \times 10^{-8}$ cm⁻¹ for HO₂ at 6638.207 cm⁻¹ and a fit residual of $\sim 5.7 \times 10^{-11}$ cm⁻¹, a 1 σ detection limit of $\sim 2.8 \times 10^8$ molecule/cm³ was deduced with the spectrum measurement.

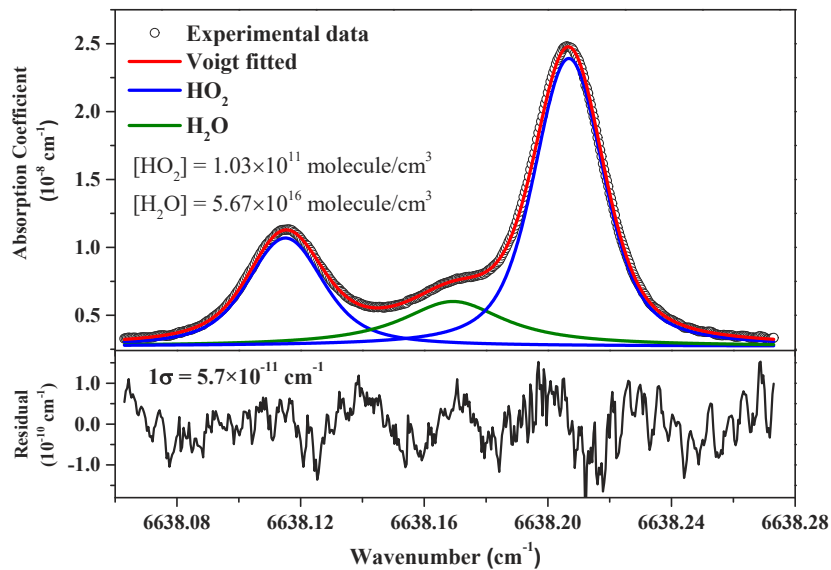


Fig. 4. CRDS spectra of HO₂ and H₂O. A multispectrum fitted Voigt line profile and the corresponding fitting residual are presented.

3.2. Sensitivity of the DFB diode laser-based CRDS system

Due to the short lifetime of HO₂ (no commercial product, it needs to be generated on-site), it is difficult to obtain very stable concentrations. Time series measurement of the zero air was performed to investigate the stability and baseline precision of the spectrometer. The result is shown in Fig. 5. The sampling time for each data point was about 0.0067 s (single ring-down event without averaging). The minimum detectable absorption coefficient (α_{\min}) can be expressed as:

$$\alpha_{\min} = \frac{\Delta\tau_{\min}}{\tau_0} \frac{1}{c\tau_0} \quad (4)$$

The averaged value of τ_0 was $136.3 \mu\text{s}$ with a standard deviation of $0.21 \mu\text{s}$. The time series measured α_{\min} was about $3.7 \times 10^{-10} \text{ cm}^{-1}$. Allan variance analysis shows that the sensitivity was improved to $3.0 \times 10^{-11} \text{ cm}^{-1}$ with 1 s data acquisition time (averaging result of 150 ring-down events). The system shows White noise dominant characteristics. When the acquisition time was extended to 10 s, the sensitivity can be lowered down to $1.5 \times 10^{-11} \text{ cm}^{-1}$, which corresponding to a HO_2 detection limit of $7.3 \times 10^7 \text{ molecule/cm}^3$.

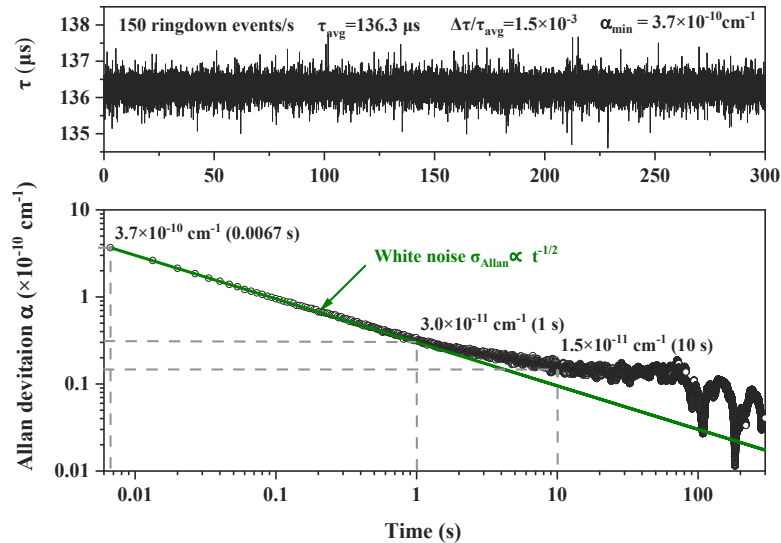


Fig. 5. Time series measurement of zero air and the corresponding Allan deviation plot of the absorption coefficient of the DFB diode laser based CRDS HO_2 -spectrometer.

3.3. Performance of the erbium-doped fiber laser-based CRDS system

In cavity ring down spectroscopy, the coupling efficiency of the laser beam into the cavity depends on the laser frequency tuning speed and the ratio of the laser linewidth to the cavity mode width. For the DFB laser system, the laser linewidth ($\sim 2 \text{ MHz}$) was approximately 1700 times larger than that of the cavity mode ($\sim 1.2 \text{ kHz}$), which results in the conversion of laser phase noise into amplitude fluctuation, making the cavity injection noisy and limiting the improvement of detection sensitivity [18,19].

To further improve the performance of the CRDS spectrometer, the DFB laser was replaced with a narrow linewidth erbium-doped fiber (EDF) laser (NKT Photonics, E15). The EDF laser has the advantages of ultra-low phase noise and narrow linewidth ($< 0.1 \text{ kHz}$). The trigger signals and ring-down curves are shown in Fig. 6. Since the laser linewidth was 10 times smaller than the cavity mode, it can be considered as a monochromatic injection. The injection efficiency of the EDF laser system was significantly improved compared to the DFB diode laser system. At 250 Hz cavity dithering frequency, the trigger probability of the ring-down events increased from 150 to 500 ring-down events per second. It is expected that the trigger rate and level can be further increased, thereby shortening the sampling time, increasing the signal-to-noise ratio of the recorded exponential decays, and further improving the detection sensitivity.

An example ring-down curve with EDF laser and its corresponding exponential fit residual are shown in Fig. 7. Compared with the DFB laser based CRDS system, the ring down time τ_0 was not changed by changing the laser source. We calculated the detector noise ($\sigma_{\text{detector noise}}$) and the

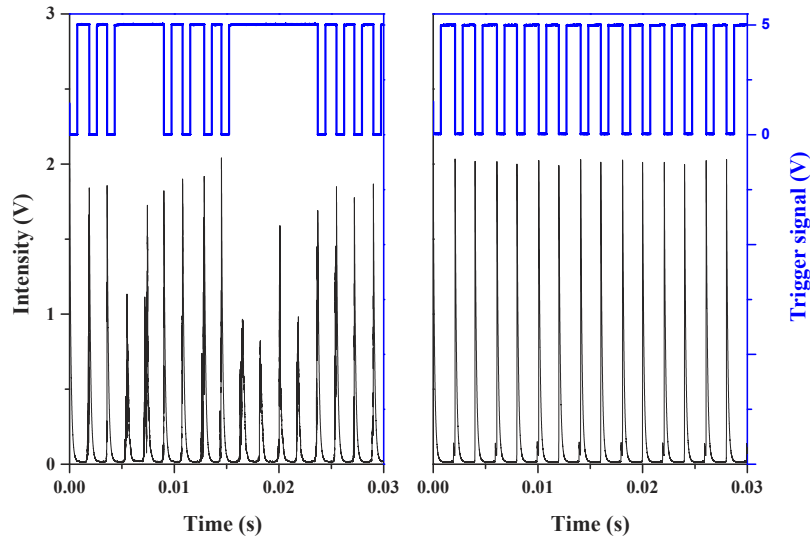


Fig. 6. Trigger signals and ring-down curves for the CRDS spectrometer with : (a) DFB and (b) EDF laser. By using a narrow linewidth EDF laser, the trigger frequency of the ring-down events was increased, and the fluctuation of the light intensity transmission was reduced.

shot noise ($\sigma_{\text{shot noise}}$) for a comparison [20,21]:

$$\sigma_{\text{detector noise}} = \left(\text{NEP} / \sqrt{2} \right) \beta G \sqrt{B}, \quad (5)$$

$$\sigma_{\text{shot noise}} = \sqrt{1/2 q G V(t) B}, \quad (6)$$

where NEP , β , G , and B are the noise-equivalent power, responsivity, transimpedance gain, and electronic bandwidth of the detector, respectively. q is the electron charge. $V(t)$ is the output voltage of the detector. The fit residual shown in Fig. 7 was comparable with the summation of the calculated detector and shot noises. From the results of averaging 500 successive fit residuals, there was no obvious structure, demonstrating the good performance of the EDF system [21,22]. The laser linewidth can be considered as the fluctuation of the phase of the laser field, and the changes of intensity and phase are coupled. The narrow linewidth EDF system reduced the intrinsic noise that caused by the instantaneous changes in the laser phase and intensity due to the spontaneous emission of the laser [18,23].

Performance evaluation of the EDF system was further analyzed with Allan variance [24]. The result is shown in Fig. 8. The sampling time for each data point was 0.002 s. Due to the narrower laser linewidth and the improvement of the coupling efficiency, the achievable detection sensitivity ($3.9 \times 10^{-11} \text{ cm}^{-1}$) of a single ring-down measurement was about one order of magnitude improved than that of the DFB diode laser ($3.7 \times 10^{-10} \text{ cm}^{-1}$). When the data averaging time extended to 0.2 s, the sensitivity of the CRDS spectrometer can be further improved to $3.9 \times 10^{-12} \text{ cm}^{-1}$, the corresponding HO_2 detection limit was about $1.9 \times 10^7 \text{ molecule/cm}^3$.

The atmospheric lifetime of HO_2 radicals is about 100 s, allowing it to transport with a sampling tube [1]. For future atmospheric application, a sample of ambient air (at 1 atm pressure) can be pumped directly into the cavity (100 mbar). The concentrations of the target gases will be roughly reduced by 10 times. Therefore, under optimistic conditions, the achievable detection limit for HO_2 in the atmosphere was estimated to be $\sim 1.9 \times 10^8 \text{ molecule/cm}^3$. Although the wall loss caused by the sampling tube needs to be corrected, the limit reported here is lower than

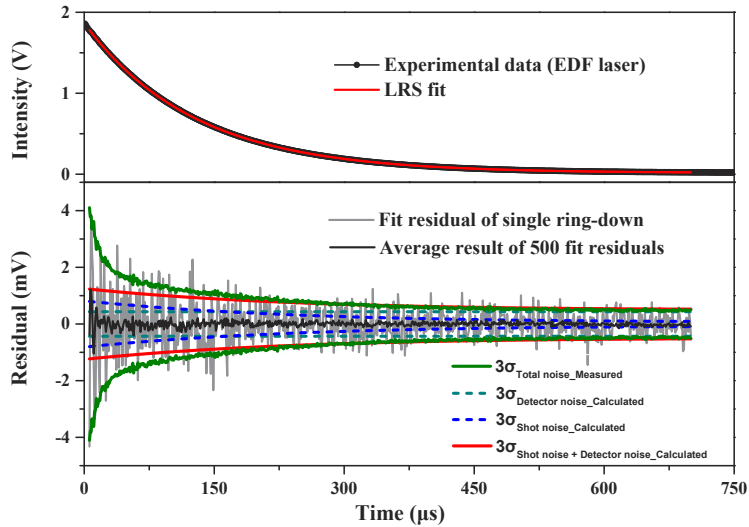


Fig. 7. Exponential fit residual for a single ring-down event using EDF laser. The calculated detector and shot noises are shown for comparison.

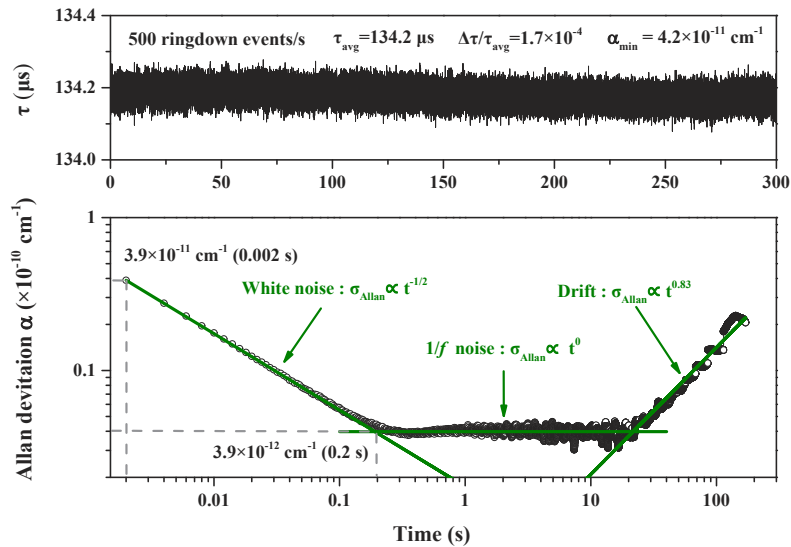


Fig. 8. Performance evaluation of the instrument with a narrow linewidth EDF laser. Time series measurement of zero air and the corresponding Allan deviation plot of the absorption coefficient are shown in the upper and lower panel, respectively.

the maximum HO₂ concentration ($\sim 2 \times 10^9$ molecule/cm³) around noon near Guangzhou in the Pearl River Delta region [25], which makes ambient applications promising.

From the time dependence analysis of the Allan variance, noise contributions of the HO₂-CRDS spectrometer can be clearly shown [24]. At the beginning, the system was dominated by White noise ($\sigma_{\text{Allan}} \propto t^{-1/2}$). The detection sensitivity can be improved by increasing the integration time. Then, $1/f$ noise dominated. The noise was independent of the data acquisition time. Increasing the sampling time did not change the detection sensitivity. After that, drift noise dominated, the noise is proportion to $t^{0.83}$. The sensitivity deteriorated as the sampling time increased.

Although limited by the $1/f$ noise, to the best of our knowledge, the sensitivity achieved in this work is the best among the traditional CRDS. To reduce the intrinsic $1/f$ noise limit, measurement can be made at high frequency. For example, Long et al. [26] demonstrated a quantum noise limited (6×10^{-14} cm⁻¹ Hz^{-1/2} with a cavity finesse of 20000) heterodyne detection method [27]. With the overcoming of the $1/f$ noise, the performance of the system is expected to be further improved.

4. Conclusion

In this paper, we report the development of a portable CRDS spectrometer for direct and absolute measurement of HO₂ radicals. With ring-down time τ_0 of 136 μ s, a detection sensitivity of $\sim 1.5 \times 10^{-11}$ cm⁻¹ (1σ , 10s) was achieved with a DFB diode laser. The corresponding HO₂ detection limit was $\sim 7.3 \times 10^7$ molecule/cm³. In addition, the use of a EDF laser to replace the DFB laser significantly reduces the amplitude fluctuation caused by laser phase noise and improve the cavity mode injection efficiency. The detection sensitivity was improved to 3.9×10^{-12} cm⁻¹ (1σ , 0.2 s), which was about one order of magnitude lower than that of the DFB diode laser based CRDS system.

Although there are many literatures reporting the use of sophisticated electronic locking techniques to achieve shot-noise performance (10^{-12} - 10^{-14} cm⁻¹ over 1 s data averaging time) [28–30,22], traditional CRDS methods still play a pivotal role in atmospheric trace detection due to their simplicity and ease of operation [21]. The use of narrow linewidth laser method reported in this work, which effectively improves the detection sensitivity by overcoming the amplitude noise of the cavity mode, is worth exploring.

In recent years, with the rapid development of high reflectivity mirror coating technology (extremely low optical loss, < 10 ppmv) [31] and laser technology (for example, frequency-stabilized laser source with 530 Hz linewidth was developed with optical feedback method) [32,33], as well as the successful combination of cavity spectroscopy with various advanced high sensitivity spectroscopy techniques such as Faraday rotation spectroscopy [34,35], spectroscopic detection of free radicals has become more and more attractive and promising. The goal of direct measurement of the absolute concentration of ambient HO₂ is feasible and is getting closer to realization. Of course, we do not rule out the use of locking technology, which will keep the instrument running at its best.

Funding. National Natural Science Foundation of China (41627810, 42022051, U21A2028); Youth Innovation Promotion Association (Y202089); HFIPS Director's Fund (YZJJ202101).

Disclosures. The authors declare no conflicts of interest.

Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

References

1. D. E. Heard and M. J. Pilling, "Measurement of OH and HO₂ in the troposphere," *Chem. Rev.* **103**(12), 5163–5198 (2003).

2. K. Lu, S. Guo, Z. Tan, H. Wang, D. Shang, Y. Liu, X. Li, Z. Wu, M. Hu, and Y. Zhang, "Exploring atmospheric free-radical chemistry in China: the self-cleansing capacity and the formation of secondary air pollution," *Natl. Sci. Rev.* **6**(3), 579–594 (2019).
3. A. T. Archibald, J. L. Neu, Y. F. Elshorbany, O. R. Cooper, P. J. Young, H. Akiyoshi, R. A. Cox, M. Coyle, R. G. Derwent, M. Deushi, A. Finco, G. J. Frost, I. E. Galbally, G. Gerosa, C. Granier, P. T. Griffiths, R. Hossaini, L. Hu, P. Jöckel, B. Josse, M. Y. Lin, M. Mertens, O. Morgenstern, M. Naja, V. Naik, S. Oltmans, D. A. Plummer, L. E. Revell, A. Saiz-Lopez, P. Saxena, Y. M. Shin, I. Shahid, D. Shallcross, S. Tilmes, T. Trickl, T. J. Wallington, T. Wang, H. M. Worden, and G. Zeng, "Tropospheric ozone assessment report: a critical review of changes in the tropospheric ozone burden and budget from 1850 to 2100," *Elem. Sci. Anth.* **8**(1), 034 (2020).
4. L. Onel, A. Brennan, M. Gianella, G. Ronnie, A. Lawry Aguila, G. Hancock, L. Whalley, P. W. Seakins, G. A. D. Ritchie, and D. E. Heard, "An intercomparison of HO₂ measurements by fluorescence assay by gas expansion and cavity ring-down spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)," *Atmos. Meas. Tech.* **10**(12), 4877–4894 (2017).
5. M. Mazurenka, A. J. Orr-Ewing, R. Peverall, and G. A. D. Ritchie, "4 Cavity ring-down and cavity enhanced spectroscopy using diode lasers," *Annu. Rep. Prog. Chem., Sect. C* **101**, 100–142 (2005).
6. S. M. Hu, "Trace gas measurements using cavity ring-down spectroscopy," in *Advances in spectroscopic monitoring of the atmosphere*, W. Chen, D. S. Venables, and M. W. Sigrist, eds. (Elsevier, 2021), pp. 413–441.
7. A. Maity, S. Maithani, and M. Pradhan, "Cavity ring-down spectroscopy: recent technological advancements, techniques, and applications," *Anal. Chem.* **93**(1), 388–416 (2021).
8. J. Thiébaud and C. Fittschen, "Near infrared cw-CRDS coupled to laser photolysis: spectroscopy and kinetics of the HO₂ radical," *Appl. Phys. B* **85**(2-3), 383–389 (2006).
9. J. Thiébaud, S. Crunaire, and C. Fittschen, "Measurements of line strengths in the 2v₁ band of the HO₂ radical using laser photolysis/continuous wave cavity ring-down spectroscopy (cw-CRDS)," *J. Phys. Chem. A* **111**(30), 6959–6966 (2007).
10. M. Djehiche, A. Tomas, C. Fittschen, and P. Coddeville, "First cavity ring-down spectroscopy HO₂ measurements in a large photoreactor," *Z. Phys. Chem.* **225**(9-10), 938–992 (2011).
11. N. Yang, B. Fang, W. Zhao, C. Wang, F. Cheng, X. Hu, Y. Chen, W. Zhang, W. Ma, G. Zhao, and W. Chen, "Optical-feedback cavity-enhanced absorption spectroscopy for OH radical detection at 2.8 μm using a DFB diode laser," *Opt. Express* **30**(9), 15238–15249 (2022).
12. M. A. Everest and D. B. Atkinson, "Discrete sums for the rapid determination of exponential decay constants," *Rev. Sci. Instrum.* **79**(2), 023108 (2008).
13. N. Sobanski, J. Schuladen, G. Schuster, J. Lelieveld, and J. N. Crowley, "A five-channel cavity ring-down spectrometer for the detection of NO₂, NO₃, N₂O₅, total peroxy nitrates and total alkyl nitrates," *Atmos. Meas. Tech.* **9**(10), 5103–5118 (2016).
14. W. Zhao, X. Xu, B. Fang, Q. Zhang, X. Qian, S. Wang, P. Liu, W. Zhang, Z. Wang, D. Liu, Y. Huang, D. S. Venables, and W. Chen, "Development of an incoherent broad-band cavity-enhanced aerosol extinction spectrometer and its application to measurement of aerosol optical hygroscopicity," *Appl. Opt.* **56**(11), E16–E22 (2017).
15. M. Schultz, M. Heitlinger, D. Mihelcic, and A. Volz-Thomas, "Calibration source for peroxy radicals with built-in actinometry using H₂O and O₂ photolysis at 185 nm," *J. Geophys. Res.* **100**(D9), 18811–18816 (1995).
16. R. U. Shah, M. M. Coggon, G. I. Gkatzelis, B. C. McDonald, A. Tasoglou, H. Huber, J. Gilman, C. Warneke, A. L. Robinson, and A. A. Presto, "Urban oxidation flow reactor measurements reveal significant secondary organic aerosol contributions from volatile emissions of emerging importance," *Environ. Sci. Technol.* **54**(2), 714–725 (2020).
17. I. E. Gordon, L. S. Rothman, R. J. Hargreaves, R. Hashemi, E. V. Karlovets, F. M. Skinner, E. K. Conway, C. Hill, R. V. Kochanov, Y. Tan, P. Wcisło, A. A. Finenko, K. Nelson, P. F. Bernath, M. Birk, V. Boudon, A. Campargue, K. V. Chance, A. Coustenis, B. J. Drouin, J. M. Flaud, R. R. Gamache, J. T. Hodges, D. Jacquemart, E. J. Mlawer, A. V. Nikitin, V. I. Perevalov, M. Rotger, J. Tennyson, G. C. Toon, H. Tran, V. G. Tyuterev, E. M. Adkins, A. Baker, A. Barbe, E. Canè, A. G. Császár, A. Dudaryonok, O. Egorov, A. J. Fleisher, H. Fleurbaey, A. Foltynowicz, T. Furtenbacher, J. J. Harrison, J. M. Hartmann, V. M. Horneman, X. Huang, T. Karman, J. Karns, S. Kass, I. Kleiner, V. Kofman, F. Kwabia-Tchana, N. N. Lavrentieva, T. J. Lee, D. A. Long, A. A. Lukashovskaya, O. M. Lyulin, V. Y. Makhnev, W. Matt, S. T. Massie, M. Melosso, S. N. Mikhailenko, D. Mondelain, H. S. P. Müller, O. V. Naumenko, A. Perrin, O. L. Polyansky, E. Raddaoui, P. L. Raston, Z. D. Reed, M. Rey, C. Richard, R. Tóbiás, I. Sadiék, D. W. Schwenke, E. Starikova, K. Sung, F. Tamassia, S. A. Tashkun, J. V. Auwera, I. A. Vasilenko, A. A. Viginin, G. L. Villanueva, B. Vispoel, G. Wagner, A. Yachmenev, and S. N. Yurchenko, "The HITRAN2020 molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transf.* **277**, 107949 (2022).
18. J. Morville, D. Romanini, M. Chenevier, and A. Kachanov, "Effects of laser phase noise on the injection of a high-finesse cavity," *Appl. Opt.* **41**(33), 6980–6990 (2002).
19. D. Romanini, I. Ventrillard, G. Méjean, J. Morville, and E. Kerstel, "Introduction to cavity enhanced absorption spectroscopy," in *Cavity-Enhanced Spectroscopy and Sensing*, G. Gagliardi and H. P. Loock, eds. (Springer, 2014), pp. 1–60.
20. R. D. van Zee, J. T. Hodges, and J. P. Looney, "Pulsed, single-mode cavity ringdown spectroscopy," *Appl. Opt.* **38**(18), 3951–3960 (1999).
21. D. A. Long, A. J. Fleisher, Q. Liu, and J. T. Hodges, "Ultra-sensitive cavity ring-down spectroscopy in the mid-infrared spectral region," *Opt. Lett.* **41**(7), 1612–1615 (2016).

22. J. Burkart, D. Romanini, and S. Kassi, "Optical feedback frequency stabilized cavity ring-down spectroscopy," *Opt. Lett.* **39**(16), 4695–4698 (2014).
23. C. H. Henry, "Theory of the Linewidth of Semiconductor-Lasers," *IEEE J. Quantum. Elect.* **18**(2), 259–264 (1982).
24. P. Werle, R. Mücke, and F. Slemr, "The limits of signal averaging in atmospheric trace-gas monitoring by tunable diode-laser absorption spectroscopy (TDLAS)," *Appl. Phys. B* **57**(2), 131–139 (1993).
25. A. Hofzumahaus, F. Rohrer, K. Lu, B. Bohn, T. Brauers, C.-C. Chang, H. Fuchs, F. Holland, K. Kita, Y. Kondo, X. Li, S. Lou, M. Shao, L. Zeng, A. Wahner, and Y. Zhang, "Amplified trace gas removal in the troposphere," *Science* **324**(5935), 1702–1704 (2009).
26. D. A. Long, A. J. Fleisher, S. Wójtewicz, and J. T. Hodges, "Quantum-noise-limited cavity ring-down spectroscopy," *Appl. Phys. B* **115**(2), 149–153 (2014).
27. J. Ye and J. L. Hall, "Cavity ringdown heterodyne spectroscopy: high sensitivity with microwatt light power," *Phys. Rev. A* **61**(6), 061802 (2000).
28. J. Ye, L.-S. Ma, and J. L. Hall, "Ultrasensitive detections in atomic and molecular physics: demonstration in molecular overtone spectroscopy," *J. Opt. Soc. Am. B* **15**(1), 6–15 (1998).
29. T. G. Spence, C. C. Harb, B. A. Paldus, and R. N. Zare, "A laser-locked cavity ring-down spectrometer employing an analog detection scheme," *Rev. Sci. Instrum.* **71**(2), 347–353 (2000).
30. D. A. Long, A. Cygan, R. D. van Zee, M. Okumura, C. E. Miller, D. Lisak, and J.T. Hodges, "Frequency-stabilized cavity ring-down spectroscopy," *Chem. Phys. Lett.* **536**, 1–8 (2012).
31. G. Winkler, L. W. Perner, G.-W. Truong, G. Zhao, D. Bachmann, A. S. Mayer, J. Fellingner, D. Follman, P. Heu, C. Deutsch, D. M. Bailey, H. Peelaers, S. Puchegger, A. J. Fleisher, G. D. Cole, and O. H. Heckl, "Mid-infrared interference coatings with excess optical loss below 10 ppm," *Optica* **8**(5), 686–696 (2021).
32. J. Burkart, D. Romanini, and S. J. Kassi, "Optical feedback stabilized laser tuned by single-sideband modulation," *Opt. Lett.* **38**(12), 2062–2064 (2013).
33. J. Burkart and S. Kassi, "Absorption line metrology by optical feedback frequency-stabilized cavity ring-down spectroscopy," *Appl. Phys. B* **119**(1), 97–109 (2015).
34. M. Gianella, S. A. Press, K. M. Manfred, H. C. Norman, M. Islam, and G. A. D. Ritchie, "Sensitive detection of HO₂ radicals produced in an atmospheric pressure plasma using Faraday rotation cavity ring-down spectroscopy," *J. Chem. Phys.* **151**(12), 124202 (2019).
35. J. Westberg and G. Wysocki, "Cavity ring-down Faraday rotation spectroscopy for oxygen detection," *Appl. Phys. B* **123**(5), 168 (2017).