



Article

Intercomparison of NO₃ under Humid Conditions with Open-Path and Extractive IBBCEAS in an Atmospheric Reaction Chamber

Meng Wang^{1,2}, Shengrong Lou^{1,2} , Weiwei Hu^{3,4}, Haichao Wang^{5,6}, Xinming Wang^{3,4} , Fengxian Fan¹, Ravi Varma⁷ , Dean S. Venables⁸ and Jun Chen^{1,*}

- ¹ Shanghai Key Laboratory of Multiphase Flow and Heat Transfer in Power Engineering, School of Energy and Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China
- ² State Environmental Protection Key Laboratory of Formation and Prevention of the Urban Air Pollution Complex, Shanghai Academy of Environmental Sciences, Shanghai 200233, China
- ³ State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
- ⁴ Guangdong Provincial Key Laboratory of Environmental Protection and Resources Utilization, Chinese Academy of Sciences, Guangzhou 510640, China
- ⁵ School of Atmospheric Sciences, Sun Yat-sen University, Guangzhou 510275, China
- ⁶ Guangdong Provincial Observation and Research Station for Climate Environment and Air Quality Change in the Pearl River Estuary, Key Laboratory of Tropical Atmosphere-Ocean System, Ministry of Education, Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai 519082, China
- ⁷ Department of Physics, National Institute of Technology Calicut, Calicut 673601, India
- ⁸ School of Chemistry and Environmental Research Institute, University College Cork, T12 YN60 Cork, Ireland
- * Correspondence: j.chen@usst.edu.cn

Abstract: We report an open-path incoherent broadband cavity-enhanced absorption spectroscopy (OP-IBBCEAS) technique for in situ simultaneous optical monitoring of NO₂, NO₃, and H₂O in a reaction chamber. The measurement precision values (1σ) are 2.9 ppbv and 2.9 pptv for NO₂ and NO₃ in 2 s, respectively, and the measurement uncertainties are 6% for NO₂ and 14% for NO₃. Intercomparison of measured concentrations of NO₂ and NO₃ by open-path and extractive IBBCEAS was carried out in the SAES-ARC reaction chamber during the reaction of NO₂ with O₃. The measurement accuracy of OP-IBBCEAS is verified by an NO₂ intercomparison and the NO₃ transmission efficiency of the extractive IBBCEAS is determined by comparison against the in situ NO₃ measurement. The relationship between H₂O absorption cross section and its mixing ratio at 295 K and 1 atm was analysed. Due to the spectral resolution of IBBCEAS system, the strong and narrow absorption lines of H₂O are unresolved and exhibit non-Beer–Lambert Law behaviour. Therefore, a correction method is used to obtain the effective absorption cross section for fitting the H₂O structure. An inappropriate H₂O absorption cross section can cause an overestimation of NO₃ concentration of about 28% in a humid atmosphere (H₂O = 1.8%). This spectroscopic correction provides an approach to obtain accurate NO₃ concentrations for open-path optical configurations, for example in chamber experiments or field campaigns. The measurement precision values are improved by a factor of 3 to 4 after applying Kalam filtering, achieving sub-ppbv (0.8 ppbv) and sub-pptv (0.9 pptv) performance in 2 s for NO₂ and NO₃, respectively.

Keywords: spectroscopy; open-path; IBBCEAS; trace pollutant detection; nitrate radical



Citation: Wang, M.; Lou, S.; Hu, W.; Wang, H.; Wang, X.; Fan, F.; Varma, R.; Venables, D.S.; Chen, J.

Intercomparison of NO₃ under Humid Conditions with Open-Path and Extractive IBBCEAS in an Atmospheric Reaction Chamber. *Remote Sens.* **2023**, *15*, 739. <https://doi.org/10.3390/rs15030739>

Academic Editor: Carmine Serio

Received: 6 December 2022

Revised: 21 January 2023

Accepted: 23 January 2023

Published: 27 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The nitrate radical (NO₃) governs the radical chemistry in the nocturnal troposphere [1,2]. The source of NO₃ is attributed to the formed through the reaction of nitrogen dioxide with ozone (Reaction (R1)):



NO_3 and N_2O_5 are generally in thermal equilibrium (Reactions (R2)) governed by the NO_2 concentration and the ambient temperature [3]:



NO_3 is lost via oxidation reaction with alkenes, aldehydes, and biogenic volatile organic compounds (VOCs; Reaction (R3)), which can lead to the formation of secondary aerosol (SOA) [4,5]:



The lifetime of NO_3 is short and its concentration is extremely low in the troposphere (in pptv range) due to its high reactivity. As a result, measurement of NO_3 is demanding, requiring high sensitivity and accuracy, together with high spatial and temporal resolution [1].

NO_3 absorbs red light efficiently via the strong $\text{B}^2\text{E}' \leftarrow \text{X}^2\text{A}_2'$ electronic transition [6]. This strong visible absorption band has been the basis for many spectroscopic approaches to NO_3 detection. In the 1970s, NO_3 radicals were first detected in the troposphere using long-path differential optical absorption spectroscopy (LP-DOAS), which was a pioneering method for measuring NO_3 in field experiments [7–11] and in chamber studies [12–14]. However, LP-DOAS measures the average mixing ratio over an optical path of several kilometres. The local mixing ratio of NO_3 at a specific site cannot be accurately quantified.

Among in-situ measurements, cavity ring-down spectroscopy (CRDS) was developed and widely deployed for laboratory studies [15,16] and field measurements of NO_3 [3,17,18]. Fiedler et al. [19] firstly proposed Incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS). The IBBCEAS (also termed BBCEAS, BBCEAS, or CE-DOAS) technique has been successfully applied for monitoring trace gas and aerosol extinction in recent years [20–28]. Extractive IBBCEAS systems have been successfully developed for the ground, vertical and airborne measurement of NO_3 and N_2O_5 [25,29–34] thanks to their high sensitivity and accuracy with high temporal resolution as CRDS. Since cavity-based instruments need to sample air into the optical cavity, losses of NO_3 on instrument surfaces must be quantified. The particle chemical compound, moisture content, air temperature and relative humidity [25,35] are the main factors impacting the transmission efficiency of NO_3 and contribute to the overall measurement uncertainty.

To avoid NO_3 sampling losses, open-path IBBCEAS (OP-IBBCEAS) was developed to measure NO_3 mixing ratios in a reaction chamber [20]. Shortly afterward, the OP-IBBCEAS was extended to other atmospheric trace gases like HONO, NO_2 , SO_2 , H_2O , IO, I_2 , BrO, Br_2 , O_3 , Formaldehyde (CH_2O), and nitrophenols et al. in the reaction chamber [21,23,36–43] and in field measurements [44–46]. Although an open-path approach avoids sampling losses, other challenges arising from the influence of aerosol extinction and water vapour on the spectral analysis should also be taken into account.

In this work, we set up a Laser-Driven Light Source (LDLS) based OP-IBBCEAS system coupled to a reaction chamber, and the design and performance are described. We use this open-path system to measure the mixing ratios of NO_2 and NO_3 and compare these measurements against those from an extractive IBBCEAS instrument. The transmission efficiency of the extractive NO_3 -IBBCEAS system was directly obtained by comparing the measured NO_3 concentrations. A correction method to obtain the effective absorption cross section of H_2O based on its mixing ratio is proposed and the influence of the water vapour mixing ratio on retrieving NO_3 is discussed. In the context of chamber experiments, the application of Kalman filtering to the OP-IBBCEAS system is explored, and the measurement precision is further improved.

2. Materials and Methods

2.1. Open-Path IBBCEAS

2.1.1. Instrument Setup

Figure 1 shows the OP-IBBCEAS instrument installed in the reaction chamber. The instrument was separated into transmitter and receiver platform. The light source is a Laser-Driven Light Source (LDLS, EQ-99X, Energetiq Technology, USA). Light from the LDLS was focused by a plano-convex lens ($f = 60$ cm) and collimated into the entrance cavity mirror by two beam steering mirrors. A green diode laser mounted on the transmitter platform was used to adjust the position of the platforms and align the optical cavity. The procedure for initial alignment of the cavity has been described previously [21]. The second cavity mirror was mounted on the receiver platform.

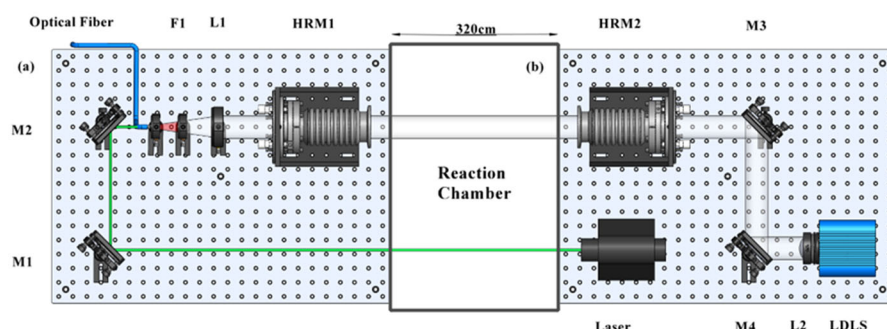


Figure 1. Schematic layout of the OP-IBBCEAS system and atmospheric simulation chamber (center). (a) The receiver platform. (b) The transmitter platform. These two platforms are installed on both sides of the chamber. M1 to M4 are beam steering mirrors. The high reflectivity mirrors HRM1 and HRM2 were mounted on the frames. F1 is an optical filter. L1 and L2 are the focus lenses.

The high-reflectivity (HR) optical cavity mirrors (Layertec GmbH) were 50 mm in diameter and had a 7 m radius of curvature. The reflectivity of the HR mirrors is greater than 0.999 from 620 to 670 nm reported by the manufacturer. The transmitted cavity light was focused by a plano-convex lens ($f = 60$ cm), filtered by a band-pass filter (FF02-675/67-25, Semrock, NY, USA), and coupled into a 100 μm -diameter optical fibre. The fibre was connected to a monochromator (Andor Kymera-328i-A, Andor Tech., Oxford Instruments, Oxford, UK) coupled with a CCD detector (Andor DU420A-BU, Andor Tech., Oxford Instruments, Oxford, UK). The monochromator uses 600 l mm^{-1} diffraction grating (500 nm blaze) and covered a wavelength range between 600 and 724 nm. The spectrometer resolution was determined by fitting the emission line of the mercury argon calibration light source (Hg-1, Ocean Optics) at 692.95 nm, corresponding to 0.54 nm. In order to minimize the dark current, the CCD detector was regulated and stabilized at -60.0 °C. For measurements at SAES, the transmitter unit and the receiver unit were installed on both sides of the cylindrical SAES-ARC chamber, giving a mirror separation d of 3.65 ± 0.04 m.

Both the transmitter and receiver platform were equipped with an adapter board to couple to the reaction chamber. One side of the adapter plate was connected to adjustable mirror mounts through 100 mm flexible bellows (50 mm inner diameter), and the other side was equipped with a 250 mm stainless steel pipe (50 mm inner diameter). The pipes served three purposes: first, The HR mirror could be contaminated by the sample air, resulting in a decrease in mirror reflectivity; purging the mirror is an efficient method to solve this problem. The inert gas could be kept in the pipe to form an air film to isolate the mirror from the sample gas. A flow of high-purity nitrogen (500 mL min^{-1}) was used to purge each cavity mirror. The path length through the reaction chamber was reduced to $d = (2.80 \pm 0.03)$ m because of the purging air. Second, the pipe on the receiver platform reduced stray light coupling into the detection system. Third, the pipes made a seal with the Teflon wall of the reaction chamber.

2.1.2. Measurement Principle

Fiedler et al. [19] first described the principle of IBBCEAS method. The extinction coefficient $\varepsilon(\lambda)$ of the sample can be determined from the reference spectrum, sample spectrum, effective cavity length and mirror reflectivity:

$$\varepsilon(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \left(\frac{1 - R(\lambda)}{d} \right) = \sum_i \sigma_i(\lambda) n_i + \alpha_{\text{Rayl}}(\lambda) + \alpha_{\text{Mie}}(\lambda) \quad (4)$$

In Equation (1), $I_0(\lambda)$ is the zero spectrum through “clean” air, $I(\lambda)$ is the spectrum with sample, λ is the wavelength, d is the effective length through the sample, $R(\lambda)$ is the mirror reflectivity, $\sigma_i(\lambda)$ and n_i are the absorption cross section and number density of i th species, $\alpha_{\text{Rayl}}(\lambda)$ and $\alpha_{\text{Mie}}(\lambda)$ is the extinction due to the Rayleigh and Mie scattering, respectively. Mie scattering from aerosols should be considered carefully when using an open path configuration in field or chamber settings.

The absorption cross section used to retrieve the mixing ratio of NO_2 was convolved from the high-resolution cross section at 293 K and 1000 mbar published by Voigt et al. [47]. The Voigt reference cross section was measured using Fourier-transform spectroscopy and had a resolution of 0.5 cm^{-1} above 435 nm (about 0.008 nm at 435 nm). The estimated uncertainty of this absorption cross section is about 4%. The absorption cross section used to retrieve the concentration of NO_3 was convolved from the cross section at 293 K reported by Yokelson et al. [6]. The resolution of the absorption cross section was around 0.1 nm between 440–694 nm. The uncertainty of this absorption cross section is about 13%. Figure 2a shows the applied absorption cross section of NO_2 and NO_3 [6,47] convolved to the instrument resolution of OP-IBBCEAS.

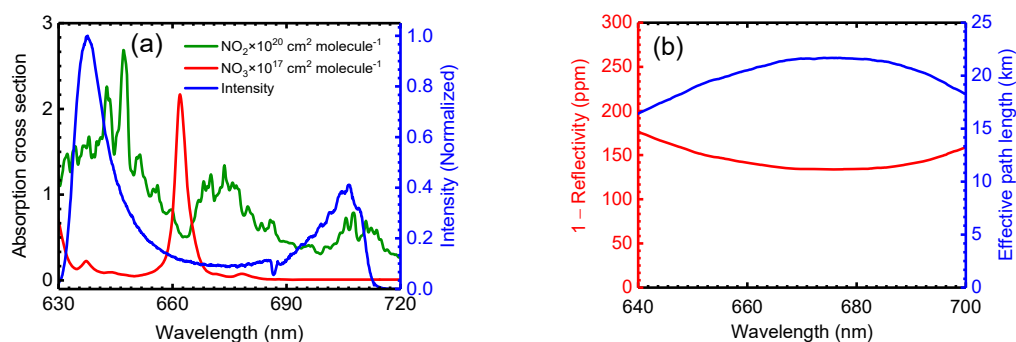


Figure 2. (a) The green and red spectrum are the absorption cross section of NO_2 and NO_3 convolved from Voigt et al. [47] and Yokelson et al. [6], respectively. The transmitted light intensity is shown as the blue line. (b) Mirror loss expressed as $(1 - R)$ and the corresponding effective path length.

2.1.3. The Mirror Reflectivity ($R(\lambda)$)

The number density of absorbing species can be quantified after determining the mirror reflectivity $R(\lambda)$ (Equation (1)). Various approaches have been taken to determine $R(\lambda)$ [18,20,21,37,48–50]. In this work, $R(\lambda)$ was determined by using a known concentration of NO_2 sample:

$$R(\lambda) = 1 - d \times \sigma_{\text{NO}_2}(\lambda) \times n_{\text{NO}_2} \times \left(\frac{I_{\text{NO}_2}(\lambda)}{I_{\text{Zero air}}(\lambda) - I_{\text{NO}_2}(\lambda)} \right) \quad (5)$$

Here, $I_{\text{Zero air}}$ and $I_{\text{NO}_2}(\lambda)$ were the transmitted light intensities through the cavity when the chamber was filled with zero air and after NO_2 was added, respectively. $\sigma_{\text{NO}_2}(\lambda)$ is the convolved NO_2 absorption cross section [47] according to the spectrograph instrument function and n_{NO_2} is the known number density of NO_2 . To determine $R(\lambda)$, NO_2 was injected into the chamber up to mixing ratios of 150 ppbv and the NO_2 concentrations were measured using a chemiluminescent NO_x analyser. Figure 2b shows the

mirror reflectivity calibration using this procedure. The reflectivity $R(\lambda)$ at 675 nm was 0.99987 ± 0.00002 ($1 - R = 130$ ppm), corresponding to an effective optical path length of 21.7 km ($d/(1 - R(\lambda))$) in the clean chamber.

2.2. Extractive IBBCEAS

• NO₂-IBBCEAS

A small extractive NO₂-IBBCEAS instrument was also used to quantify NO₂. A detailed description of this instrument can be found in [51,52]. In brief, light from a temperature-stabilized blue LED centred at 460 nm and with a full width at half maximum (FWHM) of 25 nm was coupled into a multi-mode fibre and focused into a high-finesse optical cavity. The optical cavity comprised two 25 mm-diameter high-reflectivity (HR) mirrors ($R > 0.9999$ between 365 and 415 nm) separated by 85 cm. The output light of the cavity was focussed into a multi-mode fibre and coupled into a CCD spectrometer (Maya2000, Ocean Optics, FL, USA) with a spectral resolution of 0.4 nm. Air was sampled from the reaction chamber at 1.5 L min^{-1} through a 2.0 m-long PFA tube (i.d. = 4.35 mm). The measurement precision (1σ) was 97 pptv for NO₂ over 6 s integration time and the associated uncertainty was estimated to be 6%.

• NO₃-IBBCEAS

A portable extractive NO₃-IBBCEAS instrument was also used to quantify NO₃. The instrument was based on the same principle reported above and is described in Wang et al. [25]. The light source was a temperature-stabilized red LED centred at 660 nm and with a FWHM of 25 nm. The optical cavity comprised two 25 mm diameter high-reflectivity (HR) mirrors (>0.9999 at 660 nm) separated by 50 cm. The output light of the cavity was focussed by a plano-convex lens into an optical fibre and coupled into a CCD spectrometer (QE65000, Ocean Optics, FL, USA) with a spectral resolution of 0.85 nm. Air was sampled from the chamber at 2 L min^{-1} through a PFA tube (length 1.65 m, i.d. 4.35 mm). Particulate matter was removed by an inline Teflon filter with $2 \mu\text{m}$ pore size, which was replaced before each experiment. This instrument's measurement cycle is 5 min, including 30 s to measure a reference spectrum and 4 min 30 s to record sample spectra. The reference spectrum was obtained by titrating the sample with a 99.7 ppmv NO (diluted by N₂) at 10 mL min^{-1} flow rate. In this work, the measurement precision (1σ) was 1.7 pptv for NO₃ in 6 s integration time and the associated uncertainty was estimated to be 19%.

2.3. The Reaction Chamber (SAES-ARC)

SAES-ARC is an indoor atmospheric simulation chamber located in the Shanghai Academy of Environmental Sciences. A schematic of the reaction chamber and instrumentation is shown in Figure 3a. The reaction chamber is constituted by a Teflon FEP bag of cylindrical shape with a diameter and length of 3.2 m and 2 m, respectively. The reactor volume is about 10.0 m^3 and the surface-to-volume ratio is about 2.6 m^{-1} . The reaction chamber is operated at room temperature and atmospheric pressure. The humidity can be modified by a humidification system. A total of 60 black lamps (F40BLB, Philips, Eindhoven, Netherlands) on two of the long sides of the chamber were the light source. The movable blackout curtain is installed on the outside of the chamber to keep the chamber in darkness (as required) and to protect people from the intense UV output of the black lamps. A Teflon-coated fan, mounted on one side of the chamber and 1 m above the chamber floor, ensured a homogeneous distribution of gases and particles inside the chamber. The fan was turned on for several minutes when the trace gas was injected into the chamber. A temperature and humidity sensor (HMP 110, Vaisala, Vantaa, Finland) was used to record the inside temperature and relative humidity (RH). The absolute water vapour mixing ratios were calculated from the temperature, pressure, and RH. The measurement precision of RH was $\pm 1.5\%$ and that of temperature was $\pm 0.2^\circ\text{C}$. Ozone was produced by photolyzing pure oxygen with a mercury lamp. The chamber was also equipped with a

chemiluminescence NO_x analyser (Model 42i, Thermo Scientific, Waltham, MA, USA) and a photometric O₃ analyser (EC9810, Ecotech, Melbourne, Australia).

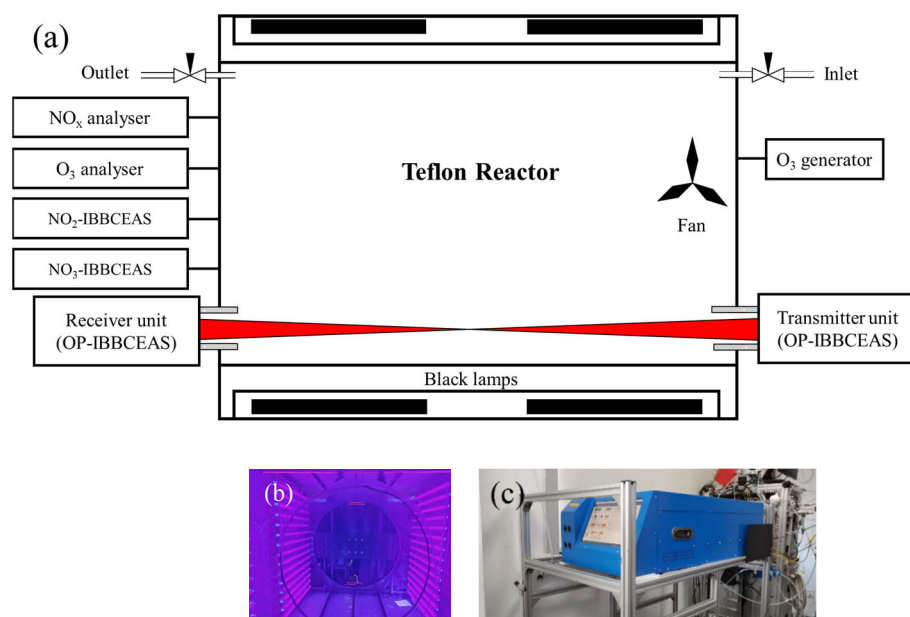


Figure 3. (a) Schematic of SAES-ARC facility. (b) SAES-ARC with black lamps on. (c) Extractive NO₃-IBBCEAS.

2.4. The Effective Cross Section Correction Method

The effective cross section correction method was used to handle the strong absorption of water vapour which overlaps the absorption of NO₃ in 662 nm region, and the absorption cross section of water varies with temperature and pressure. Moreover, the water absorption lines are not resolved by typical monochromators, leading to non-Beer-Lambert behaviour that affects the spectral analysis. When retrieving the concentration of NO₃, it is crucial to accurately account for the influence of H₂O on the spectrum [29,53].

In previous work, the effective cross section was calculated from the absorber's concentration and cavity residence time [29,30]. Here, the effective cross section was calculated according to the water vapour mixing ratio, mirror reflectivity and the high-resolution cross section of the HITRAN database [31]. In the reaction chamber study, the water vapor tends to be kept at some specific concentration, and it is sufficient to establish a series of effective absorption cross sections according to the instrument function of the spectrometer.

The flow diagram of the calculation of the effective cross section of water vapour of this work is shown in Figure 4.

1. The high-resolution cross section of water vapour has been acquired from the HITRAN database [54], and the cross section $\sigma_{\text{H}_2\text{O,high}}$ at the set temperature and pressure can be calculated using the Voigt function [55].
2. The high resolution I_0/I_{high} can be calculated by using the H₂O mixing ratio $n_{\text{H}_2\text{O}}$, the high-resolution cross section $\sigma_{\text{H}_2\text{O,high}}$, the interpolated mirror reflectivity R_{high} , together with the effective cavity length L :

$$\frac{I_0}{I_{\text{high}}} = \frac{n_{\text{H}_2\text{O}} \times \sigma_{\text{H}_2\text{O,high}} \times R_{\text{high}}}{1 - L} + 1 \quad (6)$$

3. The instrument resolution I_0/I was convolved from the high resolution I_0/I_{high} with the instrument function.

4. The instrument resolution cross section $\sigma_{\text{H}_2\text{O}}$ can be calculated at the set temperature, pressure, and mixing ratio:

$$\sigma_{\text{H}_2\text{O}} \times n_{\text{H}_2\text{O}} = \left(\frac{I_0}{I} - 1 \right) \left(\frac{1-L}{R} \right) \quad (7)$$

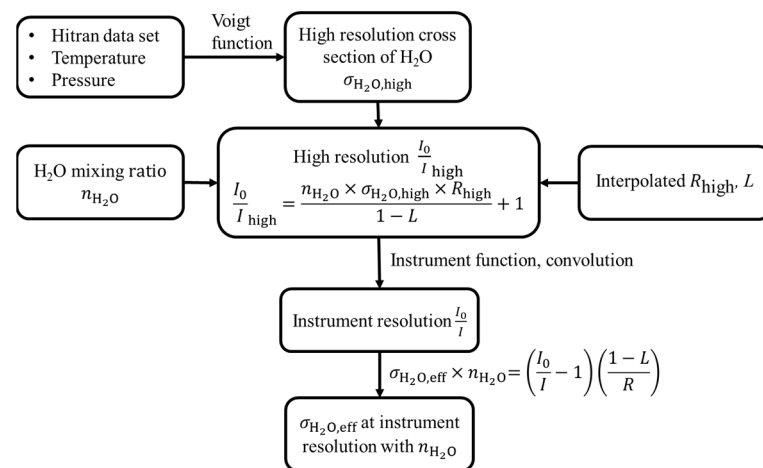


Figure 4. The flow diagram of the calculation of effective cross section of water vapor at instrumental spectrum resolution.

3. Results and Discussion

3.1. The Performance of OP-IBBCEAS

The uncertainty of retrieved mixing ratios is mainly attributed to the uncertainties in the cavity length, mirror reflectivity $R(\lambda)$, and absorption cross section. The uncertainties of the NO_2 and NO_3 cross sections are approximately 4% and 13% [6,47]; the uncertainty in the NO_2 cross section also leads to a 5% uncertainty in the calibration of $R(\lambda)$. The uncertainty in cavity length is around 1%. The associated measurement uncertainty is around $\pm 6\%$ and $\pm 14\%$ for NO_2 and NO_3 respectively calculated by the Gaussian error propagation.

The fluctuation of I_0 is usually affect the measurement precision of IBBCEAS system, which mainly attributed by the fluctuation of light source and the resonator cavity. The LDLS light source cannot easily temperature stabilized by thermoelectric cooler (TEC) control module like LED. The heat dissipation of LDLS relies on heat exchange with the environmental air. As for indoor chamber experiments, the air temperature was stabilized by air conditioners. The LDLS was turned on for more than 3–4 h to achieve the thermal equilibrium with the air before the I_0 was recorded by spectrometer. The stability of LDLS temperature also ensure the stability of I_0 throughout out the experiments.

A flexible bellow was used to connect the HR mirror frame and the chamber wall, and it can minimize the effect of chamber vibration on the finely alignment of the cavity. This can also ensure the stability of I_0 throughout out the experiments as far as possible.

The standard deviation was used to determine the measurement precision of the CEAS instrument [29,44,56,57]. The deviation analysis result is shown in Figure 5. Serious of 4000 reference spectra with 2 s integration time were continuously collected with the reaction chamber filled with zero-air. The I_0 was calculated by averaging the first 100 spectra, and the rest spectra were analysed using this I_0 . The retrieved concentrations of NO_2 and NO_3 were used for Gaussian fitting and are shown in Figure 5a,b. The 1σ standard deviation is 2.9 ppbv and 2.9 pptv for NO_2 and NO_3 in 2 s, respectively.

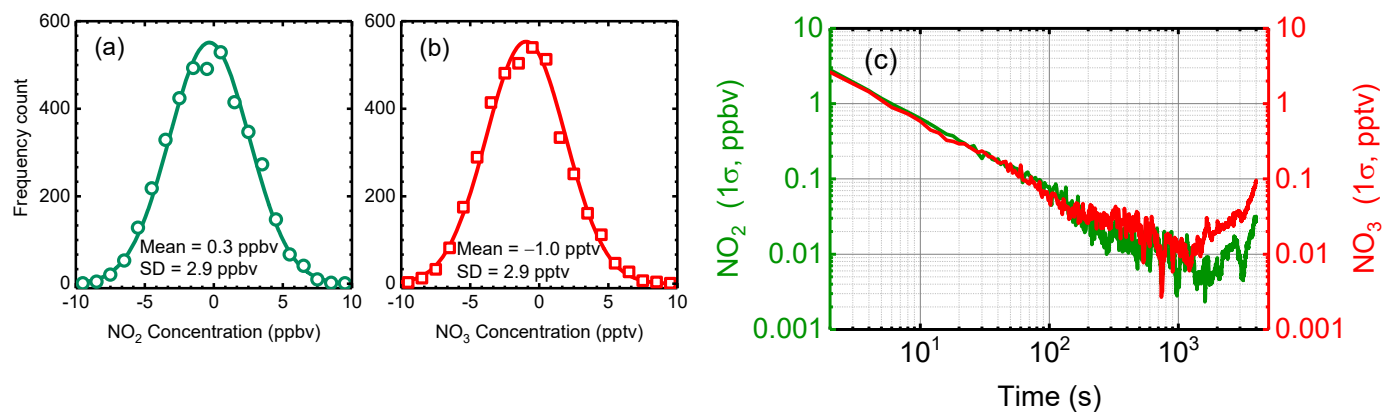


Figure 5. The standard and Allan deviation analysis result. (a) and (b) are the standard deviation of measured NO_2 and NO_3 in 2 s integration time, respectively, when the chamber was filled with zero air. (c) Allan deviation analysis result of the measurements of NO_2 and NO_3 .

Allan deviation analysis is a common method for characterizing the stability and sensitivity of an IBBCEAS system [25,28,29,44,56]. The Allan deviation in Figure 5c shows that the precision of OP-IBBCEAS measurements improves up to an averaging time of about 1000 s, at which time the precision is about 0.005 ppbv for NO_2 and about 0.01 pptv for NO_3 . At longer times, the precision decreases due to long-term drift in the system stability [24]. The drift noise of the system might come from the fluctuations in temperature and current of the light source. Deformation of the HR mirror frame caused by the change in environmental temperature may affect the alignment of the cavity, which is also a potential source of drift noise. The 1σ deviations are 2.8 ppbv and 2.6 pptv for NO_2 and NO_3 in a 2 s integration time, respectively, in agreement with the standard deviation analysis result. Table 1 summarizes the characteristics and performance of existing OP-IBBCEAS for NO_3 and NO_2 measurements. The OP-IBBCEAS instrument presented in this work has the second longest effective optical path length and achieved the best detection capability.

Table 1. Comparison of OP-IBBCEAS performances for NO_3 and NO_2 measurement under ideal conditions.

Reference	Eff. Optical Path Length (Mirror Displacement)	Reflectivity	NO_3		NO_2	
			Limit of Detection (Time Resolution)	Uncertainty	Limit of Detection (Time Resolution)	Uncertainty
Venables et al. [20]	2 km (4.5 m)	99.775% at 665 nm	4 pptv (N.A. 57 s)	14%	10 ppbv (N.A. 57 s)	11%
Varma et al. [21]	18.27 km (20.13 m)	99.9% at 660 nm	2 pptv (N.A., 5 s)	18%	2 ppbv (N.A., 5 s)	14%
Wu et al. [40]	22 km (2 m)	99.991% at 638,670 nm	7.9 pptv (N.A. 60 s)	12%	9.0 ppbv (N.A. 60 s)	9%
Yi et al. [41]	6.7 km (2 m)	99.97% at 662 nm	3.6 pptv (N.A., 60 s)	7.8%	4.1 ppbv (N.A., 60 s)	9.1%
Suhail et al. [45]	7 km (3.5 m)	99.95% at 660 nm	36 pptv (N.A. 600 s)	N.A.	N.A.	N.A.
Wang and Lu [46]	5.1 km (0.84 m)	99.985% at 660 nm	3.0 pptv (2σ , 30 s)	11–15%	N.A.	N.A.
This work	21.7 km (3.65 m)	99.987% at 675 nm	5.8 pptv (2σ , 2 s)	14%	5.8 ppbv (2σ , 2 s)	6%

3.2. Intercomparison of NO_2 and NO_3

The mirror reflectivity values of the extractive NO_2 -IBBCEAS and NO_3 -IBBCEAS instruments were determined according to the difference of Rayleigh scattering cross section between N_2 and He. The SAES-ARC chamber was flushed for 8 h with zero air at a flow rate of 60 L min^{-1} before each experiment. The purified air was supplied by a zero-air generator (ZAS100, Convenient Inc., Beijing, China). In the intercomparison experiments,

time-series measurements of NO_2 and NO_3 were simultaneously performed using the extractive NO_2 -IBBCEAS, extractive NO_3 -IBBCEAS and OP-IBBCEAS instruments.

NO_2 measurements by the extractive NO_2 -IBBCEAS and OP-IBBCEAS were compared. The time series result of NO_2 mixing ratio during a chamber experiment is shown in Figure 6a. The experiment was carried out in dry ($\text{RH} = 0.40 \pm 0.05\%$), aerosol-free air at room temperature ($22.8 \pm 1.0^\circ\text{C}$). NO_2 was added into the chamber twice at 10:48 and 11:02. After NO_2 was fully mixed, O_3 was gradually added into the chamber from 11:40, reaching 129 ppbv at 13:30. To ensure that the chamber air was homogeneously mixed, the chamber fan was turned on from 10:48 to 13:30. The chamber was flushed with zero air from 15:00. Figure 6a shows close agreement in the NO_2 concentration measured by both the OP-IBBCEAS and the extractive NO_2 -IBBCEAS.

Figure 6b shows the NO_3 concentrations retrieved by the extractive NO_3 -IBBCEAS and OP-IBBCEAS instruments, together with the NO_3 simulated by box model. The simulation was based on the initial NO_2 concentrations and constrained by the measured O_3 concentrations. Figure 6c shows the liner fitting between the measured NO_3 concentrations from the OP-IBBCEAS and extractive NO_3 -IBBCEAS (violets line), together with the concentration from OP-IBBCEAS and box model simulation (blue line). The NO_3 concentration measured by OP-IBBCEAS agrees well with box model simulation, and the linear correction coefficient is $r^2 = 0.9991$, the slope and intercept are 0.98 and 0.97 pptv, respectively. The correlation between the OP-IBBCEAS and extractive NO_3 -IBBCEAS is excellent ($r^2 = 0.9994$) and the intercept is small (1.4 pptv). However, the correlation slope is 0.74, indicating significant losses of NO_3 in the extractive system that do not occur in the open-path system across the chamber. The correlation slope was used to correct the extractive NO_3 -IBBCEAS data. The transmission efficiency obtained here was similar to the value reported by Dorn et al. [14]. Finally, the box model simulation of the NO_2 - O_3 chemical system reproduced the experimentally measured concentration–time profiles very well. Small differences in the measured NO_3 concentrations are seen during flushing; these differences likely arise from spatial heterogeneity of NO_3 concentrations in the chamber as a result of diluting chamber contents with clean air from a specific location in the chamber.

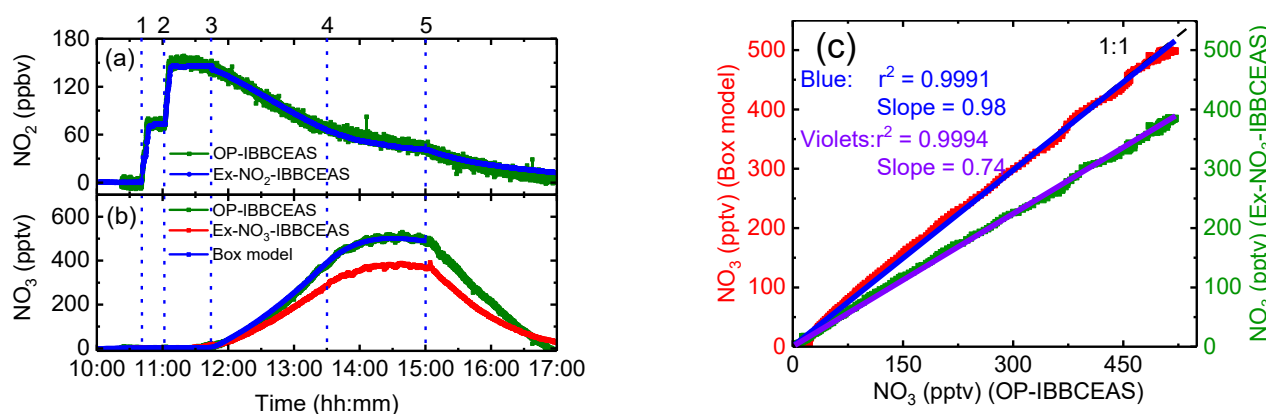


Figure 6. Time-series measurement of NO_2 , NO_3 concentrations and the NO_3 box model simulation results. (a) Time series of NO_2 concentrations retrieved by OP-IBBCEAS (green data) and extractive NO_2 -IBBCEAS (blue data). (b) Time series of NO_3 concentrations retrieved by OP-IBBCEAS (green data), extractive NO_3 -IBBCEAS (red data), and a box model simulation curve (blue data). The SAES-ARC experiment event sequence was: (1) 10:48, 75 ppbv of NO_2 added, fan on; (2) 11:02, 75 ppbv of NO_2 added; (3)–(4) 11:40–13:30, 130 ppbv O_3 added; (4) 13:30: fan off; (5) 15:00, flush on. (c) Correlation of the measured NO_3 concentrations between OP-IBBCEAS and box model simulation (Blue line), and extractive NO_3 -IBBCEAS (Violet line).

3.3. Effect of Humidity on the Spectral Analysis

3.3.1. The Cross Section of H₂O

To evaluate the interference of H₂O cross section accuracy on spectral fitting, the H₂O absorption cross sections of different mixing ratios were calculated, for which the method is described in Section 2.4. Figure 7a shows the modified absorption cross sections of H₂O at ten different H₂O mixing ratios (0.2%, 0.4%, 0.6%, 0.8%, 1.0%, 1.2%, 1.4%, 1.6%, 1.8% and 2.0%), corresponding to relative humidities of 7.7%, 15.3%, 23.0%, 30.7%, 38.3%, 46.0%, 53.7%, 61.3%, 69.0%, and 76.7% at 22 °C. From 658 to 666 nm, the absorption cross section varies differently at different wavelengths, which decreases as the wavelength increases. The change of the convolved H₂O absorption cross section with the mixing ratio of H₂O from 658.0 nm to 666.0 nm at 1 nm intervals is shown in Figure 7b. Note that the y-axis of Figure 7b is logarithmic and that the changes in the absorption cross sections at different wavelengths are not linear.

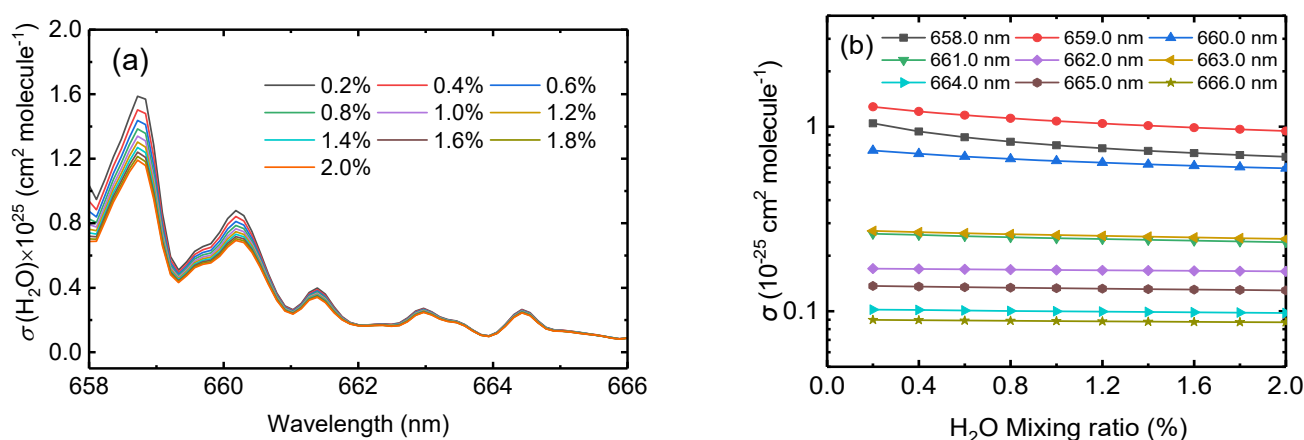


Figure 7. (a) The convolved H₂O absorption cross section at ten different mixing ratios. (b) The change of the convolved H₂O absorption cross section with the mixing ratios from 658 nm to 666 nm at 1 nm intervals. The y-axis uses a logarithmic scale here.

In the reaction chamber experiment, the H₂O concentration changes as the experiment progresses and can reach a maximum relative humidity of about 2%. The variation of H₂O absorption cross section with different concentrations cannot be ignored because even small changes in water vapor concentration affect the spectral fit and hence the quantification of trace amounts of NO₃.

3.3.2. The Influence of H₂O Cross Section

To explore the interference of water vapor cross sections on the spectral fitting, four similar chamber experiments were carried out at different water vapor concentrations, in which H₂O was added to the reaction chamber after NO₂ and O₃ were added. The effective cross section correction method was applied to acquire the number densities of NO₃, NO₂ and H₂O accurately, as described in Section 2.4.

The Levenberg–Marquardt least-squares fitting method was applied for retrieving the molecule number densities of NO₃, NO₂ and H₂O. The wavelength range from 645 to 685 nm was chosen as the optimized spectral fitting window. A third-order polynomial was applied to account for the unstructured extinction arising from scattering and O₃ absorption. Figure 8 shows an example of OP-IBBCEAS retrievals of NO₃, NO₂ and H₂O mixing ratios of 55.6 ± 2.5 pptv, 11.5 ± 2.8 ppbv, and $0.8 \pm 0.02\%$, respectively. The H₂O cross section used here was based on $n_{\text{H}_2\text{O}} = 0.78\%$. Figure 8f shows that the absorption of H₂O is well fitted by using an effective cross section correction method.

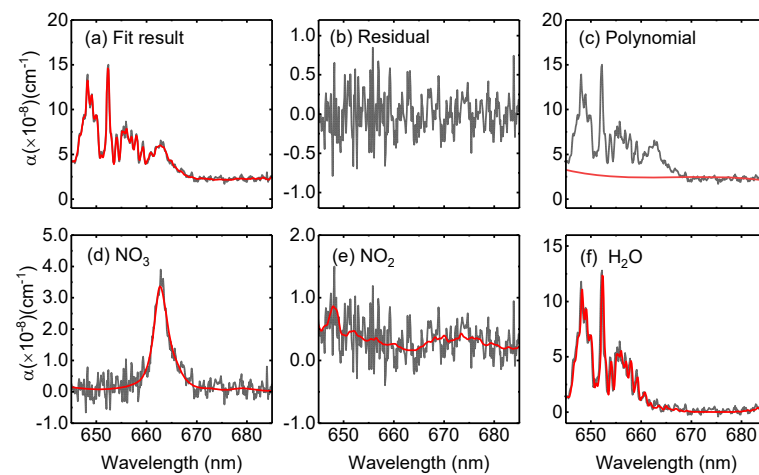


Figure 8. One spectrum fitting example of chamber experiment with a 2 s integration time. The black and red line are the measured and fitted data, respectively. (a) fit result, (b) Residual, (c) Polynomial, (d) NO_3 , (e) NO_2 , and (f) H_2O , respectively. The retrieved mixing ratios of NO_3 , NO_2 and H_2O are respectively 55.6 ± 2.5 pptv, 11.5 ± 2.8 ppbv, and $0.80 \pm 0.02\%$.

One consideration in the use of optical cavities is that the effective optical path length is non-linearly reduced in the presence of strong absorbers or scatterers [22,58,59]. Figure 9 shows the decrease of the effective optical path length. Owing to the strong absorption of 0.8% H_2O at 652 nm, the effective optical path length decreases 11%, from 19.3 km to 17.1 km. Considering NO_3 at 662 nm, the effective optical path length decreases 7%, from 20. km to 19.3 km.

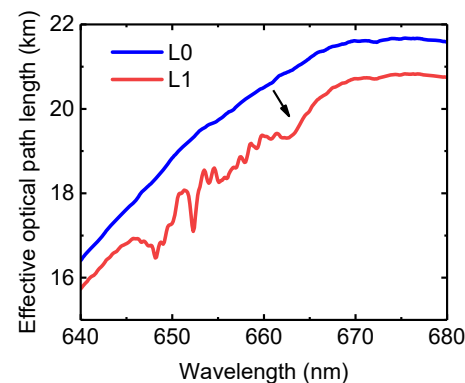


Figure 9. Example of the influence of sample composition of effective absorption optical path length: no extinction (L0) and extinction from 55.6 pptv NO_3 , 11.5 ppbv NO_2 , and 0.8% H_2O (L1).

The NO_3 retrieved by OP-IBBCEAS under different H_2O mixing ratios is shown in Figure 10a. The green and red points represent the retrieved NO_3 data with and without H_2O cross-section correction. The averaged H_2O mixing ratios measured by the humidity sensor were 0.01%, 0.78%, 1.3%, and 1.8% (RH = 0.4%, 30%, 50%, and 70% at 22 °C), respectively. The red and green points agreed well when the chamber was dry. When H_2O was added, the difference between using the effective H_2O cross section and the uncorrected cross section becomes obvious and the discrepancy increases with H_2O mixing ratio. An inappropriate H_2O absorption cross section can cause an overestimation of NO_3 concentration of about 28% in a humid atmosphere ($\text{H}_2\text{O} = 1.8\%$).

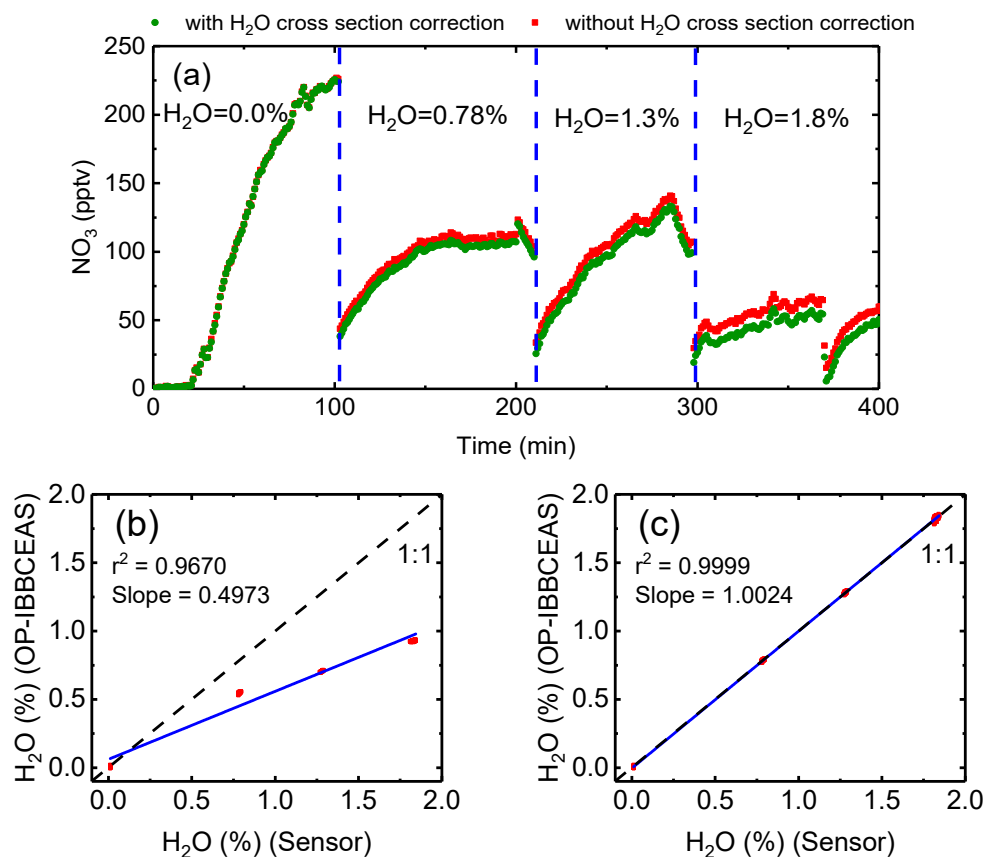


Figure 10. (a) NO₃ concentrations retrieved using OP-IBBCEAS with (green) and without (red) the H₂O cross section correction. Figures (b) and (c) show the correlation of the H₂O mixing ratio measured by a humidity sensor with that retrieved by the OP-IBBCEAS measurements. In (b) the uncorrected H₂O cross section is used, whereas the corrected H₂O cross section is used in (c).

The H₂O measurement precision (1σ) of OP-IBBCEAS is 0.02%, which is better than humidity sensor corresponding to 0.04% (RH = 1.7% at 22 °C). The correlation and regression analysis of the H₂O mixing ratio measured by the humidity sensor and OP-IBBCEAS without the correction H₂O cross section is shown in Figure 10b. The slope is 0.497 and $r^2 = 0.97$. In contrast, the regression analysis of the measured H₂O mixing ratio with the effective H₂O cross section is shown in Figure 10c. Here the agreement in the two measurements is great, the slope is 1.002 and the $r^2 = 0.9999$. The mixing ratio of H₂O is retrieved accurately after applying the effective H₂O absorption cross section, thus demonstrating the reliability and accuracy of the effective cross section correction method.

3.4. The Application of Kalman Filtering

Kalman filtering is an adaptive technique with the advantage of self-adjustment by its transfer function, and is very useful in a real measurement environment [24,60–62]. Here, Kalman filtering was applied to further improve the measurement precision. Kalman filtering has several advantages over a simple moving average. Kalman filtering is conditioned on previous data and is less affected by spikes generated by the sensor [60].

In Kalman filtering, the predicted concentration (or true value) at time k ($\hat{x}_k$) is calculated by combining the predicted concentration (or true value) at time $k-1$ ($\hat{x}_{k-1}^-$) with the measured value at time k (z_k) by using a recursive procedure [60]. This can be expressed as follows:

$$\hat{x}_k = \hat{x}_{k-1}^- + K_k(z_k - \hat{x}_{k-1}^-) \quad (8)$$

Here, the value K_k is the Kalman gain, which is obtained from the measurement noise (σ_v) and the true concentration variability (σ_w). The factor ρ is defined as the ratio of σ_v^2/σ_w^2 ,

which is the parameter used to adjust the filter. In this work, ρ was set to 50, and the variance of the first 20 values was used as the input of σ_v . Figure 11 shows the retrieved concentration of NO_2 and NO_3 when the reaction chamber was full of zero-air as the value obtained after applying Kalman filtering. The 1σ deviation with 2 s integration time (described in Section 3.1) were improved from 2.9 ppbv to 0.8 ppbv for NO_2 and 2.9 pptv to 0.9 pptv for NO_3 , respectively. The measurement precision values were improved by a factor 3.6 for NO_2 and by a factor of 3.2 for NO_3 .

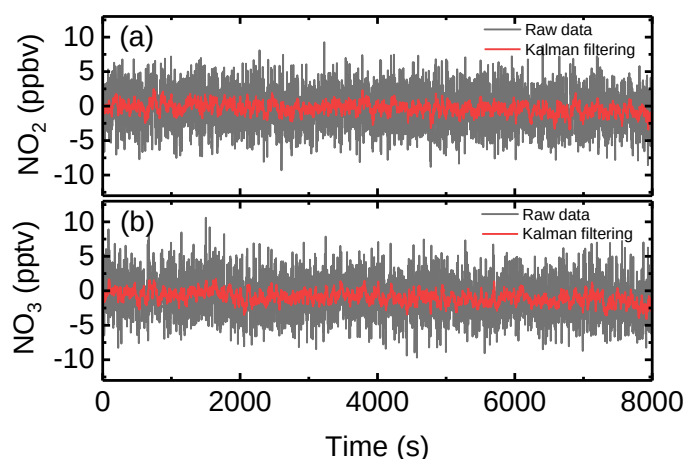


Figure 11. The raw data (grey line) measured by OP-IBBCEAS with the chamber filled with zero air, and the measured data after applying Kalman filtering (red line). (a) The measured NO_2 data with and without Kalman filtering. (b) The measured NO_3 data with and without Kalman filtering.

Figure 12 shows the reaction chamber experimental result of NO_2 and NO_3 with and without applying Kalman filtering. The spikes generated by the sensor were removed after processing Kalman filtering. The effect of Kalman filtering is more pronounced on the NO_2 data because the signal-to-noise ratio (SNR) of NO_2 is less than NO_3 . The NO_2 data also show that Kalman filtering copes well with rapid step changes in actual chamber concentration. The filtering result demonstrated that Kalman filtering is an efficient tool for reducing the measurement noise and improving the precision without affecting the time resolution.

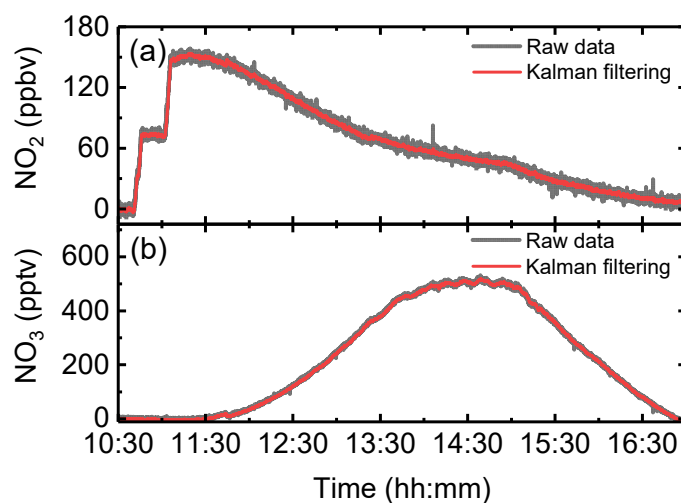


Figure 12. The raw data (grey line) measured by OP-IBBCEAS in reaction chamber experimental conditions, and the measured data after applying with Kalman filtering (red line). (a) The measured NO_2 data with and without Kalman filtering. (b) The measured NO_3 data with and without Kalman filtering.

4. Conclusions

We developed an OP-IBBCEAS for simultaneous measurements of NO₂, NO₃, and H₂O in the SAES-ARC simulation chamber based on absorption between 645 and 685 nm. The precision of the OP-IBBCEAS is 2.9 ppbv for NO₂ and 2.9 pptv for NO₃ in a 2 s (1 σ), and its corresponding uncertainty is estimated to be $\pm 6\%$ for NO₂ and $\pm 14\%$ for NO₃. Intercomparison measurements of NO₂ and NO₃ between open-path and extractive IBBCEAS were performed during the reaction of NO₂ with O₃ in the SAES-ARC. The intercomparison of NO₂ measured by OP-IBBCEAS and extractive NO₂-IBBCEAS shows good agreement. The intercomparison of measured NO₃ obtained by the OP-IBBCEAS instrument and a box model also shows excellent agreement. A 74% transmission efficiency of extractive NO₃-IBBCEAS was estimated based on regression analysis of the measured NO₃ using OP-IBBCEAS and the extractive NO₃-IBBCEAS system. A crucial advantage of the OP-IBBCEAS instrument is that it does not actively sample the air mass of interest, and there are no transmission losses in the instrument. The in-line filter membrane needs to be regularly replaced (as it does in extractive CEAS or CRDS systems) owing to accumulation of particulate matter and changes in the transmission efficiency of the filter over time. However, this OP-IBBCEAS does not allow N₂O₅ to be estimated, and it is an advantage of extractive instrument with heated inlets. As has been shown by others, the OP-IBBCEAS is a good approach for application to reaction chambers and field campaigns owing to its simple and robust design, and high precision in monitoring reactive radicals. In field campaigns, the concentrations of NO₂ and NO₃ can be well quantified by this OP-IBBCEAS, but this is not sufficient to discuss scientific questions. Some other typical pollutants like NO, CO, O₃ and NH₃ et al. should be measured as well if the researchers try to identify the source of pollutants accurately [63–65].

The effective cross section correction method was used to reduce the influence of H₂O. Comparison of the NO₃ data analyzed with and without the H₂O cross-section correction showed that the NO₃ concentration is overestimated without the H₂O absorption cross section correction. The measured H₂O mixing ratios of humidity sensor and OP-IBBCEAS were also compared. The slope and r^2 improved from 0.4973 and 0.9670 to 1.0024 and 0.9999 by correcting the effective absorption cross section of H₂O. The measurement precisions were improved by a factor of 3.6 and 3.2 for NO₂ and NO₃, respectively, after applying the Kalman filtering.

The system has good application prospects in laboratory experiments and field campaigns for in situ and NO₃ measurement. This approach also gives an accurate, in situ measurement of NO₂ rather than an indirect measurement like chemiluminescence. In addition, the H₂O measurement precision of OP-IBBCEAS is better than this hygrometer, and the accurate retrieval of H₂O vapour could be valuable in some circumstances.

Author Contributions: Conceptualization, S.L. and J.C.; methodology, M.W., S.L. and J.C.; validation, D.S.V.; formal analysis, D.S.V. and R.V.; investigation, M.W. and J.C.; resources, W.H. and X.W.; data curation, M.W. and H.W.; writing—original draft preparation, M.W.; writing—review and editing, M.W., S.L., R.V., D.S.V. and J.C.; visualization, M.W.; supervision, S.L. and J.C.; project administration, F.F. and J.C.; funding acquisition, X.W., S.L., F.F. and J.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Key Research and Development Program of China (Grant No. 2022YFC3701103, 2022YFC3700300), the High-end Foreign Expert Introduction Program (Grant No. G2022013002), and the National Natural Science Foundation of China (Grant No. 42175111).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wayne, R.P.; Barnes, I.; Biggs, P.; Burrows, J.P.; Canosa-Mas, C.E.; Hjorth, J.; Le Bras, G.; Moortgat, G.K.; Perner, D.; Poulet, G.; et al. The nitrate radical: Physics, chemistry, and the atmosphere. *Atmos. Environ. Part A Gen. Top.* **1991**, *25*, 1–203. [\[CrossRef\]](#)
2. Brown, S.S.; Stutz, J. Nighttime radical observations and chemistry. *Chem. Soc. Rev.* **2012**, *41*, 6405–6447. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Brown, S.S.; Stark, H.; Ravishankara, A. Applicability of the steady state approximation to the interpretation of atmospheric observations of NO_3 and N_2O_5 . *J. Geophys. Res. Atmos.* **2003**, *108*, 4539. [\[CrossRef\]](#)
4. Hoyle, C.R.; Boy, M.; Donahue, N.M.; Fry, J.L.; Glasius, M.; Guenther, A.; Hallar, A.G.; Hartz, K.H.; Petters, M.D.; Petaja, T.; et al. A review of the anthropogenic influence on biogenic secondary organic aerosol. *Atmos. Chem. Phys.* **2011**, *11*, 321–343. [\[CrossRef\]](#)
5. Ziemann, P.J.; Atkinson, R. Kinetics, products, and mechanisms of secondary organic aerosol formation. *Chem. Soc. Rev.* **2012**, *41*, 6582–6605. [\[CrossRef\]](#)
6. Yokelson, R.J.; Burkholder, J.B.; Fox, R.W.; Talukdar, R.K.; Ravishankara, A.R. Temperature Dependence of the NO_3 Absorption Spectrum. *J. Phys. Chem.* **1994**, *98*, 13144–13150. [\[CrossRef\]](#)
7. Platt, U.; Perner, D.; Schröder, J.; Kessler, C.; Toennissen, A. The diurnal variation of NO_3 . *J. Geophys. Res. Ocean.* **1981**, *86*, 11965–11970. [\[CrossRef\]](#)
8. Allan, B.J.; McFiggans, G.; Plane, J.M.; Coe, H.; McFadyen, G.G. The nitrate radical in the remote marine boundary layer. *J. Geophys. Res. Atmos.* **2000**, *105*, 24191–24204. [\[CrossRef\]](#)
9. Geyer, A.; Ackermann, R.; Dubois, R.; Lohrmann, B.; Müller, T.; Platt, U. Long-term observation of nitrate radicals in the continental boundary layer near Berlin. *Atmos. Environ.* **2001**, *35*, 3619–3631. [\[CrossRef\]](#)
10. Geyer, A.; Alicke, B.; Ackermann, R.; Martinez, M.; Harder, H.; Brune, W.; Di Carlo, P.; Williams, E.; Jobson, T.; Hall, S. Direct observations of daytime NO_3 : Implications for urban boundary layer chemistry. *J. Geophys. Res. Atmos.* **2003**, *108*, 4368. [\[CrossRef\]](#)
11. Stutz, J.; Alicke, B.; Ackermann, R.; Geyer, A.; White, A.; Williams, E. Vertical profiles of NO_3 , N_2O_5 , O_3 , and NO_x in the nocturnal boundary layer: 1. Observations during the Texas Air Quality Study 2000. *J. Geophys. Res. Atmos.* **2004**, *109*, D12307. [\[CrossRef\]](#)
12. Wängberg, I.; Barnes, I.; Becker, K. Product and mechanistic study of the reaction of NO_3 radicals with α -pinene. *Environ. Sci. Technol.* **1997**, *31*, 2130–2135. [\[CrossRef\]](#)
13. Bossmeyer, J.; Brauers, T.; Richter, C.; Rohrer, F.; Wegener, R.; Wahner, A. Simulation chamber studies on the NO_3 chemistry of atmospheric aldehydes. *Geophys. Res. Lett.* **2006**, *33*, L18810. [\[CrossRef\]](#)
14. Dorn, H.P.; Apodaca, R.L.; Ball, S.M.; Brauers, T.; Brown, S.S.; Crowley, J.N.; Dubé, W.P.; Fuchs, H.; Häsel, R.; Heitmann, U.; et al. Intercomparison of NO_3 radical detection instruments in the atmosphere simulation chamber SAPHIR. *Atmos. Meas. Tech.* **2013**, *6*, 1111–1140. [\[CrossRef\]](#)
15. King, M.D.; Dick, E.M.; Simpson, W.R. A new method for the atmospheric detection of the nitrate radical (NO_3). *Atmos. Environ.* **2000**, *34*, 685–688. [\[CrossRef\]](#)
16. Brown, S.S.; Stark, H.; Ciciora, S.J.; Ravishankara, A. In-situ measurement of atmospheric NO_3 and N_2O_5 via cavity ring-down spectroscopy. *Geophys. Res. Lett.* **2001**, *28*, 3227–3230. [\[CrossRef\]](#)
17. Dubé, W.P.; Brown, S.S.; Osthoff, H.D.; Nunley, M.R.; Ciciora, S.J.; Paris, M.W.; McLaughlin, R.J.; Ravishankara, A. Aircraft instrument for simultaneous, in situ measurement of NO_3 and N_2O_5 via pulsed cavity ring-down spectroscopy. *Rev. Sci. Instrum.* **2006**, *77*, 034101. [\[CrossRef\]](#)
18. Schuster, G.; Labazan, I.; Crowley, J.N. A cavity ring down/cavity enhanced absorption device for measurement of ambient NO_3 and N_2O_5 . *Atmos. Meas. Tech.* **2009**, *2*, 1–13. [\[CrossRef\]](#)
19. Fiedler, S.E.; Hese, A.; Ruth, A.A. Incoherent broad-band cavity-enhanced absorption spectroscopy. *Chem. Phys. Lett.* **2003**, *371*, 284–294. [\[CrossRef\]](#)
20. Venables, D.S.; Titus, G.; Johannes, O.; Wenger, J.C.; Ruth, A.A. High sensitivity in situ monitoring of NO_3 in an atmospheric simulation chamber using incoherent broadband cavity-enhanced absorption spectroscopy. *Environ. Sci. Technol.* **2006**, *40*, 6758. [\[CrossRef\]](#)
21. Varma, R.M.; Venables, D.S.; Ruth, A.A.; Heitmann, U.; Schlosser, E.; Dixneuf, S. Long optical cavities for open-path monitoring of atmospheric trace gases and aerosol extinction. *Appl. Opt.* **2009**, *48*, B159–B171. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Platt, U.; Meinen, J.; Pohler, D.; Leisner, T. Broadband Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS)—Applicability and corrections. *Atmos. Meas. Tech.* **2009**, *2*, 713–723. [\[CrossRef\]](#)
23. Chen, J.; Venables, D.S. A broadband optical cavity spectrometer for measuring weak near-ultraviolet absorption spectra of gases. *Atmos. Meas. Tech.* **2011**, *4*, 425–436. [\[CrossRef\]](#)
24. Fang, B.; Zhao, W.; Xu, X.; Zhou, J.; Ma, X.; Wang, S.; Zhang, W.; Venables, D.S.; Chen, W. Portable broadband cavity-enhanced spectrometer utilizing Kalman filtering: Application to real-time, in situ monitoring of glyoxal and nitrogen dioxide. *Opt. Express* **2017**, *25*, 26910–26922. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Wang, H.; Chen, J.; Lu, K. Development of a portable cavity-enhanced absorption spectrometer for the measurement of ambient NO_3 and N_2O_5 : Experimental setup, lab characterizations, and field applications in a polluted urban environment. *Atmos. Meas. Tech.* **2017**, *10*, 1465–1479. [\[CrossRef\]](#)
26. Duan, J.; Qin, M.; Ouyang, B.; Fang, W.; Li, X.; Lu, K.; Tang, K.; Liang, S.; Meng, F.; Hu, Z. Development of an incoherent broadband cavity-enhanced absorption spectrometer for in situ measurements of HONO and NO_2 . *Atmos. Meas. Tech.* **2018**, *11*, 4531–4543. [\[CrossRef\]](#)

27. Liu, J.; Li, X.; Yang, Y.; Wang, H.; Kuang, C.; Zhu, Y.; Chen, M.; Hu, J.; Zeng, L.; Zhang, Y. Sensitive Detection of Ambient Formaldehyde by Incoherent Broadband Cavity Enhanced Absorption Spectroscopy. *Anal. Chem.* **2020**, *92*, 2697–2705. [\[CrossRef\]](#)
28. Wang, M.; Varma, R.; Venables, D.S.; Zhou, W.; Chen, J. A Demonstration of Broadband Cavity-Enhanced Absorption Spectroscopy at Deep-Ultraviolet Wavelengths: Application to Sensitive Real-Time Detection of the Aromatic Pollutants Benzene, Toluene, and Xylene. *Anal. Chem.* **2022**, *94*, 4286–4293. [\[CrossRef\]](#)
29. Langridge, J.M.; Ball, S.M.; Shillings, A.J.L.; Jones, R.L. A broadband absorption spectrometer using light emitting diodes for ultrasensitive, in situ trace gas detection. *Rev. Sci. Instrum.* **2008**, *79*, 123110. [\[CrossRef\]](#)
30. Benton, A.; Langridge, J.; Ball, S.; Bloss, W.; Dall'Osto, M.; Nemitz, E.; Harrison, R.M.; Jones, R. Night-time chemistry above London: Measurements of NO₃ and N₂O₅ from the BT Tower. *Atmos. Chem. Phys.* **2010**, *10*, 9781–9795. [\[CrossRef\]](#)
31. Kennedy, O.; Ouyang, B.; Langridge, J.; Daniels, M.; Bauguette, S.; Freshwater, R.; McLeod, M.; Ironmonger, C.; Sendall, J.; Norris, O. An aircraft based three channel broadband cavity enhanced absorption spectrometer for simultaneous measurements of NO₃, N₂O₅ and NO₂. *Atmos. Meas. Tech.* **2011**, *4*, 1759–1776. [\[CrossRef\]](#)
32. Wang, H.; Lu, K.; Chen, X.; Zhu, Q.; Qi, C.; Song, G.; Jiang, M.; Xin, L.; Shang, D.; Tan, Z. High N₂O₅ Concentrations Observed in Urban Beijing: Implications of a Large Nitrate Formation Pathway. *Environ. Sci. Technol. Lett.* **2017**, *4*, 416–420. [\[CrossRef\]](#)
33. Chen, X.; Wang, H.; Lu, K.; Li, C.; Zhai, T.; Tan, Z.; Ma, X.; Yang, X.; Liu, Y.; Chen, S. Field determination of nitrate formation pathway in winter Beijing. *Environ. Sci. Technol.* **2020**, *54*, 9243–9253. [\[CrossRef\]](#)
34. Nam, W.; Cho, C.; Perdignes, B.; Rhee, T.S.; Min, K.E. Development of a broadband cavity-enhanced absorption spectrometer for simultaneous measurements of ambient NO₃, NO₂, and H₂O. *Atmos. Meas. Tech.* **2022**, *15*, 4473–4487. [\[CrossRef\]](#)
35. Fuchs, H.; Dubé, W.P.; Ciciora, S.J.; Brown, S.S. Determination of Inlet Transmission and Conversion Efficiencies for in Situ Measurements of the Nocturnal Nitrogen Oxides, NO₃, N₂O₅ and NO₂, via Pulsed Cavity Ring-Down Spectroscopy. *Anal. Chem.* **2008**, *80*, 6010–6017. [\[CrossRef\]](#)
36. Gherman, T.; Venables, D.S.; Vaughan, S.; Orphal, J.; Ruth, A.A. Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy in the near-Ultraviolet: Application to HONO and NO₂. *Environ. Sci. Technol.* **2008**, *42*, 890–895. [\[CrossRef\]](#)
37. Chen, J.; Wenger, J.C.; Venables, D.S. Near-ultraviolet absorption cross sections of nitrophenols and their potential influence on tropospheric oxidation capacity. *J. Phys. Chem. A* **2011**, *115*, 12235–12242. [\[CrossRef\]](#)
38. Ashu-Ayem, E.R.; Nitschke, U.; Monahan, C.; Chen, J.; Darby, S.B.; Smith, P.D.; O'Dowd, C.D.; Stengel, D.B.; Venables, D.S. Coastal Iodine Emissions. 1. Release of I-2 by *Laminaria digitata* in Chamber Experiments. *Environ. Sci. Technol.* **2012**, *46*, 10413–10421. [\[CrossRef\]](#)
39. Hoch, D.J.; Buxmann, J.; Sihler, H.; Poehler, D.; Zetzsch, C.; Platt, U. An instrument for measurements of BrO with LED-based Cavity-Enhanced Differential Optical Absorption Spectroscopy. *Atmos. Meas. Tech.* **2014**, *7*, 199–214. [\[CrossRef\]](#)
40. Wu, T.; Coeur-Tourneur, C.; Dhont, G.; Cassez, A.; Fertein, E.; He, X.; Chen, W. Simultaneous monitoring of temporal profiles of NO₃, NO₂ and O₃ by incoherent broadband cavity enhanced absorption spectroscopy for atmospheric applications. *J. Quant. Spectrosc. Radiat. Transf.* **2014**, *133*, 199–205. [\[CrossRef\]](#)
41. Yi, H.; Wu, T.; Wang, G.; Zhao, W.; Fertein, E.; Coeur, C.; Gao, X.; Zhang, W.; Chen, W. Sensing atmospheric reactive species using light emitting diode by incoherent broadband cavity enhanced absorption spectroscopy. *Opt. Express* **2016**, *24*, A781–A790. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Yi, H.; Cazaunau, M.; Gratien, A.; Michoud, V.; Pangui, E.; Doussin, J.-F.; Chen, W. Intercomparison of IBBCEAS, NitroMAC and FTIR analyses for HONO, NO₂ and CH₂O measurements during the reaction of NO₂ with H₂O vapour in the simulation chamber CESAM. *Atmos. Meas. Tech.* **2021**, *14*, 5701–5715. [\[CrossRef\]](#)
43. Yi, H.; Meng, L.; Wu, T.; Lauraguais, A.; Coeur, C.; Tomas, A.; Fu, H.; Gao, X.; Chen, W. Absolute determination of the chemical kinetic rate constant by optically tracking the reaction on the second time-scale using cavity enhanced absorption spectroscopy. *Phys. Chem. Chem. Phys.* **2022**, *24*, 7396–7404. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Wu, T.; Chen, W.; Fertein, E.; Cazier, F.; Dewaele, D.; Gao, X. Development of an open-path incoherent broadband cavity-enhanced spectroscopy based instrument for simultaneous measurement of HONO and NO₂ in ambient air. *Appl. Phys. B Lasers Opt.* **2012**, *106*, 501–509. [\[CrossRef\]](#)
45. Suhail, K.; George, M.; Chandran, S.; Varma, R.; Venables, D.S.; Wang, M.; Chen, J. Open path incoherent broadband cavity-enhanced measurements of NO₃ radical and aerosol extinction in the North China Plain. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2019**, *208*, 24–31. [\[CrossRef\]](#)
46. Wang, H.; Lu, K. Monitoring Ambient Nitrate Radical by Open-Path Cavity-Enhanced Absorption Spectroscopy. *Anal. Chem.* **2019**, *91*, 10687–10693. [\[CrossRef\]](#)
47. Voigt, S.; Orphal, J.; Burrows, J.P. The temperature and pressure dependence of the absorption cross-sections of NO₂ in the 250–800 nm region measured by Fourier-transform spectroscopy. *J. Photochem. Photobiol. A Chem.* **2002**, *149*, 1–7. [\[CrossRef\]](#)
48. Schmidl, G.; Paa, W.; Triebel, W.; Schippel, S.; Heyer, H. Spectrally resolved cavity ring down measurement of high reflectivity mirrors using a supercontinuum laser source. *Appl. Opt.* **2009**, *48*, 6754–6759. [\[CrossRef\]](#)
49. Fullam, D.P.; Shoji, K.; Venables, D.S. Using integrated absorption to calibrate optical cavity spectrometers. *Anal. Methods* **2015**, *7*, 3298–3301. [\[CrossRef\]](#)
50. Washenfelder, R.A.; Attwood, A.R.; Flores, J.M.; Zarzana, K.J.; Rudich, Y.; Brown, S.S. Broadband cavity-enhanced absorption spectroscopy in the ultraviolet spectral region for measurements of nitrogen dioxide and formaldehyde. *Atmos. Meas. Tech.* **2016**, *9*, 41–52. [\[CrossRef\]](#)

51. Wu, T.; Zhao, W.; Chen, W.; Zhang, W.; Gao, X. Incoherent broadband cavity enhanced absorption spectroscopy for in situ measurements of NO₂ with a blue light emitting diode. *Appl. Phys. B Lasers Opt.* **2009**, *94*, 85–94. [\[CrossRef\]](#)
52. Chen, Y.; Yang, C.; Zhao, W.; Fang, B.; Xu, X.; Gai, Y.; Lin, X.; Chen, W.; Zhang, W. Ultra-sensitive measurement of peroxy radicals by chemical amplification broadband cavity-enhanced spectroscopy. *Analyst* **2016**, *141*, 5870–5878. [\[CrossRef\]](#)
53. Ball, S.M.; Jones, R.L. Broad-band cavity ring-down spectroscopy. *Chem. Rev.* **2003**, *103*, 5239–5262. [\[CrossRef\]](#)
54. Rothman, L.S.; Gordon, I.E.; Barbe, A.; Benner, D.C.; Bernath, P.F.; Birk, M.; Boudon, V.; Brown, L.R.; Campargue, A.; Champion, J.P.; et al. The HITRAN 2008 molecular spectroscopic database. *J. Quant. Spectrosc. Radiat. Transf.* **2009**, *110*, 533–572. [\[CrossRef\]](#)
55. McLean, A.B.; Mitchell, C.E.J.; Swanston, D.M. Implementation of an efficient analytical approximation to the Voigt function for photoemission lineshape analysis. *J. Electron. Spectrosc. Relat. Phenom.* **1994**, *69*, 125–132. [\[CrossRef\]](#)
56. Allan, D.W. Statistics of atomic frequency standards. *Proc. IEEE* **1966**, *54*, 221–230. [\[CrossRef\]](#)
57. Li, C.M.; Wang, H.C.; Chen, X.R.; Zhai, T.Y.; Chen, S.Y.; Li, X.; Zeng, L.M.; Lu, K.D. Thermal dissociation cavity-enhanced absorption spectrometer for measuring NO₂, RO₂NO₂, and RONO₂ in the atmosphere. *Atmos. Meas. Tech.* **2021**, *14*, 4033–4051. [\[CrossRef\]](#)
58. Horbanski, M.; Pöhler, D.; Lampel, J.; Platt, U. The ICAD (iterative cavity-enhanced DOAS) method. *Atmos. Meas. Tech.* **2019**, *12*, 3365–3381. [\[CrossRef\]](#)
59. Tang, J.Y.; Li, Y.J.; Li, X.L.; Jing, S.A.; Huang, C.; Zhu, J.P.; Hu, Q.Y.; Wang, H.L.; Lu, J.; Lou, S.R.; et al. Intermediate volatile organic compounds emissions from vehicles under real world conditions. *Sci. Total Environ.* **2021**, *788*, 147795. [\[CrossRef\]](#)
60. Leleux, D.; Claps, R.; Chen, W.; Tittel, F.; Harman, T. Applications of Kalman filtering to real-time trace gas concentration measurements. *Appl. Phys. B* **2002**, *74*, 85–93. [\[CrossRef\]](#)
61. Chen, W.; Yi, H.; Wu, T.; Zhao, W.; Lengignon, C.; Wang, G.; Fertein, E.; Coeur, C.; Wysocki, G.; Wang, T. Photonic sensing of reactive atmospheric species. *Encycl. Anal. Chem.* **2017**, 1–60. [\[CrossRef\]](#)
62. Tang, K.; Qin, M.; Fang, W.; Duan, J.; Meng, F.; Ye, K.; Zhang, H.; Xie, P.; He, Y.; Xu, W. Simultaneous detection of atmospheric HONO and NO₂ utilising an IBBCEAS system based on an iterative algorithm. *Atmos. Meas. Tech.* **2020**, *13*, 6487–6499. [\[CrossRef\]](#)
63. Bian, X.; Zhou, S.; Sun, X.; Yu, B.; Li, J. Continuous measurement of NO₂ in flue gas employing cavity-enhanced spectroscopy sensing system. *Measurement* **2022**, *201*, 111729. [\[CrossRef\]](#)
64. Li, J.; Reiffs, A.; Parchatka, U.; Fischer, H. In situ measurements of atmospheric CO and its correlation with NO_x and O₃ at a rural mountain site. *Metrol. Meas. Syst.* **2015**, *22*, 25–38. [\[CrossRef\]](#)
65. Thompson, A.M.; Cicerone, R.J. Possible perturbations to atmospheric CO, CH₄, and OH. *J. Geophys. Res. Atmos.* **1986**, *91*, 10853–10864. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.