1 **A Portable Nitrogen Dioxide Instrument Using Cavity-Enhanced Absorption**

2 **Spectroscopy**

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11 **Abstract**

12 The Portable (2.7 kg) Cavity-enhanced Absorption of Nitrogen Dioxide (PCAND) instrument for

13 measuring *in situ* nitrogen dioxide (NO_2) was developed using incoherent, broadband cavity-

14 enhanced absorption spectroscopy (IBBCEAS). An LED light source centered at 408 nm was

15 coupled to a cavity 15 cm in length, achieving an effective optical pathlength of ~520 m. Our

16 precision was measured as 94 pptv (1 s). To date, we have flown this instrument on 3 balloon and

17 1 UAV test flights. This instrument records data to an SD card and outputs data (via an RS232

18 port) to external devices including a commercial radiosonde (iMet) for real-time data downlink.

19 **1   Introduction**

20 Nitrogen dioxide (NO_2) is a major contributor to air pollution in the Earth's troposphere. Its main

21 source is a byproduct of combustion from the burning of fossil fuels (Spinei, E. *et al.* 2014). NO_2

22 has been monitored from satellite instruments (like OMI, TROPOMI, and GEMS) for a decade

23 (Miyazaki, K. *et al.* 2017, Duncan, B. *et al.* 2015, Martin, R.V. *et al.* 2003, Cooper, M.J. *et al.* 2020),

24 providing a global understanding of emissions and air quality. However, satellite retrievals of the

25 total column NO_2 rely on estimates of the vertical distribution of NO_2 based on models or

26 climatology (Cersosimo, A. *et al*, 2020). These *a priori* estimates are a major source of uncertainty

27   in making retrievals of NO_2 columns from satellite measurements (Cooper, M.J. *et al*. 2020, Dang,

28   R. *et al*. 2023).

29

30   Direct measurement of the vertical profile can verify and improve these *a priori* estimates.

31   Aircraft instruments cannot typically make a continuous vertical profile of the atmospheric

32   column. Therefore, an instrument small enough to fly on a balloon (or drone) is needed.

33   Techniques for measuring in situ NO_2 include Laser Induced Fluorescence (LIF)(Thornton, J.A. *et*

34   *al.* 2000), various-optical, absorption methods (like IBBCEAS)(Womack, C.C. *et al*. 2022, Min K.E.

35   *et al*. 2016), and chemical techniques (like chemiluminescence)(Ryerson, T.B. *et al*. 2000).

36   Although all these techniques have their pros and cons for use, we chose to focus on optical,

37   absorption methods for several reasons. First, we have successful experience using IBBCEAS in a

38   previous, ozone (O_3) based instrument (Hannun, *et al.*, 2020). Second, stability and ease of

39   calibration are desirable, which we found to be the case with the O_3 instrument. Third, the

40   technique can be scaled to a small enough size and weight to fly (via balloon or drone) into the

41   free troposphere. An instrument using LIF to measure NO_2 would (in our experience) not be

42   suitable for our purposes. Its size and weight would be too great to work with a small weather

43   balloon, despite LIF having greater sensitivity than IBBCEAS. Previously, a small NO_2 instrument

44   was developed by the Royal Netherlands Meteorological Institute (Dutch: Koninklijk Nederlands

45   Meteorologisch Instituut, KNMI) (Sluis, et al., 2010). That instrument uses chemiluminescence to

46   measure NO_2, with a reported precision of 7.7 ppbv/sec. Although chemiluminescence

47   instruments fit our size and weight criteria, they suffer from a lengthy calibration procedure

48   before every flight. Additionally, an instrument using chemiluminescence does not have the

49   desired sensitivity we require.

50

51   A description of our instrument using IBBCEAS follows. Performance metrics will show our

52   instrument meets the Federal Aviation Administrations (FAA) uncontrolled, maximum allowable

53   weight (~2.7 kg) for a balloon payload. In addition, we record sensitivity to NO_2 that exceeds the

54   KNMI sonde by more than an order of magnitude. A description of our calibration procedure is

55   detailed showing its simplicity. Finally, we demonstrate an atmospheric vertical profile
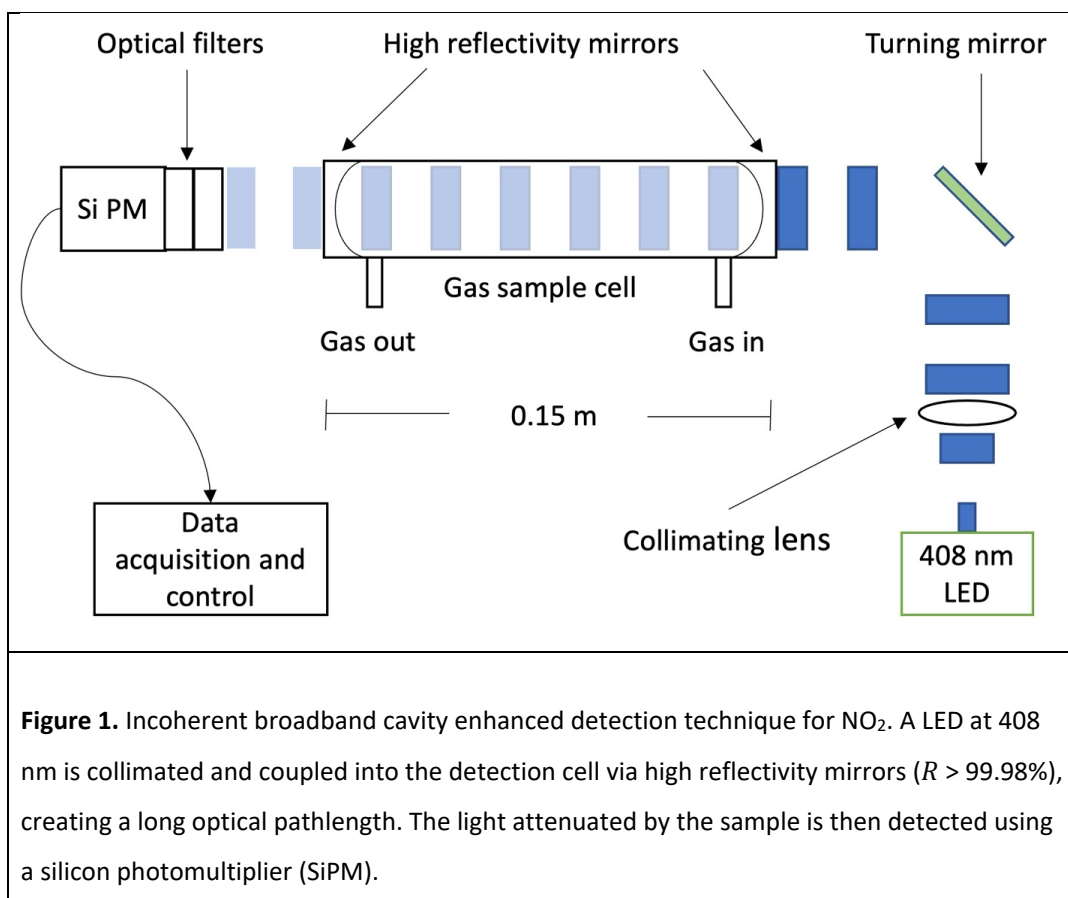
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56   measurement from one of our balloon flights. We also validate our instrument via a ground-

57   based comparison with another established NO_2 instrument.

58   **2   Principle of operation**

59   IBBCEAS is an established technique for the detection of trace gases (Fiedler *et al.*, 2003; Ball *et

60   al.*, 2004; Washenfelder *et al.*, 2008) including NO_2 (Min *et al.*, 2016). We use an LED as our

61   incoherent, broadband light source centered at 408 nm. This is coupled to an optical cavity with

62   highly reflective mirrors on either end. IBBCEAS leverages the mirror reflectivity to turn a

63   physically short path length (15 cm) of the cavity into an effective optical pathlength of ~520 m.

64   This effective pathlength increases the probability of NO_2 absorption in the cavity, thereby

65   increasing the sensitivity (94 pptv @ 1 s) of the instrument.

66

67   Shown in Figure 1, output from an LED is collimated into the gas sample cell (cavity) where it first

68   passes through the leftmost mirror. Both mirrors have highly reflective coatings (>99.9%) on

69   curved surfaces (r=250 mm) facing towards each other. Only a small fraction of light enters the

70   cell, but the light (photons) bounces back and forth between both mirrors thousands of times on

71   average before exiting the rightmost mirror. Photons that exit are then detected by a silicon

72   photomultiplier (SiPM). A transconductance amplifier is then used to convert small amounts of

73   current from the SiPM into measurable voltage levels. A micro controller with a 12-bit analog to

74   digital convertor digitizes this voltage. The micro controller is both a data acquisition system and

75   a controller of the LED and 3-way valve. A digital lock-in scheme is used to remove background

76   light by modulating the LED at 100 Hz with a large duty cycle (70%).

Figure 1. Incoherent broadband cavity enhanced detection technique for NO_2. A LED at 408 nm is collimated and coupled into the detection cell via high reflectivity mirrors ($R > 99.98\%$), creating a long optical pathlength. The light attenuated by the sample is then detected using a silicon photomultiplier (SiPM).

Trace gas absorption (using IBBCEAS) is a measurement of light attenuation. As light is absorbed and scattered (via Rayleigh), an attenuation of light is seen at the SiPM. The Beer-Lambert absorption coefficient, α_{abs}, is directly related to the light intensity exiting the cavity (Washenfelder *et al.*, 2008; Hannun *et al.*, 2020) through the equations:

$$\alpha_{abs} = \left(\frac{I_0 - I}{I}\right)\left(\frac{1-R}{d} + \alpha_{Ray}\right) \tag{1}$$

$$\alpha_{cav} = \left(\frac{1-R}{d}\right) \tag{2}$$

$$L_{\text{eff}} = \left(\frac{1}{\alpha_{cav}}\right) \tag{3}$$

87   Here I_0 is the intensity of light in the absence of any absorbing molecules, I is the intensity of

88   light including absorbing molecules, R is the mirror reflectivity, d is the physical distance between

89   cavity mirrors, and α_{Ray} is the extinction due to Rayleigh scatter. The term $(1-R)/d$ is the

90   theoretical cavity loss, α_{cav}. L_{eff} represents the maximum effective pathlength. In the case of

91   mirrors with R=0.9997, the maximum theoretical L_{eff} for our 15 cm cell would be 450 m.

92   **3   Instrument description**

93   PCAND is housed in a small aluminum box measuring 38 cm length x 22 cm width x 7 cm height

94   with a total weight of 2.7 kg. Inside the box (Figure 2) is an optical plate where all the instrument

95   components are mounted. Power comes from an 11.1 volt Lithium Ion rechargeable battery with

96   2200 mAh (24 Wh) of storage. Table 1 summarizes the PCAND design and performance

97   characteristics.

98

99   Table 1. Summary of PCAND performance capabilities

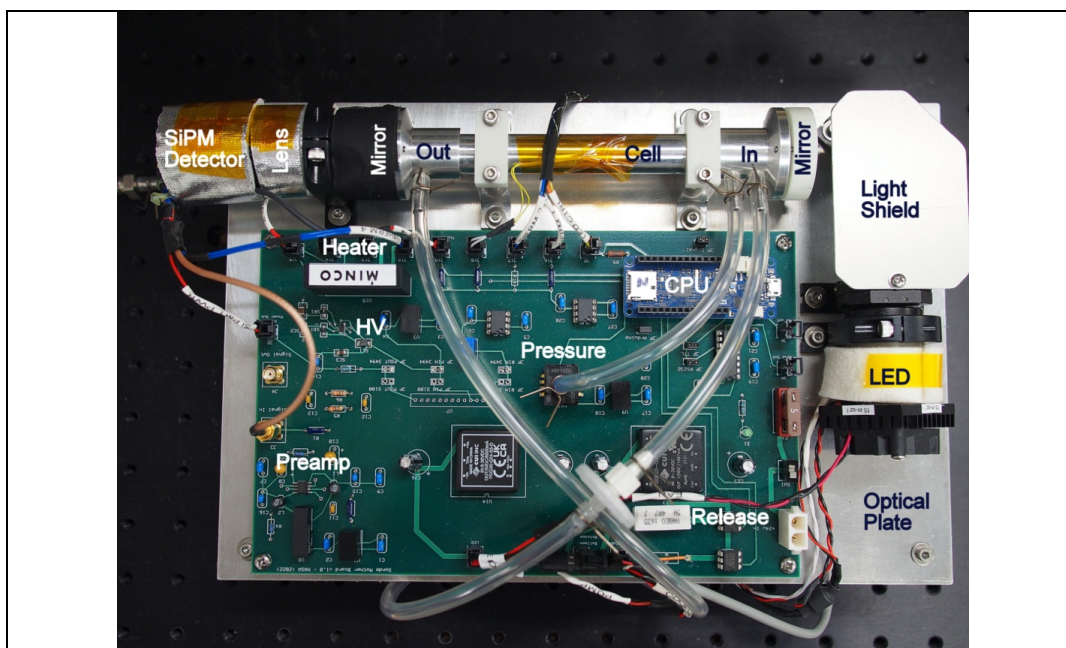| Specification	Value
Size	38 x 22 x 7 cm
Weight	2.7 kg
Power	< 6 W
Data rate	1 Hz
Precision (1σ, 1Hz)	2.3 x 10^9 molec. cm^{-3}
Accuracy	6.0%
Time response	3 s

100

Figure 2. A top view of the NO$_2$ instrument. Major components include A) the optical plate, which consists of the LED assembly, light shield, turning mirror (under light shield), the optical cell, end mirrors, collimating lens, and SiPM detector; B) The electronics motherboard with detector preamp, heater controller, pressure sensor, balloon release circuit, and the data acquisition system (CPU). Not shown is the nafion tubing used to dry the air before entering the instrument.

101

3.1 Optical components

3.1.1 LED assembly

104 A UV LED (λ_{max} = 408 nm, FWHM = 30 nm) (Thorlabs M310D1) is mounted to a custom heat sink

105 and temperature controlled to 25 °C with a thermo-electric cooler controller (Thorlabs

106 MTD415T). Constant current to the LED is supplied by a low noise controller (Thorlabs

107 MLD203CLN). The LED assembly includes a 15 mm focal length collimating lens (Thorlabs LA1074-

108 A) followed by a turning mirror (Thorlabs PF10-03-F01) to direct light into the sample cell.

109

110 *3.1.2 Sample cell*

111 The sample cell is manufactured from an aluminum alloy tube measuring 15 cm in length with a

112 1.4 cm inner diameter. The cell mirrors (Layertec 103654) have a reflectivity of $R > 99.9\%$ over

113 the detected spectral range (Figure 3) and a 250 mm radius of curvature. Mirrors are held to the

114 cell ends with bezel mounts on flanges with face seal o-ring glands. Although the mounts

115 themselves are non-adjustable, they are fabricated to hold the mirrors in a way that maximizes

116 their centricity to the cell ends. Furthermore, the incoherent light source negates the need for

117 rigid mirror alignment. A pressure transducer (Honeywell ASDXACX015PAAA5) measures the cell

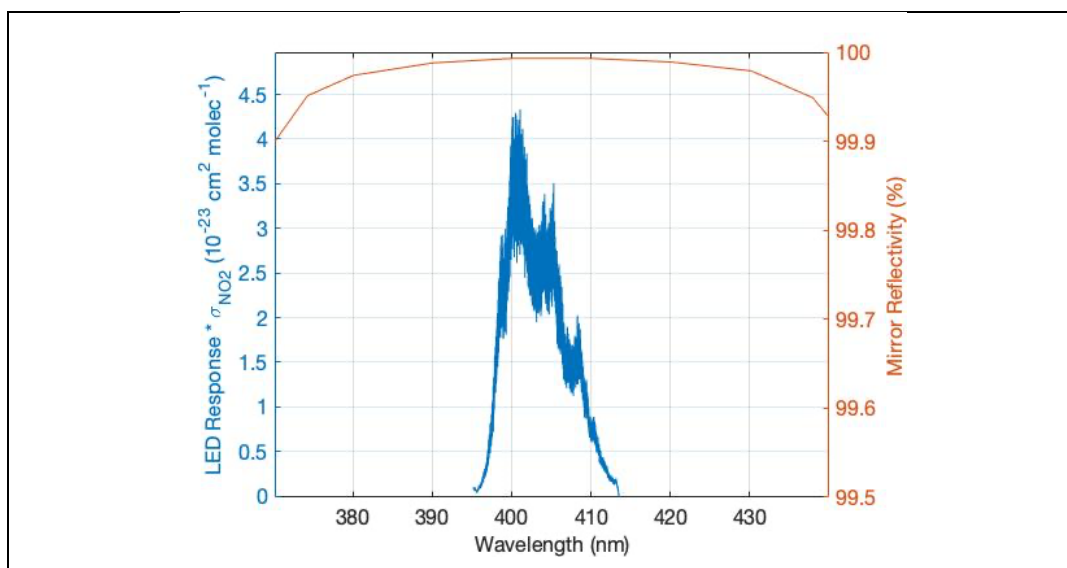118 pressure from a port near the cell inlet.

119

Figure 3. Normalized LED spectral response x NO_2 cross-section vs mirror reflectivity (99.98%

@ 408 nm). The LED (λ_{max} = 408 nm, FWHM = 30 nm) response was measured using a grating

spectrometer with the instrument SiPM and associated detector optics. The absorption cross-

section of NO_2 (for this instrument) is the integration of the above product (with a resolution

of 0.0005 nm) which yields 6.0419 x 10^{-19} cm^2 /molecule.

120

121 *3.1.3 SiPM assembly*

122 Following exit from the sample cell, light enters an optical bandpass filter (Semrock FF01-405/10-

123 25), then a lens (Thorlabs LA1252-A) focuses the beam onto a Silicon Photo Multiplier (SiPM -

124 Onsemi 30035) detector. The detector is biased by ~29 volts DC via a LT3494A boost converter.

125 This voltage sets the gain of this device. Signal from the SiPM is amplified through a

126 transimpedance amplifier based on a low noise, ADA4625-2 op-amp. The SiPM assembly is

127 thermally stabilized by heating it to a 35 °C setpoint using a Minco CT335 heater controller. The

128 temperature of the SiPM is monitored with a 10K thermistor mounted adjacent to the heater.

129 Temperature of the detector is held to within 0.1 °C of the setpoint using the Minco controller.

130 **3.2 Flow system**

131 The PCAND instrument uses a small, 12 volt diaphragm pump (Parker E134-11-120) to achieve a

132 1.4 standard liters per minute (SLM) flow rate. Flush time is approximately 3 seconds as evident

133 from Figure 4. A 3-way valve (ASCO 411L3212HV) is used to switch the flow between sample air

134 and scrubbed air (via an inline charcoal filter). The charcoal filter removes any NO_2 from the flow

135 and gives us our I_0 (reference) measurement every 30 seconds for 5 seconds, leaving us sample

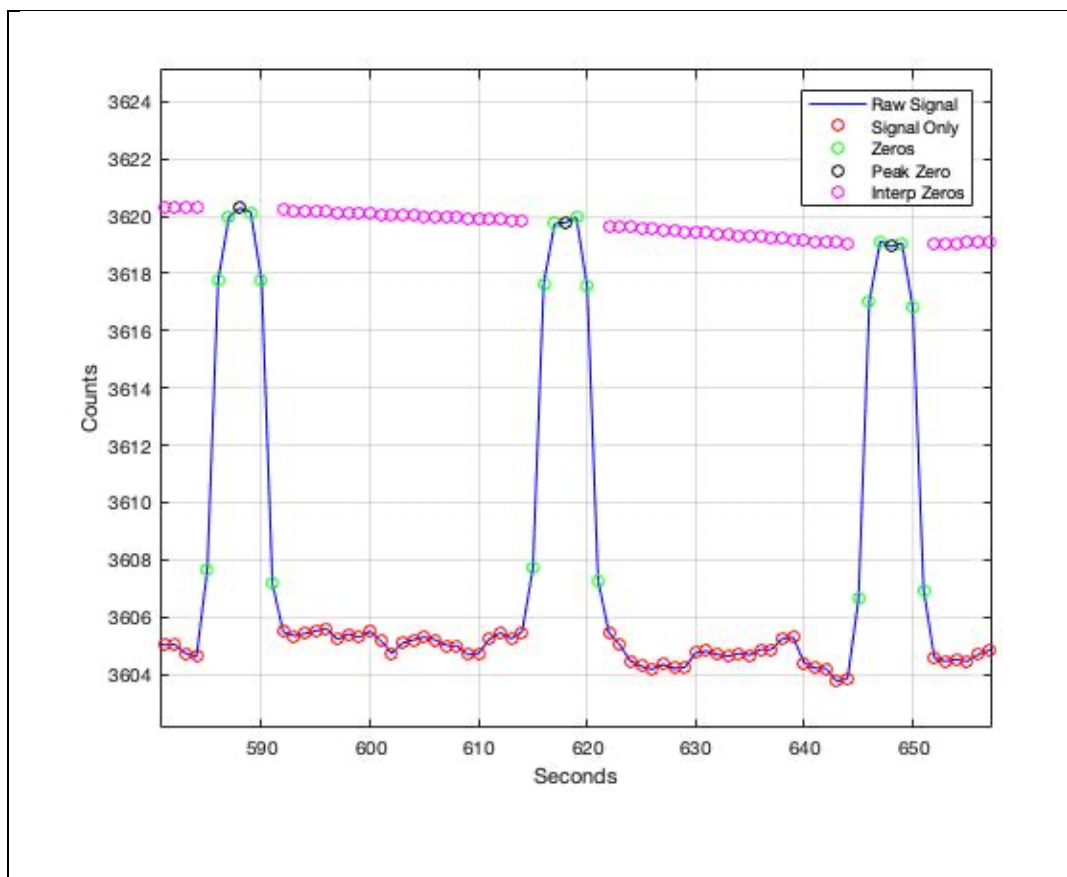136 air measurements 50 seconds out of every minute.

137

138

Figure 4. Cadence used to make real-time measurements of I_z (signal with no absorbers) vs I (signal with absorbers) is 7 seconds for I_z and 23 seconds for I. We found this was a good cadence allowing 3 seconds to achieve peak I_z and 3 seconds to return to I. A charcoal filter is switched into the airflow to achieve the I_z measurement.

139

140   We expect a small interference from water vapor. H2O vapor has a cross-section of 3 x 10^{-17}

141   cm^2 /molecule at 405 nm (Lampel *et al.*, 2015; 2017). An atmospheric abundance of H_2O = 1%

142   contributes the same absorption as 50 pptv of NO_2. In addition, we notice stronger attenuation

143   that is not consistent with gas phase absorption like that reported in ozone instruments using

144   UV absorption (Wilson *et al.*, 2006). In principle the presence of water vapor should not affect

145   the measurement if the abundance is constant between the sample and the scrubbed air.

146   However, the scrubber material (activated charcoal) can add or remove water vapor to the

147   sampled air depending on the prior humidity. Because of this interference, water vapor is

148   removed using two 30 cm lengths of 0.3 cm diameter Nafion Dewline tubing held in an

149   enclosure with drierite. The dry air sample eliminates any contribution of water vapor in the

150   measurement.

151

152   PCAND uses fluorinated ethylene propylene (FEP) lined thermoplastic tubing for all internal

153   plumbing. A 2-micron teflon membrane filter is positioned immediately before the cell inlet to

154   keep small particles from entering the cell and potentially dirtying the mirrors.

155   **3.3   Data acquisition**

156   PCAND uses an Arduino MKR Zero microcontroller for 3-way valve control, LED modulation, and

157   data acquisition. Arduino actuation of the valve is made through a CoolCube R valve controller,

158   which reduces the holding current needed to keep the valve in its open state. LED modulation is

159   produced by the Arduino through the LED controller at a 100 Hz rate. This modulation has a 70%

160   duty cycle used to achieve a digital lock-in to remove any background light from the absorption

161   measurement. We oversample the absorption signal 42k samples / second to increase the native

162   Arduino internal 12-bit measurement to an effective (averaged over a second) ~21-bit

163   measurement. Data is recorded both to an SD card and sent to an RS-232 port. The latter is useful

164   for both instrument testing and for connecting to an external iMet radiosonde where the data is

165   merged for RF data downlink by the radiosonde.

166   **3.4   Data processing**

167   The PCAND absorbance calculation uses equation 1, but accounts for the differential cell pressure

168   between the sample flow and the zero flow, which is restricted by the scrubber. Including the

169   Rayleigh scattering for both zero air and sample air, Eq. 1 is rewritten as equation 4 (Min *et al.*

170   2016 ; Hannun *et al.*, 2020) :

171

172    $$\alpha_{NO2} = \left(\frac{I_Z}{I} - 1\right)\left(\alpha_{cav} + \alpha_{Ray,Z}\right) + \Delta\alpha_{Ray} \qquad (4)$$

173    $$\Delta\alpha_{Ray} = \alpha_{Ray,Z} - \alpha_{Ray,S} \qquad (5)$$

174 $\qquad \alpha_{Ray} = N_{air}\sigma_{Ray}$ (6)

175 $\qquad \alpha_{NO2} = N_{NO2}\sigma_{NO2}$ (7)

176 $\qquad \alpha_{Ray,S} = \left(\frac{I_Z}{I} - 1\right)\alpha_{cav}$ (8)

177

178 Zero air is NO_2 scrubbed air where I_Z substitutes for I_0 (from equation 1). Rayleigh cavity

179 extinction is broken into 2 parts ($\alpha_{Ray,Z}$ and $\alpha_{Ray,S}$) describing zero air and sample air cavity

180 extinction respectively. In both cases, the Rayleigh scattering cross-section (σ_{Ray}), weighted by

181 the SiPMT response curve (Figure 3), is used (Bucholtz, 1995). The NO_2 number density

182 (concentration) is found by knowing the absorption cross-section of NO_2 (σ_{NO2}) (Vandalae, 1998).

183 **4   Performance**

184 **4.1   Sensitivity and calibration**

185 The PCAND effective pathlength of the optical cavity determines the instruments sensitivity to

186 NO_2. Highly reflective mirrors on either end of the cavity are statically mounted, so no adjustment

187 of their position is required. In practice, the alignment is stable over months of operation. After

188 the initial alignment, calibration is needed to determine the effective pathlength given the mirror

189 positions. We can use equation 4 with known quantities of NO_2 to determine the effective

190 pathlength (Figure 5a). We can also use Rayleigh scattering alone to solve for effective pathlength

191 (Figure 5b). This requires varying the pressure of zero air (in the absence of NO_2) to generate a

192 data set of absorption attenuation (I) vs number density of zero air. It also requires we solve for

193 equation 8 after it has been reduced from equation 4. To do this, we must assume $\alpha_{Ray,Z}$ is taken

194 at vacuum, so $\alpha_{Ray,Z}$ goes to zero leaving only $\alpha_{Ray,S}$. We must calculate (I_z) at vacuum using

195 our data set. This leaves us with equation 8 to solve for effective pathlength (equation 3). Using

196 known quantities of NO_2 and equation 4 yields a pathlength of 519 ± 2 m. Using the Rayleigh

197 scattering method and equation 8 yields a pathlength of 524 ± 1 m. The two methods of

198 calibration are within < 1% of each other and both yield pathlengths that agree to within 2σ

199 uncertainty for each fit. Therefore, we choose to use the Rayleigh scattering method in future

200 calibrations (when needed) of PCAND. Note that due to the small Rayleigh cross-section of air at

201 408 nm, sigma = 1.5 x 10^{-26} cm^{-2}/molecule (Bucholz, 1995) the calibration using air is susceptible

202 to leaks and contamination. Adequate care must be taken to ensure that the system is free of

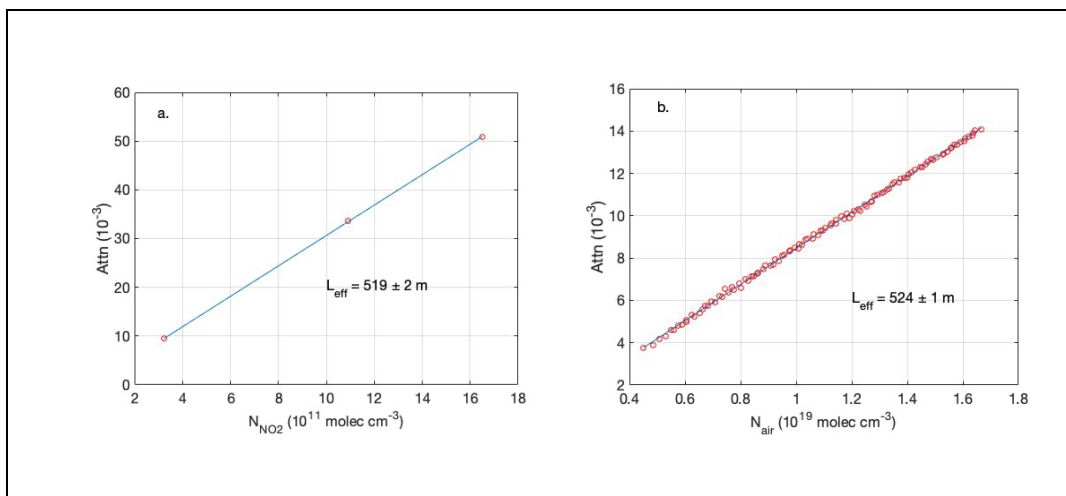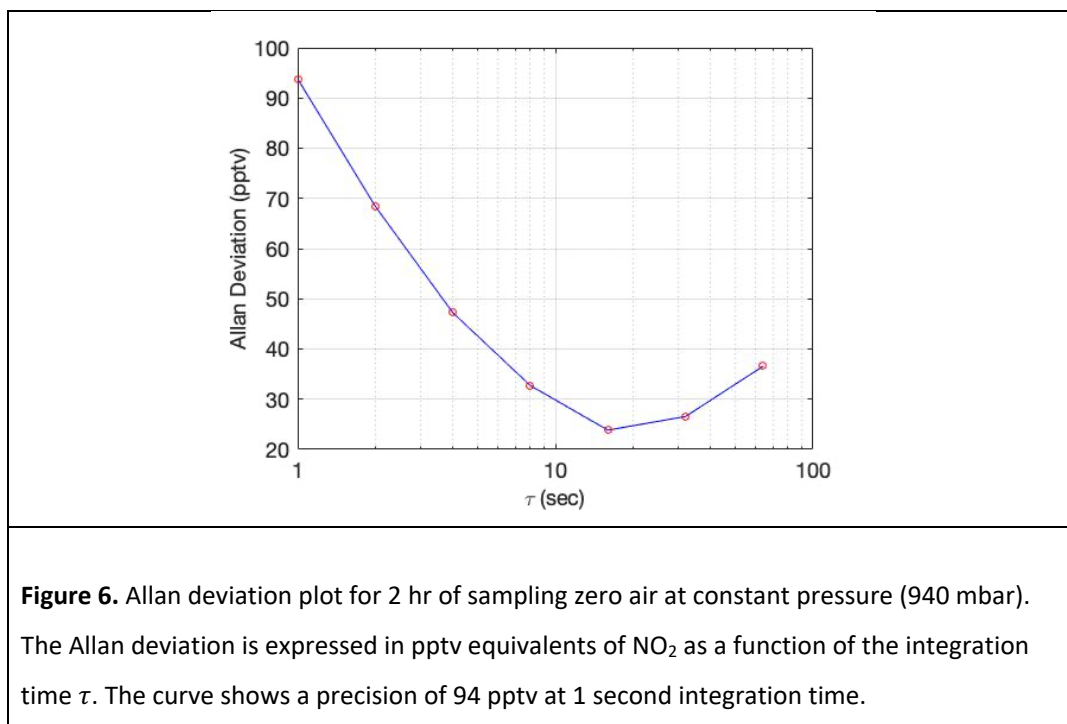203 leaks and that the air is pure.

Figure 5. NO_2 Sonde calibration: a) The effective pathlength (L_{eff}) as determined by attenuation (Attn) due to known additions of NO_2 from a reference tank of NO_2 mixed with zero air. The slope yields the effective pathlength as determined from Equation 1 in the text using the known NO_2 absorption cross section; b) Attenuation due to Rayleigh scatter over a range of cell pressures. The slope of attenuation as a function of number density gives the pathlength using the known Rayleigh scattering cross-section for zero air. The pathlength from each calibration agreed to within 2σ uncertainty for each fit.

204

205 **4.2   Precision and accuracy**

206 The PCAND precision was determined by flowing zero air (under constant pressure of 920 mbar)

207 into the cavity for 2 hours while accumulating 1Hz data. Figure 6 is an Allan deviation plot showing

208 a 1 Hz precision of 94 pptv and a 10 s precision of 30 pptv. The 1 Hz precision translates to 2.3 x

209 10^9 molecules cm^{-3} of NO_2 at 1 atmosphere.

210

Figure 6. Allan deviation plot for 2 hr of sampling zero air at constant pressure (940 mbar). The Allan deviation is expressed in pptv equivalents of NO_2 as a function of the integration time τ. The curve shows a precision of 94 pptv at 1 second integration time.

211

212 The accuracy of PCAND measurements depends on NO_2 and Rayleigh cross section uncertainties,

213 pressure sensor uncertainty, thermistor uncertainty, and cavity extinction uncertainty. The NO_2

214 absorption cross-section uncertainty is reported to be 3% (Spinei, 2014; Vandalae 1998). We use

215 3% for the Rayleigh scattering cross-section uncertainty (Bucholtz, 1995). From data sheets, we

216 conclude temperature and pressure measurements to have uncertainties of 0.5% and 2%

217 respectively. We also measured cavity extinction slope uncertainty at 1%. Together, the total

218 uncertainty when propagated through equation 4 comes to 6 % when applied to the final NO_2

219 number density.

4.3 Response time

221 Response time is a direct function of gas flush time in our cell given our small vacuum pump. A

222 flow rate of 1.4 SLM is achieved with our pump resulting in a response time of approximately 3

223 seconds (Figure 4). Given our cadence of 5 second zero followed by 25 second sample, we can

224 see (by eye) it takes ~3 seconds for the signal to stabilize with zero air. A larger pump could

225 shorten this response time at the expense of more mass and power needed.

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226 **4.4 Photolysis Effects**

227 The photolysis quantum yield is 0.22 at 408 nm (*Troe, 2000)*, so we expect some fraction of the

228 NO_2 in the cell to photolyze, $NO_2 + h\nu \rightarrow NO + O$. In static cells the photolysis of NO_2 has been

229 shown to be a concern (Platt *et al., 2019*) In the case of our detection, it is unlikely that a

230 significant fraction of NO_2 will be photolyzed because the sample flows through the cell quickly

231 with a flush time of approximately 1 s and the number of photons available for photolysis is

232 small.

233 We can estimate the number of photons in the cell from the detector signal. The SiPM has a

234 radiant sensitivity of 4×10^5 A/W and a photon detection efficiency of 50%. Based on our

235 detection signal of 2×10^{-5} A, we estimate the optical power is roughly 10^{-10} W and calculate a

236 photon flux of 2×10^9 photons/s. A typical absorbance with 1 ppb NO_2 in the cell is 10^{-3}, thus

237 we expect that roughly 2×10^6 photons/s are absorbed by the 1 ppb NO_2 in the cell. At 900 hPa

238 the number density of 1 ppb NO_2 is roughly 2.2×10^{10} molecules/cm^3. The absorption of 2×10^6

239 photons would result in the photolysis of 4.4×10^5 NO_2 molecules, or 2×10^{-5} of the available

240 NO_2 molecules. While this number is quite low for our conditions, it is worth noting that with

241 slower flows and higher photon fluxes the photolysis could be significant and secondary

242 chemistry could be a concern.

243 **5 Field demonstration**

244 PCAND was launched on 3 low altitude (~7 km) balloon flights for demonstration purposes during

245 the summer of 2022. PCAND was physically linked (via RS232 cable) to a commercial weather

246 sonde for real-time data downlink (via the weather sonde). Results from the second flight (Figure

247 7) launched on 18 August 2022 show a vertical profile of NO_2 indicative of that time of year with

248 high concentrations of NO_2 near the ground. This flight occurred at 8 am local time when the

249 boundary layer was still close to the ground. The temperature deviation in the instrument box

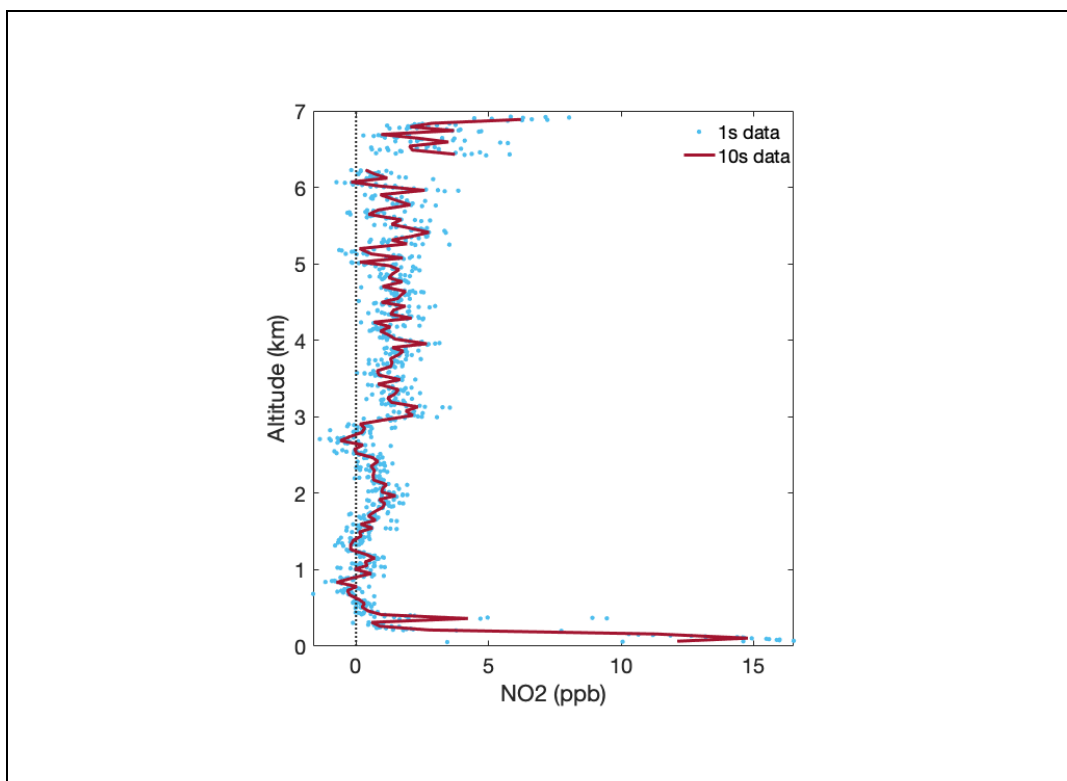250 during flight to 7km was less than 1 °C.

251

252

253

Figure 7. NO2 Sonde flight data from 18 August 2022 balloon launch. Programmed cut-down of balloon at 7 km to achieve payload recovery. Significant concentrations of NO₂ appear near the surface and again at cut-down (~7 km) altitude.
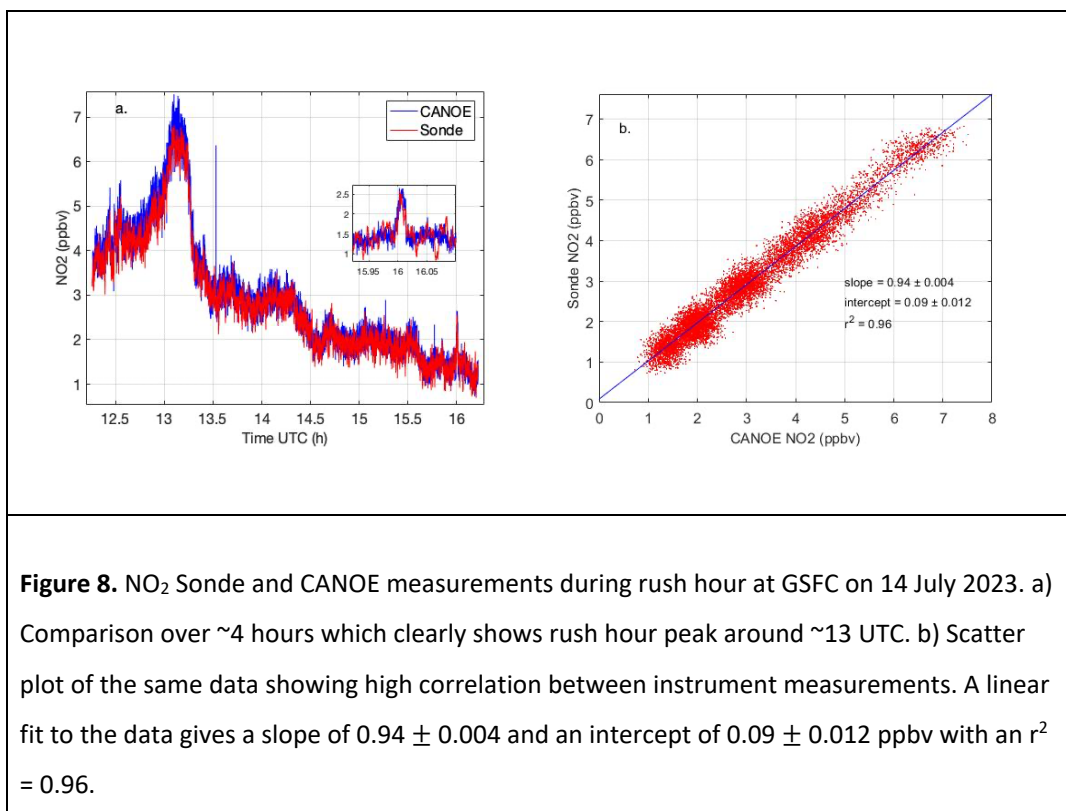
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5.1 Validation with CANOE

257

258 PCAND was validated with another NO₂ instrument called CANOE (Compact Airborne Nitrogen

259 diOxide Experiment). CANOE was based on the design of a similar instrument called CAFE (St.

260 Clair *et al.*, 2019) (Compact Airborne Formaldehyde Experiment). The only difference between

261 CANOE and CAFE are the laser wavelengths (532 nm for CAFE vs 355 nm for CANOE) and PMT

262 detectors used. CANOE is an LIF instrument which has been deployed on several airborne

263 campaigns including Dynamics and Chemistry of the Summer Stratosphere (DCOTSS) and Fire

264   Influence on Regional to Global Environments and Air Quality (FIREX-AQ). CANOE has been

265   calibrated to known cylinders of NO_2 concentration. Figure 8 shows a ~4-hour data set where

266   PCAND and CANOE shared the same inlet port sampling the air during a morning in the DC greater

267   metropolitan area. Clearly, a rush hour peak of NO_2 is seen trailing off by noon. Figure 8a shows

268   good agreement between the measurements with a slope of 0.94 ± 0.004 and an intercept of

269   0.09 ± 0.012 ppbv NO_2 (r^2 = 0.96).

Figure 8. NO_2 Sonde and CANOE measurements during rush hour at GSFC on 14 July 2023. a)
Comparison over ~4 hours which clearly shows rush hour peak around ~13 UTC. b) Scatter
plot of the same data showing high correlation between instrument measurements. A linear
fit to the data gives a slope of 0.94 ± 0.004 and an intercept of 0.09 ± 0.012 ppbv with an r^2
= 0.96.

270   **6   Summary and conclusions**

271   PCAND provides very high sensitivity to NO_2 for such a small package using broadband cavity-

272   enhanced UV absorption at 408 nm. PCAND has a precision of ~94 pptv s^{-1} with an accuracy of

273   6.0%. Although PCAND was designed for portable, battery powered operation (as needed for a

274   sonde or drone flight), it could easily be used in either ground or lab-based measurements. It was

275   successfully tested on 3 balloon flights producing NO_2 vertical profiles for each. A comparison

276   with another (calibrated) NO_2 instrument (CANOE) showed strong agreement over a ~4-hour

277   period.

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