

Supporting Information

Measurements of Peroxy Radicals

Using Chemical Amplification-Cavity Ringdown Spectroscopy

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1. CRDS instrument setup

The CRDS measurements of NO₂ are carried out at ~405.23 nm near its peak absorption. As described before (1), the 532-nm output from a Nd:YAG laser pumps a dye laser to produce radiation near 810 nm, which is then doubled to ~405 nm. The 405-nm laser radiation enters the cavity ring-down chamber (0.90 m in length) and the output light is detected by a photomultiplier. The cavity mirrors are separated by 0.90 m and have a reflectivity of ~99.985% at 405 nm (Research Electro-Optics, diameter = 20 mm, and ROC = 1 m). The typical ring-down time for a cavity filled with zero air is 15 μs. The ring-down signal is collected on a 14-bit 200 MS/s oscilloscope card (Gage); each ring-down curve is fitted with a fast algorithm in combination with the data collection software on National Instruments Labview.(1) The gas flow from the PERCA reactor enters in the ring-down cavity after passing through a 0.45-μm particle filter.(1) Buffer gas is not required to protect the mirror surfaces since the air sample is sufficiently filtered, and thus the air sample filled the entire optical path ($L=l_s$). After removing the background and interferences signals, NO₂ measurements with a limit of detection of 150 pptv/10s (S/N=3) can be achieved.(1) Reliable NO₂ measurements could be obtained by this method without the need for frequent calibration with a calibration gas.(1)

Calibration of PERCA

In order for the chemical amplifier to function as a viable instrument for the measurement of atmospheric peroxy radicals, the number of NO₂ molecules produced per peroxy radical, i.e., the chain length CL, must be determined accurately. This number is dependent on many factors

such as the rates of reactions, removal processes of the radicals, and the reaction time. Under the specified conditions, the sensitivity of the system to peroxy radicals can be assessed quantitatively. Therefore, the first important part in this project is to calibrate and obtain a reasonable CL.

Figure 1 shows the experimental setup for the calibration measurement. In the calibration step, the continuous and stable HO_2 radical source is used as the standard. The zero air flow carries a small amount (~ 600 ppbv) of H_2O_2 vapor from the permeation tube(2) and then passes through a quartz tube heated with a heating tape up to 600°C , which produces a continuous source of HO_2 radicals.

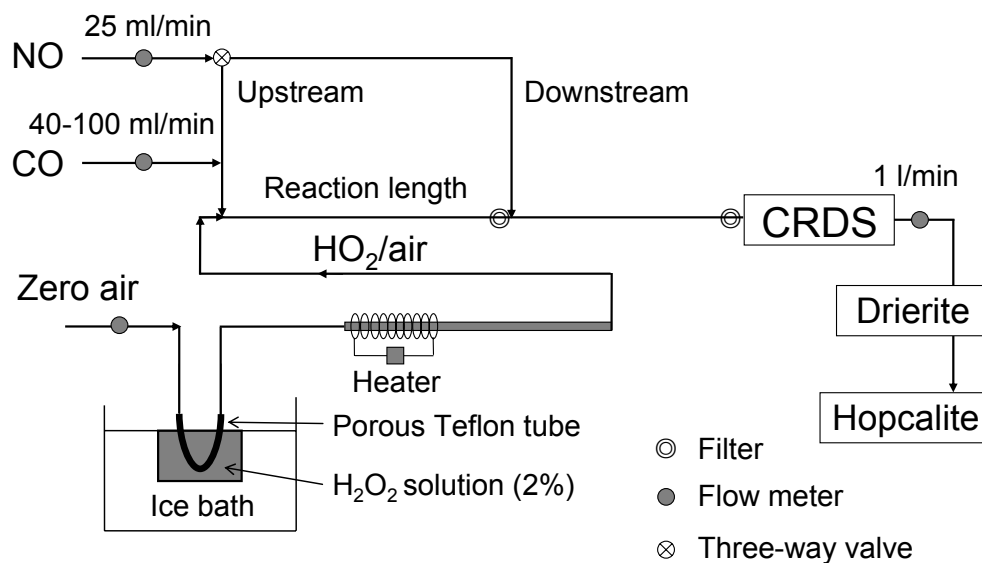


Figure 1. Schematic diagram of the HO_2 calibration system.

In our experiment, five measurements on NO_2 are carried out to obtain the CL and instrumental sensitivity to HO_2 . These five signals are shown in the schematics of the calibration

processes in Figure 2. S_1 is the background level from zero air. S_2 is the CRDS reading for the downstream configuration with only NO and calibration air (HO_2) in the reactor; this corresponds to the background NO_2 impurity in the NO reagent gas and the zero sample gas, with HO_2 removed by the Teflon filter at the end of the 2-m flow reactor tubing. S'_2 is the NO_2 signal of the upstream configuration with only NO and calibration air (HO_2) in the reactor, in which HO_2 is converted to NO_2 (without amplification) by reaction with NO in the flow system. S_3 is the signal of the downstream configuration with NO, CO, and calibration air (HO_2) in the reactor; this corresponds to the background NO_2 level without amplification, as HO_2 is removed by the filter at the end of the flow system. S'_3 is the signal in the upstream configuration with NO, CO and calibration air (HO_2) in the reactor (with amplification). The difference signal, $(S'_2 - S_2)$, is from the NO_2 that is converted from the HO_2 radicals in the source; as the HO_2 radicals can be quantitatively converted to NO_2 in the excess amount of NO, this difference signal is effectively equal to the HO_2 concentration. Therefore the output of the HO_2 radical source is determined

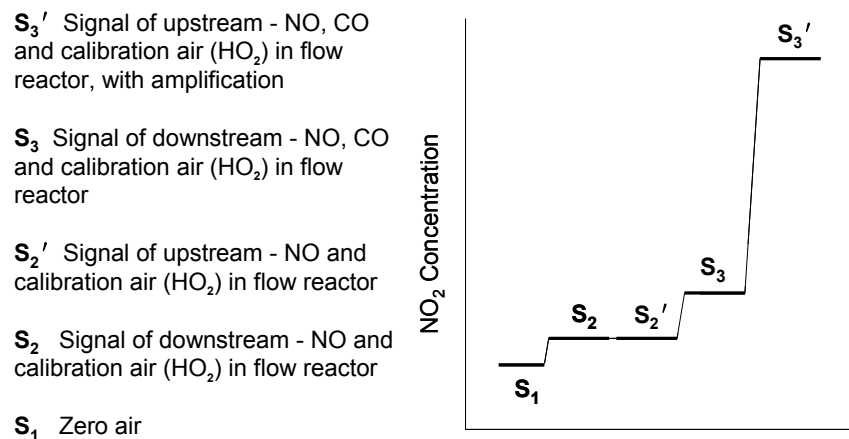


Figure 2: Schematics of calibration model

from these two measurements (S'_2-S_2); the concentration of HO_2 in the flow source is found to be in the range of 0.5-3 ppbv. (S'_3-S_3) is the amplified NO_2 signal from the HO_2 radicals in the radical source. The ratio between the amplified signal and the radical concentration gives the chain length of the chemical amplifier:

$$\Delta[\text{NO}_2]/[\text{HO}_2] = (S'_3-S_3)/(S'_2-S_2) = \text{CL} \quad (1)$$

In the calibration processes, optimized signals require a stable zero-air baseline (S_1), and the difference between S_2 and S'_2 need to be measured accurately because it is small. With the high sensitivity of CRDS for NO_2 detection (<1 ppbv), a reliable (S'_2-S_2) can be readily obtained.

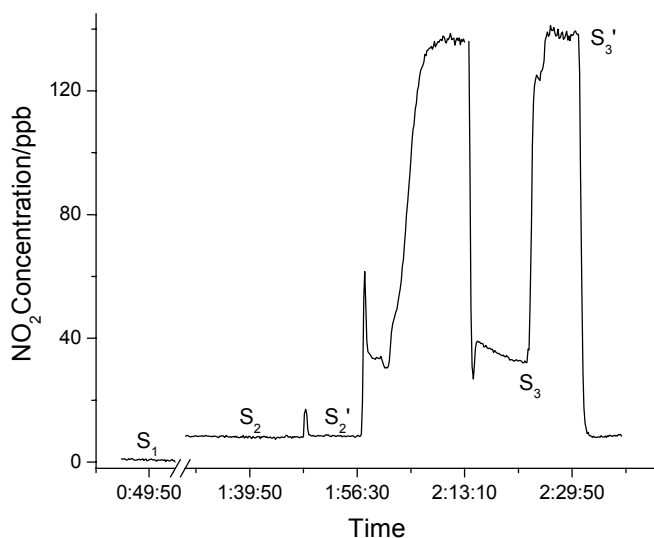


Figure 3. Experimental calibration data.

Figure 3 shows an example of the experimental calibration data. The evidence of PERCA, (S'_3-S_3), is quite pronounced. After several repeated measurements, the chain length is determined to be 150 with a 90% confidence interval of 50, $\text{CL} = 150 \pm 50$. Our CL value is close

to the value of 190 reported by Sadanaga et al. using a similar PERCA flow system.(3)

Our CL is obtained with low concentration of HO₂ of ~ 0.5 ppb, close to the measured ambient level. It was shown that at higher concentration of HO₂ ($>10^{11}$ cm⁻³), the CL may be significantly reduced (4). However, the large CL observed in this study indicates that the HO₂ radical concentration is reasonably low, and the derived CL could be used for ambient measurements.

The CL for the RO₂ radicals is slightly different from that of HO₂, as the RO₂ radicals are converted to HO₂ via reactions with NO and O₂ with an efficiency that depends upon the structures of RO₂ and the intermediate RO radicals. Cantrell and co-workers discussed the factors that control the efficiency with which the RO₂ radicals are converted into the HO₂ radicals.(5-7) Those factors include (1) branching ratio for RO₂ + NO → RO + NO₂ relative to RO₂ + NO → RONO₂; (2) competition of the reactions of the alkoxy radicals with oxygen (in the PERCA chain reactions) and with NO (removal of the RO radicals from the PERCA reactions); and (3) removal of the alkoxy radicals from PERCA due to their unimolecular decomposition or isomerization to hydroxyl substituted radicals.(6,7) The different efficiencies of converting the RO₂ radicals to HO₂ could be related to their different numbers of carbon atoms and reactivities that depend on temperature, pressure and NO concentration. In the calculations by Cantrell and co-workers,(5,6) it was shown that in clean to moderately polluted atmospheres the conversion efficiencies of selected peroxy radicals to HO₂ in the chemical amplifier are about 0.9. This indicates that the CL's of the RO₂ radicals could be assumed to be about 90% of that of HO₂.

References

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