

Ethane-Based Chemical Amplification Measurement Technique for Atmospheric Peroxy Radicals

Ezra C. Wood,*^{,†}[©] Benjamin L. Deming,^{‡,§} and Shuvashish Kundu[‡]

[†]Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104, United States

[‡]Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, United States

Supporting Information

ABSTRACT: Peroxy radicals play important roles in the atmospheric oxidation of organic compounds and the formation of ozone and secondary organic aerosol. There are few peroxy radical measurement techniques; the most common, chemical amplification using CO and NO, requires the use of toxic reagents, and its calibration factor is very sensitive to relative humidity. We present a new method for quantifying atmospheric peroxy radicals, ECHAMP (Ethane CHemical AMPlifier). Sampled air is mixed with NO and C_2H_6 (rather than CO), effecting a series of reactions that ultimately produces 25 molecules of NO₂ per sampled peroxy radical under dry conditions. This "amplification"



factor decreases to 17 at a relative humidity of 50%, yielding a 1σ precision for 90 s average measurements of 0.8–2.5 ppt depending on the atmospheric variability of ozone. We demonstrated the utility of the new technique with measurements in Bloomington, IN, in July 2015.

INTRODUCTION

Peroxy radicals (HO₂ and RO₂, where R is an organic backbone) are key species in atmospheric chemistry. Their reaction with NO to form NO₂ leads to net formation of ozone in the troposphere,¹ and their fates are closely connected to the formation of secondary organic aerosol particles.^{2,3} Model predictions of peroxy radicals do not always match measured concentrations, especially in forests where there are high concentrations of biogenic volatile organic compounds (VOCs).^{4,5} Such discrepancies have been attributed to radical loss⁴ or production⁵ processes missing from models. Despite their importance, there are few techniques capable of measuring total peroxy radicals, and measurement intercomparions have shown mixed results.⁶⁻¹⁰ The most common method of quantifying total peroxy radicals is the chemical amplification technique,¹¹⁻¹⁴ also known as "CHAMP" (CHemical AMPlifier)¹⁵ or "PERCA" (PERoxy radical Chemical Amplifier).^{16,17} Ambient air is mixed with high concentrations of CO (3-10%)and NO (\sim 3 ppm), effecting the following radical propagation cycle:

$$HO_2 + NO \rightarrow OH + NO_2$$
 (1)

$$OH + CO + O_2 \rightarrow CO_2 + HO_2$$
(2)

The NO₂ formed is then quantified by one of several techniques. Organic peroxy radicals are detected after conversion to HO₂ by reaction with NO, though formation of organic nitrates (RONO₂) and organic nitrites (RONO) reduces the sampling efficiency.¹⁸ The chain length, the number of NO₂ molecules produced per sampled radical, can be as high as 200 at 0% relative humidity. Since the introduction of this chemical amplification technique in 1981,¹¹ numerous versions that use the same CO and NO chemistry have been developed

with subsequent detection of the NO $_2$ amplification product by several different analytical methods.^{13,14,19–21}

There are several drawbacks to the CO-based amplifier. (1) The high concentrations of CO required are extremely toxic. Mixing ratios of 3-10% are used in the reaction chambers, which requires using a cylinder of 100% CO. Inhalation of 0.2% CO can lead to death within 2 h.²² CO is also explosive at concentrations between 12 and 85% in air. Although the flow rates used, typically ~100 sccm per channel, are relatively low and with proper safeguards the likelihood of a large leak is low, the ramifications of such a leak could be catastrophic. The use of CO is a serious logistical impediment to deploying traditional chemical amplifiers. (2) The amplification factor is very sensitive to relative humidity (RH). In many systems, the sensitivity is reduced by a factor of >4 when operating at 75% RH compared to 0% RH. This also increases the measurement uncertainty due to the additional uncertainty of the RH effect itself. There is also disagreement among groups that operate CO-based amplifiers regarding the suitability of this RH correction.^{6,17,20,23,24} (3) The detection sensitivity to individual peroxy radicals varies because of the formation of RONO₂ and RONO following the reaction of sampled RO₂ with excess NO. In particular, a large fraction of CH_3O_2 (~25%) that is sampled is converted into CH₃ONO rather than detected by chemical amplifiers when using the typical NO mixing ratio of 3 ppm.

Reiner et al.²⁵ presented a major modification to this amplification chemistry, whereby the CO was replaced by SO_2 and rather than detecting NO_2 their chemical ionization mass

Received:	November 15, 2016
Revised:	December 9, 2016
Accepted:	December 13, 2016
Published:	December 13, 2016

Environmental Science & Technology Letters

spectrometer detected H_2SO_4 .²⁵ Although this decreased the chain length by an order of magnitude, it still led to excellent sensitivity that is not affected by RH.²⁶ Partial peroxy radical speciation information can also be provided by modulation of the NO/O₂ ratio.²⁷

In this paper, we present a new chemical amplification method [Ethane CHemical AMPlifier (ECHAMP)] that uses ethane (C_2H_6) rather than CO, with detection of the NO₂ product by cavity-attenuated phase shift spectroscopy (CAPS). Because of its relatively benign impact on health, ethane is not classified as a criteria pollutant or a hazardous air pollutant by the U.S. Environmental Protection Agency. The amplification factor of ECHAMP is almost 7 times lower than that of the CO-based amplification technique under dry conditions, but one-quarter as large at 50% RH. Use of much safer ethane greatly facilitates field deployments, and the lower NO mixing ratio used leads to a higher detection efficiency for CH₃O₂ and other alkyl peroxy radicals. We show measurements of ambient peroxy radicals in Bloomington, IN, during July 2015 using our prototype ECHAMP instrument.

MATERIALS AND METHODS

The overall flow design and operation of the ECHAMP instrument are based on our previously described CO-based chemical amplifier²⁴ with a few important modifications described herein. Air is sampled at 0.88 SLPM into two identical 0.43 cm inner diameter (ID) fluorinated ethylene propylene (FEP) tubes and immediately mixed with 45 sccm of NO (20 ppm in N_2) and either 45 sccm of N_2 or 45 sccm of C_2H_6 (30% in N₂) via an "upstream" perfluoroalkoxy (PFA) tee; 45 sccm of C₂H₆ or N₂ is added via a second tee 15 cm downstream. The sampled air then flows through an additional 64 cm of 0.4 cm ID FEP tubing, a PTFE filter (United filtration BKN-60), and 7 m of 0.4 cm ID FEP tubing and finally enters the CAPS detectors (Aerodyne Research, Inc.) that are housed inside a laboratory at a flow rate of 1.0 SLPM. The mixing ratios of NO and C₂H₆ in the reaction chambers are 1.0 ppm and 2.3% between the two addition points and 4.5% lower downstream of the second addition. The lower explosive limit of C_2H_6 in air is 3.0%. When a reaction chamber is operated in "ROx" or amplification mode, the ethane is added upstream and the nitrogen is added downstream. In "Ox" or background mode, these are reversed: nitrogen is added upstream and ethane downstream.²⁴ Further details regarding the inlet, purification of the C2H6 and NO, and other aspects of the gas flows are provided in the Supporting Information.

Calibration and Amplification Factor. Peroxy radical measurements by all chemical amplifiers rely on accurate calibrations with known concentrations of peroxy radicals. We calibrated the sensor with two different radical sources: one based on photolysis of acetone vapor and another based on photolysis of water vapor. The former creates a mixture of CH_3O_2 and $CH_3C(O)O_2$ radicals and has been described previously.²⁴ Briefly, radicals produced by acetone photolysis are quantified by reaction with excess NO and measurement of the NO₂ produced (without amplification). The water photolysis method is a more common HOx calibration method and used by many chemical amplifiers and laser-induced fluorescence instruments.^{13,28–31} Briefly, humidified air is exposed to 184.9 nm ultraviolet (UV) radiation from a mercury lamp, creating an equimolar mixture of OH and HO₂:

$$H_2O + 184.9 \text{ nm} \rightarrow H + OH \tag{3}$$

$$H + O_2 \to HO_2 \tag{4}$$

OH is quantitatively converted to either HO_2 or $C_5H_8(OH)O_2$ by reaction with added CO or isoprene, respectively. Further details of our implementation of the water photolysis method and comparison to the acetone photolysis method are described in the Supporting Information.

RESULTS AND DISCUSSION

The amplification factors (F) for both ethane-based and CObased chemical amplifiers as a function of RH are shown in Figure 1. At 0% RH, the amplification factor for the ethane



Figure 1. RH dependence of the chain length of both the CO-based and C_2H_6 -based amplifier. At typical ambient relative humidity values (40–85%), the amplification factor of the ethane-based amplifier is within a factor of 4 of that of the CO-based amplifier. The RH is defined as that entering the reaction chamber (before dilution with the dry reagents). Each point is the result of a calibration curve. The error bars are \pm 5% for the C_2H_6 amplifier and \pm 12% for the CO amplifier.

system is 7 times lower than that of the CO system. Its amplification factor, however, is less sensitive to RH than that of the CO amplification system. At 50% RH, the amplification factor for the ethane system is 30% lower than that at 0% RH and is 4 times lower than the CO system's amplification factor at 50% RH.

Amplification Chemistry. In "ROx" mode (i.e., with the NO and C_2H_6 added to the sampled air immediately at the "upstream" tee), the following radical propagation reactions occur:

$$O_2 + NO \rightarrow OH + NO_2$$
 (1)

$$OH + C_2 H_6 \rightarrow H_2 O + C_2 H_5 \tag{5}$$

$$C_2H_5 + O_2 + M \to C_2H_5O_2 + M$$
 (6)

$$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2 \tag{7}$$

$$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2 \tag{8}$$

net reaction:

$$C_2H_6 + 2O_2 + 2NO \rightarrow CH_3CHO + H_2O + 2NO_2$$
(9)

Organic peroxy radicals that create HO_2 upon reaction with NO are also detected by the radical sensor:

$$RO_2 + NO \rightarrow RO + NO_2$$
 (10)



Figure 2. Mixing ratios of RO₂ + HO₂, NO, NO₂, and O₃ and j_{NO_2} measurements in a forest near Bloomington, IN, during the IRRONIC field campaign (local time). With the exception of the HO₂ + RO₂ measurements for which 15 min averages are shown, all other measurements are 1 min averages. Units for the j_{NO_2} axis are inverse seconds.

$$RO + O_2 \rightarrow R'HO + HO_2$$
 (11)

where R'HO is a carbonyl compound. Decomposition of RO radicals can also form HO₂ or OH radicals that then participate in reactions 1-5.

In background mode, in which the air is mixed with NO and N_2 at the upstream tee and the ethane is not added until 130 ms later at the downstream tee, RO_2 and HO_2 radicals are converted into HONO by reactions 10, 11, and 1 and, finally, the reaction of OH with NO to form HONO. In strict terms, the amplification factor *F* can be defined as the amount of NO_2 produced in amplification mode per radical sampled. Because NO_2 is produced from reactions 1 and 7 in both amplification mode and background mode, however, we instead define *F* as the quotient of the difference in NO_2 concentration between amplification and background modes and the sampled peroxy radical concentration (see the section on calibration).

We use a chemical kinetics numerical integration model to predict the impact of experimental conditions on the amplification factor (details in the Supporting Information). The major termination reactions at 0% RH are listed below in order of importance according to the model:

$$C_2H_5O + NO + M \rightarrow C_2H_5ONO + M$$
(12)

$$C_2H_5O_2 + NO + M \rightarrow C_2H_5ONO_2 + M$$
(13)

 $HO_2 + NO + M \rightarrow HNO_3 + M$ (14)

$$HO_2 + wall \rightarrow loss$$
 (15)

At a NO mixing ratio of 1 ppm, 2.9% of the ethoxy radicals (C_2H_5O) react with NO to form C_2H_5ONO rather than propagate by reaction with oxygen (reaction 8).³² Similarly, 1.9% of the reaction of ethyl peroxy radicals $(C_2H_5O_2)$ with NO will form ethyl nitrate (reaction 13) rather than C_2H_5O and NO₂.³³ Reactions 12 and 13 account for a combined 86% of the total radical termination at 0% RH, while formation of HNO₃ from HO₂ and NO (reaction 14) accounts for only 9%. At 75% RH, reaction 14 accounts for 43% of total radical termination because of the increase in its rate constant caused by HO₂·H₂O adducts.^{34–36} This is also the cause of the RH dependence of CO-based chemical amplifiers' chain length.^{23,37} Although reaction 14 also affects the ethane amplifier, because of the presence of the faster radical termination steps (C_2H_5ONO and $C_2H_5ONO_2$ formation), the overall result is that the ethane amplifier has an amplification factor at 0% RH that is much lower than that of the CO amplifier, but does not decrease as much with increasing RH. At RH values commonly found in the troposphere during the day (40-85%), the amplification factor of the ethane amplifier is within a factor of 4 of that of the CO amplifier.

Letter

The ambient ROx concentration (ROx = $OH + HO_2 + RO_2 + RO)$ is determined by eq 1:

$$[ROx] = \Delta NO_2 / F \tag{I}$$

where ΔNO_2 is the difference between the two reaction chambers' NO_2 measurements (one in amplification mode and the other in background mode) and *F* is the laboratory-determined amplification factor.

Ambient Measurements. We deployed the ECHAMP system along with supporting measurements of NO, NO₂, and O₃ in Bloomington, IN, during July 2015 as part of the Indiana Radical, Reactivity and Ozone Production Intercomparison (IRRONIC) field project. NO was measured with a Thermo model 42i-TL chemiluminescence sensor; NO₂ was measured with a separate CAPS sensor, and O₃ was measured with a 2B Tech model 202 UV absorption sensor. j_{NO_2} was measured with a spectroradiometer. Figure 2 shows 4 days of measurements during the IRRONIC field project. Concentrations followed a diurnal pattern similar to that of j_{NO_2} , usually peaking between 13:00 and 16:00 local time at 20–50 ppt, and were <5 ppt at night. Analysis of these measurements along with those recorded with a laser-induced fluorescence instrument will be presented in other papers.

Uncertainty and Detection Limit. As was the case with our earlier CO-based amplifier,²⁴ there are three main sources of uncertainty. All uncertainty values quoted are at the 2σ level: (1) the calibration of the two CAPS sensors to NO₂ (5%), (2) uncertainty associated with the peroxy radical calibrations and the RH "correction" (on the basis of the uncertainty in the fit of the calibration curves, this is 5% for the former²⁴ and 15% for the latter for a combined uncertainty, calculated in quadrature, of 16%; for the July 2015 data set shown below, however, this is increased to 25% because of problems encountered with the field calibration source that have since been rectified),³⁸ and (3) uncertainty related to the variable response of the instrument to different types of peroxy radicals, estimated to be 9%.

For the field measurements described below, the total 2σ uncertainty is thus 27%, though we expect future data sets to have an uncertainty of <20%.

Environmental Science & Technology Letters

The third point above underscores an attribute of the ECHAMP method: its relative sensitivity to RO2 radicals compared to HO₂ is higher than that of CO-based amplifiers because of the lower NO mixing ratio used (1 ppm for ECHAMP vs 3 ppm for PERCA). RO₂ radicals are detected by chemical amplifiers only if they eventually form HO₂ following reaction with NO (e.g., R10 and R11). The extent to which this occurs depends on the competing fates of the intermediate alkoxy radical (RO): reaction with O_{24} reaction with NO to form alkyl nitrites (RONO), and isomerization/decomposition. At 3 ppm NO, only 75% of CH₃O₂ radicals are detected by chemical amplifiers because of the formation of CH₃ONO as determined by the relevant literature rate constants [i.e., $k_{\text{CH}_{3}\text{O}+\text{O}_{2}}[\text{O}_{2}]/(k_{\text{CH}_{3}\text{O}+\text{O}_{2}}[\text{O}_{2}] + k_{\text{CH}_{3}\text{O}+\text{NO}}[\text{NO}])]$. In contrast, at 1 ppm NO, 90% of CH₃O₂ is expected to be detected. This advantageous use of lower NO mixing ratios is not an attribute of the ethane amplification chemistry itself and could be applied to CO-based amplifiers, though at reduced sensitivity.

The precision and detection limit are theoretically limited by the precision of the CAPS NO2 sensors and the RH-dependent amplification factor of the C_2H_6 -NO chemistry (eq 1).²⁴ With a CAPS NO₂ 1 σ precision of 10 ppt for a 45 s average and an amplification factor of 17 (at 50% RH), the theoretical 1σ precision for a 90 s measurement is $\sqrt{2(10)}/17 = 0.8$ ppt, leading to predicted detection limits of 1.6 ppt for 90 s averages and 0.5 ppt for 15 min averages (signal-to-noise ratio of 2). During ambient sampling, however, fast variations in the O₃ mixing ratio and imperfect matching of the time response of the two reaction chambers, transit tubing, and CAPS internal volumes usually degrade this 1σ precision by a factor of 3, to 2.5 ppt for 90 s averages and 0.8 ppt for 15 min averages.²⁴ Given daytime mixing ratios of 10-40 ppt, the resulting signal-tonoise ratios for the 15 min averaged daytime measurements in Figure 2 typically range from 10 to 50. Additional figures demonstrating instrument precision and data processing are provided in the Supporting Information.

Given the relative ease of deploying this instrument with the new ethane-based chemistry and the success of its first deployment, we have discontinued use of the traditional CO amplification chemistry and plan to use the ECHAMP method for future studies of atmospheric peroxy radicals.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00438.

Further details of the reagent gas purification, inlet design, amplification chemistry modeling, dependence of amplification factor on experimental conditions, water vapor photolysis calibration method, measurement precision, and amplification by isoprene (PDF)

AUTHOR INFORMATION

Corresponding Author

*Department of Chemistry, Drexel University, 3141 Chestnut St., Disque Hall 303, Philadelphia, PA 19104. E-mail: Ezra. Wood@drexel.edu. Phone: 215.895.1681.

ORCID [©]

Ezra C. Wood: 0000-0002-9533-215X

Present Address

[§]B.L.D.: Department of Chemistry, University of Colorado, Boulder, CO 80309.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (AGS 1443842). We are grateful to J. Flynn and B. Lefer of the University of Houston (Houston, TX) for the spectroradiometer data.

REFERENCES

(1) Kleinman, L. I. The dependence of tropospheric ozone production rate on ozone precursors. *Atmos. Environ.* **2005**, *39* (3), 575–586.

(2) Kroll, J. H.; Seinfeld, J. H. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.* **2008**, *42*, 3593–3624.

(3) Ng, N. L.; Chhabra, P. S.; Chan, A. W. H.; Surratt, J. D.; Kroll, J. H.; Kwan, A. J.; McCabe, D. C.; Wennberg, P. O.; Sorooshian, A.; Murphy, S. M.; Dalleska, N. F.; Flagan, R. C.; Seinfeld, J. H. Effect of NOx level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes. *Atmos. Chem. Phys.* **2007**, *7* (19), 5159.

(4) Griffith, S. M.; Hansen, R. F.; Dusanter, S.; Stevens, P. S.; Alaghmand, M.; Bertman, S. B.; Carroll, M. A.; Erickson, M.; Galloway, M.; Grossberg, N.; et al. OH and HO_2 radical chemistry during PROPHET 2008 and CABINEX 2009 - Part 1: Measurements and model comparison. *Atmos. Chem. Phys.* **2013**, *13* (11), 5403– 5423.

(5) Wolfe, G. M.; Cantrell, C.; Kim, S.; Mauldin Iii, R. L.; Karl, T.; Harley, P.; Turnipseed, A.; Zheng, W.; Flocke, F.; Apel, E. C.; et al. Missing peroxy radical sources within a summertime ponderosa pine forest. *Atmos. Chem. Phys.* **2014**, *14* (9), 4715–4732.

(6) Andrés-Hernández, M. D.; Stone, D.; Brookes, D. M.; Commane, R.; Reeves, C. E.; Huntrieser, H.; Heard, D. E.; Monks, P. S.; Burrows, J. P.; Schlager, H.; Kartal, D.; Evans, M. J.; Floquet, C. F. A.; Ingham, T.; Methven, J.; Parker, A. E. Peroxy radical partitioning during the AMMA radical intercomparison exercise. *Atmos. Chem. Phys.* **2010**, *10* (21), 10621.

(7) Burkert, J.; Behmann, T.; Andrés Hernández, M.; Stöbener, D.; Weißenmayer, M.; Perner, D.; Burrows, J. Measurements of peroxy radicals in a forested area of Portugal. *Chemosphere: Global Change Sci.* **2001**, 3 (3), 327–338.

(8) Fuchs, H.; Brauers, T.; Häseler, R.; Holland, F.; Mihelcic, D.; Müsgen, P.; Rohrer, F.; Wegener, R.; Hofzumahaus, A. Intercomparison of peroxy radical measurements obtained at atmospheric conditions by laser-induced fluorescence and electron spin resonance spectroscopy. *Atmos. Meas. Tech.* **2009**, *2* (1), 55–64.

(9) Ren, X.; Edwards, G. D.; Cantrell, C. A.; Lesher, R. L.; Metcalf, A. R.; Shirley, T.; Brune, W. H. Intercomparison of peroxy radical measurements at a rural site using laser-induced fluorescence and Peroxy Radical Chemical Ionization Mass Spectrometer (PerCIMS) techniques. J. Geophys. Res. 2003, 108 (D19), 4605.

(10) Ren, X.; Mao, J.; Brune, W. H.; Cantrell, C. A.; Mauldin Iii, R. L.; Hornbrook, R. S.; Kosciuch, E.; Olson, J. R.; Crawford, J. H.; Chen, G.; Singh, H. B. Airborne intercomparison of HO_X measurements using laser-induced fluorescence and chemical ionization mass spectrometry during ARCTAS. *Atmos. Meas. Tech.* **2012**, *5* (8), 2025. (11) Cantrell, C.; Stedman, D. A possible technique for the measurement of atmospheric peroxy radicals. *Geophys. Res. Lett.* **1982**, *9* (8), 846–849.

(12) Hastie, D. R.; Weissenmayer, M.; Burrows, J. P.; Harris, G. W. Calibrated chemical amplifier for atmospheric ROx measurements. *Anal. Chem.* **1991**, *63* (18), 2048–2057.

(13) Horstjann, M.; Andrés Hernández, M. D.; Nenakhov, V.; Chrobry, A.; Burrows, J. P. Peroxy radical detection for airborne

Environmental Science & Technology Letters

atmospheric measurements using absorption spectroscopy of NO₂. Atmos. Meas. Tech. 2014, 7 (5), 1245.

(14) Kartal, D.; Andrés-Hernández, M. D.; Reichert, L.; Schlager, H.; Burrows, J. P. Technical Note: Characterisation of a DUALER instrument for the airborne measurement of peroxy radicals during AMMA 2006. *Atmos. Chem. Phys.* **2010**, *10*, 3047–3062.

(15) Cantrell, C. A.; Shetter, R. E.; Calvert, J. G. Dual-Inlet chemical amplifier for atmospheric peroxy radical measurements. *Anal. Chem.* **1996**, *68* (23), 4194–4199.

(16) Green, T. J.; Reeves, C. E.; Brough, N.; Edwards, G. D.; Monks, P. S.; Penkett, S. A. Airborne measurements of peroxy radicals using the PERCA technique. *J. Environ. Monit.* **2003**, *5* (1), 75–83.

(17) Sommariva, R.; Brown, S. S.; Roberts, J. M.; Brookes, D. M.; Parker, A. E.; Monks, P. S.; Bates, T. S.; Bon, D.; de Gouw, J. A.; Frost, G. J.; et al. Ozone production in remote oceanic and industrial areas derived from ship based measurements of peroxy radicals during TexAQS 2006. *Atmos. Chem. Phys.* **2011**, *11* (6), 2471–2485.

(18) Clemitshaw, K. C.; Carpenter, L. J.; Penkett, S. A.; Jenkin, M. E. A calibrated peroxy radical chemical amplifier for ground-based tropospheric measurements. J. Geophys. Res. **1997**, 102 (D21), 25405.

(19) 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* (20), 5870–5878.

(20) Liu, Y.; Zhang, J. Atmospheric Peroxy Radical Measurements using Dual-Channel Chemical Amplification Ravity Ringdown Spectroscopy. *Anal. Chem.* **2014**, *86* (11), 5391–5398.

(21) Sadanaga, Y.; Matsumoto, J.; Sakurai, K.-i.; Isozaki, R.; Kato, S.; Nomaguchi, T.; Bandow, H.; Kajii, Y. Development of a measurement system of peroxy radicals using a chemical amplification/laser-induced fluorescence technique. *Rev. Sci. Instrum.* **2004**, 75 (4), 864–872.

(22) Goldstein, M. Carbon monoxide poisoning. J. Emerg. Nurs. 2008, 34 (6), 538-542.

(23) Mihele, C. M.; Hastie, D. R. The sensitivity of the radical amplifier to ambient water vapour. *Geophys. Res. Lett.* **1998**, 25 (11), 1911–1913.

(24) Wood, E. C.; Charest, J. Chemical Amplification – Cavity Attenuated Phase Shift Spectrometer Measurements of Peroxy Radicals. *Anal. Chem.* **2014**, *86* (20), 10266–10273.

(25) Reiner, T.; Hanke, M.; Arnold, F. Atmospheric peroxy radical measurements by ion molecule reaction-mass spectrometry: A novel analytical method using amplifying chemical conversion to sulfuric acid. *J. Geophys. Res.* **1997**, *102* (D1), 1311–1326.

(26) Edwards, G. D.; Cantrell, C. A.; Stephens, S.; Hill, B.; Goyea, O.; Shetter, R. E.; Mauldin, R. L.; Kosciuch, E.; Tanner, D. J.; Eisele, F. L. Chemical ionization mass spectrometer instrument for the measurement of tropospheric HO_2 and RO_2 . *Anal. Chem.* **2003**, 75 (20), 5317–5327.

(27) Hornbrook, R. S.; Crawford, J. H.; Edwards, G. D.; Goyea, O.; Mauldin Iii, R. L.; Olson, J. S.; Cantrell, C. A. Measurements of tropospheric HO_2 and RO_2 by oxygen dilution modulation and chemical ionization mass spectrometry. *Atmos. Meas. Tech.* **2011**, *4* (4), 735–756.

(28) Dusanter, S.; Vimal, D.; Stevens, P. S.; Volkamer, R.; Molina, L. T. Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign Part 1: Deployment of the Indiana University laser-induced fluorescence instrument. *Atmos. Chem. Phys.* **2009**, *9* (5), 1665–1685.

(29) Faloona, I. C.; Tan, D.; Lesher, R. L.; Hazen, N. L.; Frame, C. L.; Simpas, J. B.; Harder, H.; Martinez, M.; Di Carlo, P.; Ren, X. R.; et al. A laser-induced fluorescence instrument for detecting tropospheric OH and HO₂: Characteristics and calibration. *J. Atmos. Chem.* **2004**, 47 (2), 139–167.

(30) Sadanaga, Y.; Matsumoto, J.; Sakurai, K.; Isozaki, R.; Kato, S.; Nomaguchi, T.; Bandow, H.; Kajii, Y. Development of a measurement system of peroxy radicals using a chemical amplification/laser-induced fluorescence technique. *Rev. Sci. Instrum.* **2004**, *75* (4), 864.

(31) Schultz, M.; Heitlinger, M.; Mihelcic, D.; Volz-Thomas, A. Calibration source for peroxy radicals with built-in actinometry using

 H_2O and O_2 photolysis at 185 nm. J. Geophys. Res. **1995**, 100 (D9), 18811–18816.

(32) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J.; IUPAC Subcommittee. Subcommittee, I., Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II; gas phase reactions of organic species. *Atmos. Chem. Phys.* **2006**, *6* (11), 3625– 4055.

(33) Ranschaert, D. L.; Schneider, N. J.; Elrod, M. J. Kinetics of the $C_2H_5O_2 + NO_x$ Reactions: Temperature Dependence of the Overall Rate Constant and the $C_2H_5ONO_2$ Branching Channel of $C_2H_5O_2 + NO$. J. Phys. Chem. A **2000**, 104 (24), 5758–5765.

(34) Butkovskaya, N.; Kukui, A.; Le Bras, G. HNO_3 Forming Channel of the HO_2 + NO Reaction as a Function of Pressure and Temperature in the Ranges of 72–600 Torr and 223–323 K. J. Phys. Chem. A **2007**, 111 (37), 9047–9053.

(35) Butkovskaya, N.; Kukui, A.; Pouvesle, N.; Le Bras, G. Formation of nitric acid in the gas-phase HO_2 + NO reaction: Effects of temperature and water vapor. *J. Phys. Chem. A* **2005**, *109* (29), 6509–6520.

(36) Butkovskaya, N.; Rayez, M.-T.; Rayez, J.-C.; Kukui, A.; Le Bras, G. Water vapor effect on the HNO₃ yield in the HO₂ + NO reaction: experimental and theoretical evidence. *J. Phys. Chem. A* **2009**, *113* (42), 11327–11342.

(37) Reichert, L.; Hernández, A.; Stöbener, D.; Burkert, J.; Burrows, J. Investigation of the effect of water complexes in the determination of peroxy radical ambient concentrations: Implications for the atmosphere. J. Geophys. Res. 2003, 108 (D1), ACH 4-1–ACH 4-16, DOI: 10.1029/2002]D002152.

(38) Kundu, S.; Deming, B.; Lew, M.; Stevens, P. S.; Dusanter, S.; Sklaveniti, S.; Leonardis, T.; Locoge, N.; Flynn, J.; Wood, E. Peroxy radical measurements by ethane - nitric oxide chemical amplification (ECHAMP) during the IRRONIC field campaign in a forest atmosphere in Indiana. 2016, manuscript in preparation.