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Atmospheric Measurement Techniques
Discussions

A new technique for the direct detection of HO_2 radicals using bromide chemical ionization mass spectrometry (Br-CIMS): initial characterization

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Abstract

Hydroperoxy radicals (HO_2) play an important part in tropospheric photochemistry, yet photochemical models do not capture ambient HO_2 mixing ratios consistently. This is likely due to a combination of uncharacterized chemical pathways and measurement limitations. The indirect nature of current HO_2 measurements introduces challenges in accurately measuring HO_2, therefore a direct technique would help constrain HO_x chemistry in the atmosphere. In this work we evaluate the feasibility of using chemical ionization mass spectrometry (CIMS) and propose a direct HO_2 detection scheme using bromide as a reagent ion. Ambient observations were made with a high resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) in Atlanta over the month of June 2015 to demonstrate the capability of this direct measurement technique. Observations displayed expected diurnal profiles, reaching daytime median values of ~7 ppt between 1 p.m. and 3 p.m. local time. The HO_2 diurnal was found to be dictated by morning-time vehicular NO_x emissions and shows a slow decrease into the evening. Measurement sensitivities of 4.95±1.00 Hz/ppt per 10^6 bromide ion counts (^{79}Br) were observed. The relatively low baseline allowed for 3σ lower detection limits of 0.7 ppt for 1 minute integration times. Mass spectra of ambient measurements showed the $^{79}BrHO_2^-$ peak was the major component of the signal at nominal mass-to-charge 112, suggesting high selectivity for HO_2 at this mass-to-charge. More importantly, this demonstrates that high resolution instrumentation is not necessary to conduct these measurements.

1. Introduction

Hydroperoxy radicals (HO_2) play an important role in the photochemistry of the troposphere. They are primarily formed from the OH initiated oxidation of CO and other volatile organic compounds (VOCs), with contributions from ozonolysis of alkenes, nitrate radical oxidation of VOCs, and photolysis of aldehydes (e.g., HCHO) (Geyer et al., 2003;Cooke et al., 2010;Volkamer et al., 2010;Alam et al., 2013;Stone et al., 2014). HO_2 is a reservoir species for OH, which is the primary daytime oxidant, and facilitates the photochemical production of ozone via reaction with NO. Additionally, the relative abundance of HO_2 to NO_x plays a critical role in the fate of peroxy radicals (RO_2) and the production of low-volatility products in secondary organic aerosol (SOA) formation (Ziemann and Atkinson, 2012; Orlando and Tyndall, 2012). For instance, reactions of HO_2 with RO_2 serve as the main source of atmospheric organic hydroperoxides, which are important constituents of SOA (Docherty et al., 2005).

Because HO_2 are short lived ($\tau \leq 1$ min) (Heard and Pilling, 2003), measurements are useful in evaluating model photochemical schemes with the exclusion of confounding phenomena, such as atmospheric transport. However, accurate measurements have proven difficult due to the naturally low abundance of HO_2. HO_2 also possess weak spectral lines, which has posed challenges for spectroscopic techniques, though some spectroscopic measurements have been made, primarily in the laboratory. (Radford et al., 1974) employed a more sensitive laser-assisted technique, laser magnetic resonance (LMR) spectroscopy in the laboratory to measure HO_2. Milhelcic et al. (1985, 2003) used Matrix Isolation Electron Spin Resonance (MIESR), where HO_2 are collected for a period of 30 minutes on a D_2O matrix at 77 K before detection. Both techniques directly measure HO_2 but their applicability to atmospheric observations is limited. LMR may be impractical due to instrumentation needs while MIESR suffers from poor time resolution.

More recent methods such as peroxy radical chemical amplification (PERCA) (Cantrell and Stedman, 1982;Cantrell et al., 1984), chemical ionization mass spectrometry (CIMS) (Hanke et al., 2002;Edwards et al., 2003;Hornbrook et al., 2011), and laser induced fluorescence (LIF) (Stevens et al., 1994;Brune et al., 1995) provide lower detection limits at high temporal resolution. However, these techniques do not measure HO_2 directly, requiring HO_2 to be titrated with NO, which introduces additional complexity.

The PERCA technique, for example, detects NO_2 produced from radical chain reactions of HO_2 with NO and OH with CO to produce multiple NO_2 molecules from each HO_2 present in the sample, effectively amplifying the signal. However, addition of NO to a sample stream containing organic peroxy radicals results in additional HO_2 production, which precludes speciation of HO_2 from other peroxy radicals, though previous attempts to speciate the two have been made (Miyazaki et al., 2010).

Chemical ionization techniques such as ROx Chemical Conversion/CIMS (ROxMAS) and Peroxy radical CIMS (PerCIMS) also rely on the addition of NO to the sample stream, titrating HO_2 to OH which subsequently reacts with added SO_2 to produce H_2SO_4. The H_2SO_4 is then ionized by nitrate ions (NO_3^-) at atmospheric pressure to produce a stable HSO_4^- ion for detection. PerCIMS suffers from positive artifacts from the contribution of the RO_2+NO reaction to the measured HO_2 concentration. Hornbrook et al. (2011) successfully speciated HO_2 and HO_2+RO_2 measurements by modulating the relative NO and O_2 concentrations in the reaction region, suppressing conversion of some peroxy radicals to ~15%. However, RO_2 contribution to HO_2 mixing ratios derived from unsaturated hydrocarbons such as isoprene is not suppressed by the oxygen dilution modulation scheme.

The LIF technique, which converts HO_2 to OH for direct detection at 308 nm laser excitation, does not require additional chemical conversion steps, which allows for shorter reaction times. However, LIF instruments have previously been shown to also experience similar artifacts, with magnitudes dependent on the effective reaction time allowed after NO addition before detection and on the precursor of the RO_2 (Fuchs et al., 2011;Whalley et al., 2013).

Given the uncertainties associated with indirect methods of HO_2 measurement and the time resolution required for atmospheric measurements, especially airborne measurements, a direct measurement of HO_2 at fast integration times would benefit efforts aiming to measure and model HO_2 to understand atmospheric photochemistry. The exclusion of measurement artifacts would aid in evaluating the gap between measured and modeled HO_2 concentrations in forested regions, where HO_2 measured to modeled ratios are highly variable (Stone et al., 2012). In this work, we evaluated the potential of various chemical ionization schemes and provide proof of concept for the Br^- associative ionization of HO_2 to form a $Br^-(HO_2)$ adduct as a direct way of measuring HO_2 using chemical ionization mass spectrometry. This technique provides selective, fast time resolution measurements of HO_2. Ambient measurements were conducted in Atlanta in June 2015 to demonstrate technique performance.

2. Instrument description

A High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS, Aerodyne Research, Inc.) and a house-built quadrupole CIMS were used for laboratory characterizations of reagent ions for the measurement of HO_2. Ambient data were collected using the HR-ToF-CIMS exclusively. The High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS, Aerodyne Research, Inc.) consists of an atmospheric pressure interface with five differentially pumped stages, utilizing two scroll pumps and a multi-stage turbomolecular pump backed by a Vacuubrand MD1 diaphragm pump. The instrument design has been described in detail by Bertram et al. (2011). Fig. 1 shows a schematic of the HR-ToF-CIMS. HO_2 are measured by introducing 2 sLPM of sample into the ion-molecule reaction region through a 0.5 mm orifice and mixed with Br^- reagent produced by passing 10 sccm of a 0.2% CF_3Br/N_2 mixture carried by ~2 sLPM N_2 gas through a cylindrical 10 mCi Po-210 alpha radiation source. HO_2 present in the sample cluster with Br^- to form $Br^-(HO_2)$ adducts which are transmitted by a series of ion optics and speciated by the time-of-flight spectrometer. The isotopic abundance of bromine is such that the adduct is detected at two nominal mass-to-charge ratios, *m/z* 112 and *m/z* 114 corresponding to the Br^{79} and Br^{81} isotopes, respectively. The adducts have fractional mass-to-charge ratios of 111.9165 and 113.9144 Th. In order to demonstrate the generalizability of the technique to instruments with unit mass resolution, only the integrated peak data is used in this paper, though the high resolution capabilities were exploited to diagnose and address possible artifacts during the method development. The high resolution mass spectra are also used to unambiguously identify the $BrHO_2^-$ adducts.

3. Laboratory characterizations and reagent ion selection

Prior to the selection of Br^- for our ionization scheme, a number of negative reagent ions were evaluated for their ability to detect HO_2. The reagent ions attempted included O_2^-, SF_6^-, Cl^-, and I^-. Because of their low electron affinities, O_2^- and SF_6^- were utilized in an attempt to produce the HO_2^- ion directly via charge exchange. However, HO_2^- was not observed in laboratory characterization experiments. It is likely that the HO_2^- ion was formed but was not detected due to its low electron affinity (Ramond et al., 2002), which results in high reactivity. The SF_6^- ionization did yield a cluster at mass-to-charge 52, which was assigned as HO_2F^- in the high resolution mass spectrum. However, the signal was not quantitatively reproducible and did not remain constant for a given HO_2 concentration. Additionally, the form of the cluster is more likely to be $O_2^-(HF)$ than $F^-(HO_2)$ (Seeley et al., 1996), which may compromise the selectivity of the measurement, as O_2^- ions are not uniquely formed from the ionization of HO_2.

Chloride and Iodide reagent ions were generated from HCl and CH_3I mixtures, respectively. The $Cl^-(HO_2)$ cluster was not observed. The characterizations involving chloride reagent ions in the laboratory were conducted using the quadrupole CIMS. Unlike the other ions, which were evaluated the the HR-ToF-CIMS as well as the quadrupole CIMS, Cl^- was not revisited with the HR-ToF-CIMS instrument.

The I^- reagent ion, which has been used extensively to measure both organic and inorganic species (Huey et al., 1995;Slusher et al., 2004;Lee et al., 2014;Woodward-Massey et al., 2014;Brophy and Farmer, 2015;Faxon et al., 2015;Nah et al., 2016;Lee et al., 2016), was found to cluster with HO_2, appearing at mass-to-charge 160, consistent with observations by Veres et al. (2015). However, we observed that additions of NO_2 (Scott-Marrin, 100 ppm v/v N_2) to a clean N_2 gas matrix resulted in an increase of 1 cps per ppb NO_2 per 10^6 cps I^- in the *m/z* 160 signal. A 20 ppb addition results in a 20 cps increase in the *m/z* 160 signal, equivalent to ~4 ppt of HO_2. The addition of NO_2 showed in increase in a peak (*m/z* 159.992) not associated with HO_2 that we could not identify. The addition of NO_2 did not affect the high resolution $I^-(HO_2)$ signal but is expected to be a significant artifact for instruments lacking sufficient resolving power. We suspect that some of the behavior exhibited in the I^- system may be due to the formation of methyl peroxy radicals (CH_3O_2), which result as a side product of the electron capture of CH_3I. To attempt to resolve this issue, a CF_3I mixture was prepared and used as an I^- source to avoid the production of CH_3O_2. However, strong clustering of I^- with CF_3I suppressed iodide ion abundance which prevented the formation of the $I^-(HO_2)$ product ion.

Unlike the other reagent ions, the Br^- ionization scheme was found to be sensitive to HO_2, the measurements were reproducible, and there were no observed positive artifacts, making this an ideal scheme for measurements of HO_2. To evaluate potential positive artifacts as observed using iodide, NO_2 was added to N_2 gas sample and measured using the bromide reagent, but no increase in the $BrHO_2^-$ (nominal *m/z* 112 and *m/z* 114) signals was observed. Parts per million mixing ratios of ozone were also introduced into the inlet in a clean N_2 matrix but did not cause any changes in the $Br^-(HO_2)$ cluster signal. While Br^- has the disadvantage of having a ~50% natural isotopic abundance with nominal *m/z* 79 and 81, HO_2 calibrations performed as described in Sect. 4 showed similar absolute sensitivities for the $I^-(HO_2)$ and $^{79}Br^-(HO_2)$ clusters using I^- and Br^- reagents, respectively. A synthesized mixture containing primarily ^{79}Br could nearly double the sensitivity at the *m/z* 112 cluster if necessary, giving Br^- an inherent advantage over I^- with respect to sensitivity. The $^{79}Br^-(HO_2)$ cluster was used preferentially over the $^{81}Br^-(HO_2)$ cluster for ambient data because *m/z* 114 has a contribution from the isotope of a large *m/z* 113 CF_3COO^- signal which arises from impurities in PFA Teflon. Iodide ionization was attempted once more during ambient sampling, which will be discussed in Sect 5.2.

4. HO_2 Calibrations

HO_2 calibrations were conducted by water photolysis at 184.9 nm using a mercury UV lamp as previously described by a number of studies e.g. (Tanner et al., 1997;Holland et al., 2003;Smith et al., 2006;Dusanter et al. 2008). Humidified and dry zero air gas streams from a pure air generator (AADCO 747-14) were mixed to vary the relative humidity of the gas. The gas stream was introduced through a square flow tube (15.6 x 15.6 x 520 mm) and exposed to UV radiation through a small slit. HO_2 concentrations were calculated using Eq. (1),

$$[HO_2]=q\varphi\sigma[H_2O]\tau, \tag{1}$$

where q, ϕ, σ, and τ represent the quantum yield, UV lamp photon flux at 184.9 nm, water absorption cross-section, and irradiation time, respectively. The quantum yield was assumed to be unity and a value of 7.22 x 10^{-20} cm^2 was used for the water absorption cross section (Creasey, 2000). The lamp photon flux was measured using a Hamamatsu Phototube (Hamamatsu Photonics), and found to be 2.6 x 10^{13} photons cm^{-2} s^{-1}. A bandpass filter (HORIBA Scientific) was used to selectively transmit at 185 nm. The dew point of the gas was measured using a LICOR LI-840A CO_2/H_2O gas analyzer. The irradiation time was calculated based on the flow velocity which was measured using a Dwyer pitot tube and magnehelic. The time after irradiation before introduction into the instrument was minimized (t~60 ms) to avoid additional HO_2 generation from reaction of OH with trace CO present in the N_2 gas. It was calculated that less than 8% of the OH formed would react with CO to produce additional HO_2 assuming a CO concentration of 500 ppb. The HO_2 concentrations were kept low to calibrate for atmospherically relevant ranges and avoid non-linearity in the calibration curve due to depletion of HO_2 through HO_2 radical-radical recombination. At the HO_2 mixing ratios employed, less than 1% of HO_2 are estimated to be lost to recombination.

Fig. 2 shows the HO_2 calibration curve for *m/z* 112. The curve is linear with a slope of 4.95±1.00 which represents the sensitivity in Hz/ppt for a $^{79}Br^-$ ion count of 10^6 cps. An intercept of 27±5 is observed for the calibration which is not explained by errors in any of the parameters used to calculate the expected HO_2 concentrations in Eqn. 1. Instead, there appears to be a constant HO_2 photolytic source independent of water photolysis. The unidentified source requires the presence of water vapor but does not scale with the absolute water vapor mixing ratio. The magnitude of the HO_2 formation from this unknown source scales linearly with the UV lamp flux. The intercept does not affect the sensitivity and is not used to calculate the HO_2 mixing ratio. The uncertainty in the sensitivity is derived from the combined uncertainties of the parameters used in Eq. 1, resulting in a 1σ uncertainty of 20%.

5. Ambient Measurements

To demonstrate the applicability of the Br^- ionization scheme to ambient HO_2 measurements, a field study was conducted in June, 2015 (6/9/2015-6/25/2015) in Atlanta at an urban background site located on the roof (30-40 m above ground) of the Ford Environmental Science & Technology building on the Georgia Tech campus, which has been used for previous ambient studies (Hennigan et al., 2008;Xu et al., 2015a;Xu et al., 2015b). The site is about 840 m west of Interstate-75/85 and is therefore affected by traffic emissions. The instrument was located outside in an enclosure, allowing a short inlet of approximately five inches to avoid HO_2 losses on the walls of the sample tubing. Data was collected at a 1 Hz frequency and averaged to 1 minute data points. A solenoid valve was used to perform periodic additions of 4 ppm NO (Scott-Marrin) into the sample stream every 10 minutes on a 10% duty cycle to obtain the measurement background. The signal response to the NO addition is immediate and very short periods of time (<20 s) are required, though longer baseline periods were used here for ease of data analysis. The *m/z* 112 signal was normalized to a $^{79}Br^-$ count of 10^6 cps to account for temporal changes in reagent ion abundance.

Various co-located instruments were deployed for simultaneous measurements of O_3, NO, NO_2, and HNO_4. NO concentrations were measured using a Teledyne 200EU chemiluminescence monitor while NO_2 was measured by a Cavity Attenuated Phase Shift NO_2 monitor (Aerodyne Research, Inc.). Ozone was measured using a Teledyne Model T400 UV absorption analyzer. Pernitric acid (HNO_4), formed from the reaction of HO_2 with NO_2 was also monitored using a house-built Quadrupole Chemical Ionization Mass Spectrometer (Q-CIMS) with an Iodide-adduct ionization scheme and observed at *m/z* 206. A similar configuration of the instrument has been described previously by Slusher et al. (2004). Previous measurements of HNO_4 using I^- have been conducted by Veres et al. (2015). Meteorological data, including temperature, humidity, and solar UV radiation were recorded using a Vantage Pro2 weather station.

5.1 Bromide-CIMS measurements of HO_2

Fig. 3 shows the diurnal profile of HO_2, as well as the diurnals of the UV radiation intensity, NO and O_3 concentrations. The difference in the time between peak actinic flux and peak HO_2 concentration is due to the suppression of HO_2 by the presence of NO from morning-time traffic emissions. The HO_2 rises once the NO concentration is sufficiently low and peaks between 1 and 3 p.m. with a mixing ratio of ~7 ppt, comparable to previous studies in other urban areas (Emmerson et al., 2005;Kanaya et al., 2007;Dusanter et al., 2009). The 3σ limit of detection was calculated to be 0.7 ppt for a 1 minute integration time based on laboratory calibrations and baselines observed during ambient sampling, which is sufficiently low for atmospherically important HO_2 concentrations. The slow decay of HO_2 may partially be explained by HO_2 production from oxidation of biogenic volatile organic compounds (BVOCs), which are abundant in the Southeast United States (Geron et al., 2000;Guenther et al., 2006), as well as a decrease in boundary layer height However, additional measurements would be required to constrain sources and sinks.

HNO_4 and NO_2 measurements were used to calculate an inferred HO_2 concentration for comparison with the measured HO_2 concentrations. The HNO_4 and HO_2 are assumed to be in thermal equilibrium for the calculation. The assumption is expected to be valid in Atlanta due to significant NO_2 concentrations (6-29 ppb). Their respective diurnal profiles are shown in

Fig. 4. The measurements agree well qualitatively. However, during the measurement period, the HO_2 mixing ratio calculated based on HNO_4 measurements was consistently higher than the measured HO_2 by a factor of 5. This is likely due to a combination of factors, including a positive bias in the HNO_4 measurement and uncertainties associated with the HO_2 sensitivity during ambient sampling. The sensitivity of the direct HO_2 measurement was determined in the laboratory and online calibrations were not conducted. It is possible that the sensitivity during ambient measurements was lower due to specific sampling conditions. In particular, the instrument experienced temperature fluctuations between 20 and 40°C. We performed laboratory experiments to evaluate the effect of temperature on instrument sensitivity and found a 20% decrease in sensitivity at 40°C as compared to the sensitivity at 20°C. Furthermore, environmental conditions resulted in corrosion of the critical orifice on the HR-ToF-CIMS, which lowered the sample flow by 35%. The sensitivity was not corrected for the lower sample flow as the time at which the sample flow decreased was not known with certainty. A detailed comparison of HO_2 inferred from HNO_4 and HO_2 directly measured by the Br^- ionization warrants future investigation, considering both methods are currently under development. Nevertheless, the good qualitative agreement observed between both methods, as well as the consistency of the measured HO_2 diurnal profile with expectation demonstrates that Br^- chemical ionization is a promising technique for ambient HO_2 measurements.

A final but important observation during our ambient measurements was that the measurement background differed between different backgrounding methods. We compared the measurement backgrounds obtained using two backgrounding methods: NO chemical titration by standard NO additions, and physical scrubbing using a metal wool scrubber. The NO titration of HO_2 resulted in lower background signals than physical scrubbing. Furthermore, additions of NO to the sample air after physical scrubbing further decreased the HO_2 signal. This suggests that there is internal HO_2 generation within the instrument. Laboratory characterizations were conducted to explore the discrepancy. In the laboratory, adding NO to a clean N_2 sample matrix also decreased the observed HO_2 background signal. The differences in HO_2 backgrounds observed between the different backgrounding methods and NO additions to N_2 gas were similar, representing ~4 ppt of HO_2 generated inside the instrument. The HO_2 is likely produced from ion-molecule reactions of trace gases in the N_2 used for ion generation. The measured HO_2 profiles in Fig. 3 and Fig. 4 have already been corrected by subtraction of internal HO_2 generation.

5.2 Iodide-CIMS measurements of HO_2

Despite artifacts observed in the measurements of laboratory-generated HO_2, iodide ionization measurements were conducted during a short ambient sampling period (07/25/2015 6:00 P.M. to 7/27/2015 10:00 A.M.) to assess its viability in a real air matrix for the measurement of HO_2. We observed that the measured $I^-(HO_2)$ signals were not consistent with the expected behavior of HO_2. The time series did not show a clear diurnal, nor was the signal effectively suppressed by NO additions. During noon-time, NO additions had no effect on *m/z* 160, and caused it to increase during other times of the day. The high resolution capability of the HR-ToF-CIMS allowed for the peak assignment of $I^-(HO_2)$ with high accuracy but the time-series of the high resolution peak displayed a similar behavior to that of the low resolution data. Additionally, a peak (*m/z* 159.9989 Th) which may pertain to the NO_2 related artifact observed during earlier laboratory characterizations is present (Fig. 5). Because the sampling period was short, the possibility of using iodide for HO_2 measurements may warrant further exploration. However, our laboratory and ambient measurements suggest that for iodide to be viable, high resolution capability will be necessary for accurate measurements due to artifacts caused by the presence of NO_2. This is not the case for Br^-. Fig. 5 shows the mass spectra of Br^- and I^- at the mass-to-charge ratios where the HO_2 clusters are observed. The Br^- spectrum shows that the $BrHO_2^-$ cluster is the dominant species at *m/z* 112. The minor peak observed is always present and does not vary significantly over the course of the day. Furthermore, the peak does not respond to NO additions, making NO backgrounds effective at eliminating any contribution to the signal from this peak. Thus, the measurement of HO_2 with Br^- does not require high resolution capability.

6. Conclusions and Future Work

HO_2 are important contributors to photo-chemical schemes in the atmosphere. In this work, we investigated the feasibility of a direct chemical ionization measurement of HO_2. We evaluated a number of negative reagent ions (O_2^-, SF_6^-, Cl^-, I^-, Br^-) using a HR-ToF-CIMS and found that detection of HO_2 using charge exchange ionization will not be feasible in the real atmosphere. However, associative ionization of HO_2 via clustering was found to be a promising mechanism for the direct measurement of atmospheric HO_2. Among the reagent ions evaluated, Br^- was found to be the best candidate for the measurement of HO_2, providing improved selectivity over I^-. The HO_2 sensitivities as measured at *m/z* 160 and *m/z* 112 using iodide and bromide, respectively, were found to be similar, giving Br^- an inherent advantage in sensitivity, as an isotopically pure $CF_3{}^{79}Br$ mixture should nearly double the sensitivity at *m/z* 112. Using Br^- also allows for the measurement of HO_2 at a lower *m/z* which decreases the likelihood of measurement interferences.

Ambient measurements were conducted in Atlanta in June 2015 to demonstrate the performance and capability of the instrument. The sensitivity using Br^- (4.95±1.00 Hz/ppt per 10^6 ^{79}Br ion counts) was sufficient for ground-based measurements as the observed baselines were relatively low. Furthermore, the absolute sensitivity for HO_2 may also be significantly improved by using a radioactive source with higher activity, provided that measures are taken to suppress the increased background due to internal HO_2 generation. The measured HO_2 diurnal behaves in a manner consistent with the associated NO_x and HNO_4 measurements, though there exist no previous measurements for HO_2 in Atlanta available for a more quantitative comparison. Future work will focus on optimizing the instrument sensitivity to HO_2, conducting instrument intercomparisons, and further exploring Br^- ionization for the measurement of other atmospherically important species.

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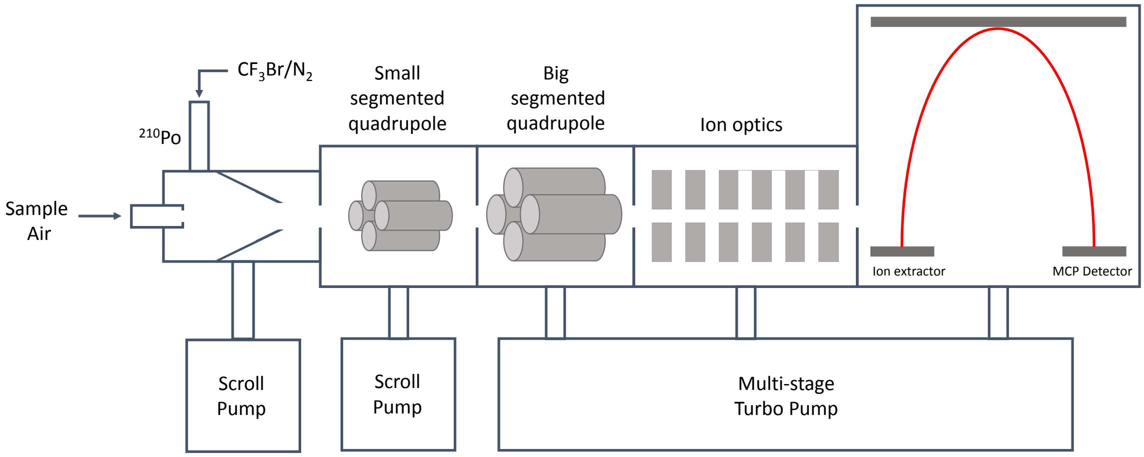

Figure 1: Schematic of the High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer. Sample air enters the flow tube through a 0.5 mm orifice where it is ionized. Collision dissociation occurs in the small segmented quadrupole. Products ions are transferred through the big segmented quadrupole and a series of ion lenses to the time-of-flight analyzer.

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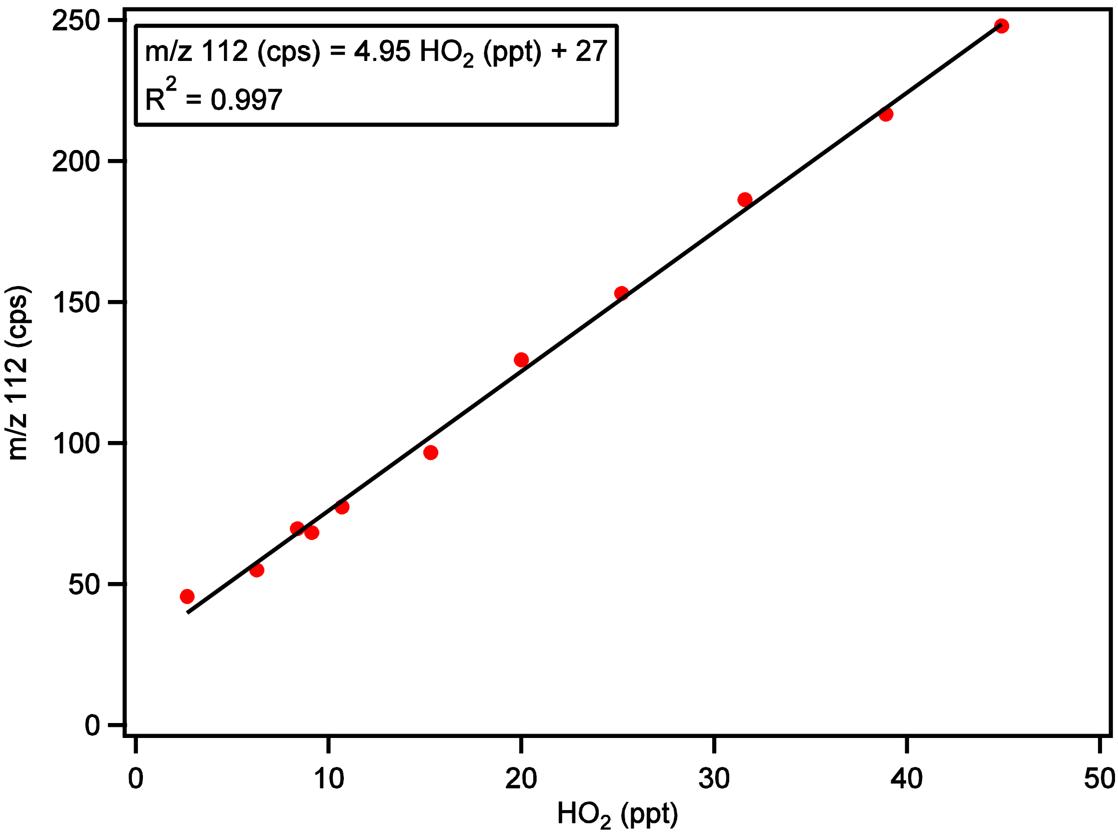

Figure 2: HO_2 calibration curve for the $^{79}BrHO_2^-$ cluster as observed at nominal *m/z* 112. The slope represents the sensitivity in Hz/ppt. HO_2 mixing ratios are calculated using Eqn. 1. The error associated with the sensitivity is 20% which arises from the combined uncertainty of the calibration parameters (Eqn. 1).

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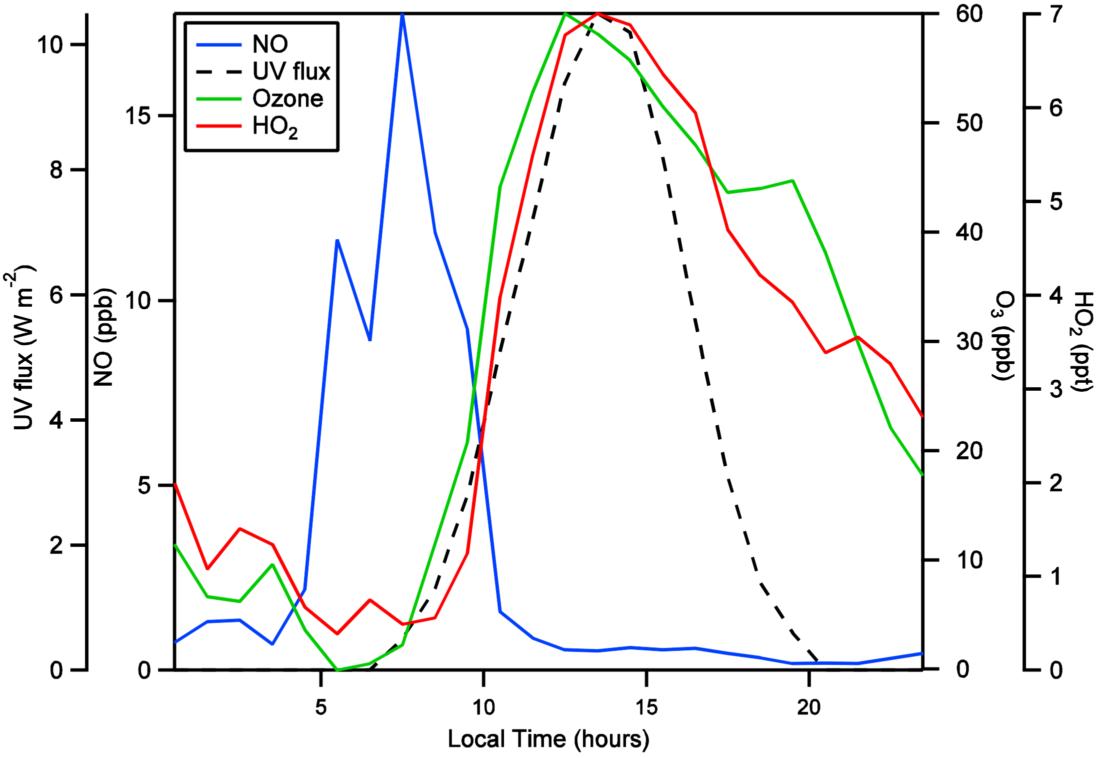

Figure 3: Diurnal profiles of HO_2, NO, O_3 and UV flux in Atlanta, June 15th – June 18th, 2015.

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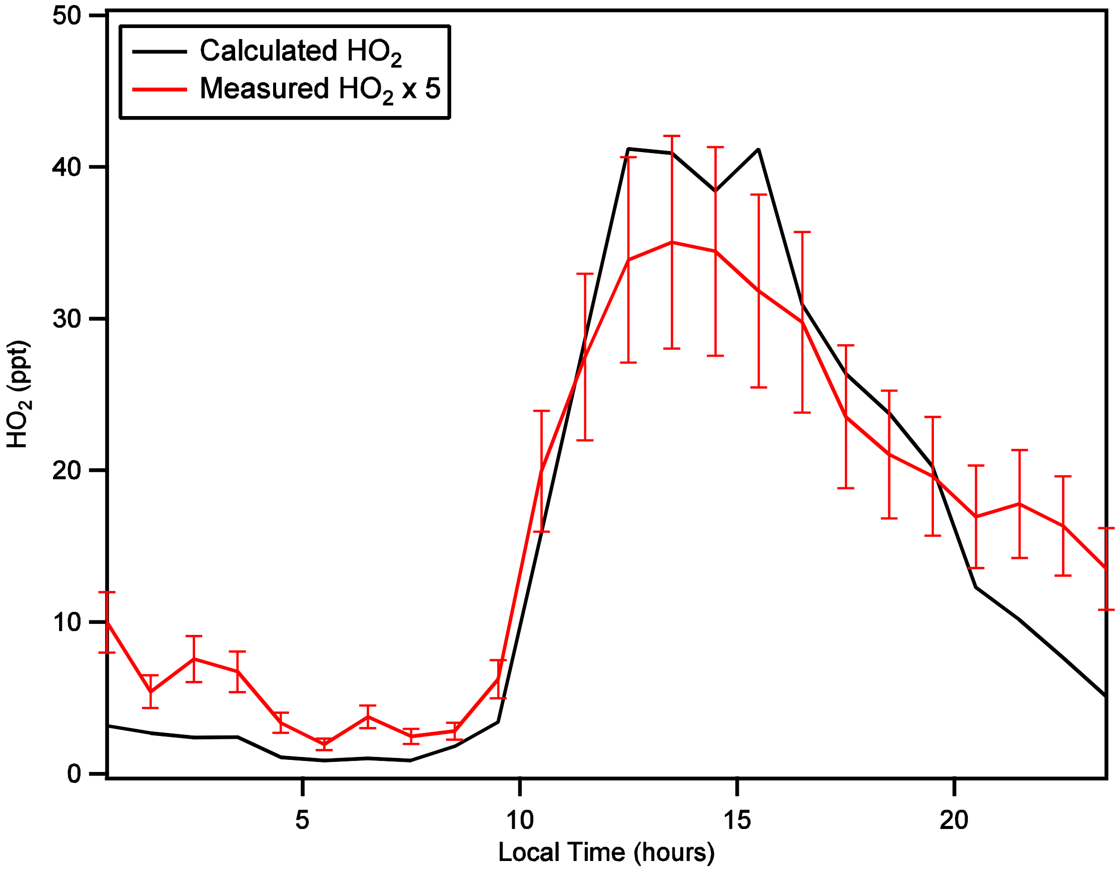

Figure 4: Comparison of HO_2 diurnal profiles (6/15/2015 to 6/18/2015) for measured HO_2 and HO_2 calculated assuming an equilibrium between HO_2 and HNO_4. The measured HO_2 signal has been corrected by subtracting the contribution from internal generation of HO_2.

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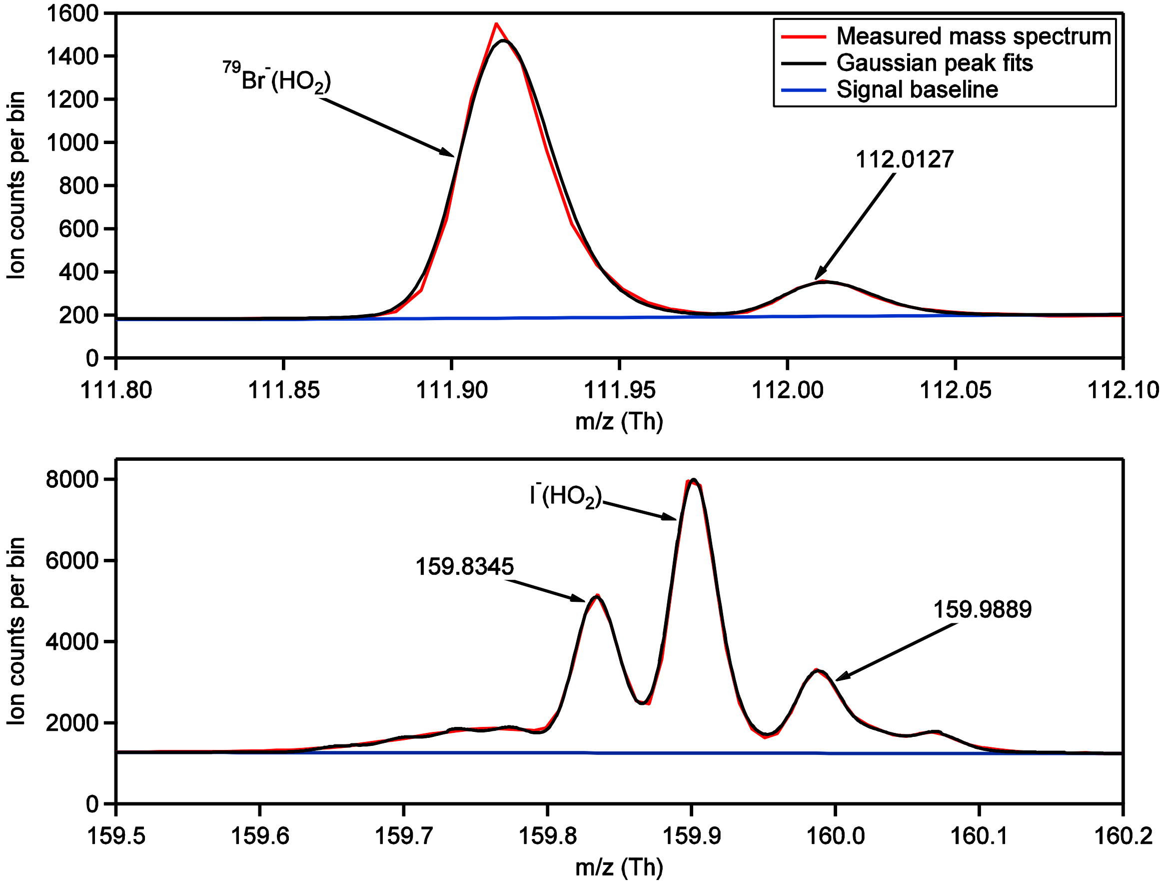

Figure 5: High resolution mass spectra of nominal m/z 112 for the Br^- ionization of HO_2 (top) and m/z 160 for the I^- ionization of HO_2 (bottom).