A new technique for the direct detection of HO₂ radicals using bromide chemical ionization mass spectrometry (Br-CIMS): initial characterization

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Abstract. Hydroperoxy radicals (HO₂) play an important role in tropospheric photochemistry. 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). HO₂ is a reservoir species for OH, the primary daytime oxidant, and facilitates the photochemical production of ozone via its reaction with NO. Additionally, the relative abundance of HO₂ to NOₓ plays a critical role in the fate of peroxy radicals (RO₂) and the production of low-volatility products in secondary organic aerosol (SOA) formation (Orlando and Atkinson, 2012). For instance, reactions of HO₂ with RO₂ serve as the main source of atmospheric organic hydroperoxides, which are important constituents of SOA (Docherty et al., 2005).

HO₂ is also critical for the evaluation of model photochemical schemes. Because HO₂ is short lived (Heard and Pilling, 2003), HO₂ measurements allow for evaluation of model photochemistry with the exclusion of confounding phenomena, such as atmospheric transport. However, accurate measurements have proven difficult due to the naturally low abundance of HO₂. HO₂ also possess weak spectral lines, which has posed challenges for spectroscopic techniques. Nevertheless, some spectroscopic measurements have been made, primarily in the laboratory. Radford et al. (1974) employed laser magnetic resonance (LMR) spec-
troscopy in the laboratory to measure HO$_2$ while Mihelcic et al. (1985, 2003) used matrix isolation electron spin resonance (MIESR). The latter requires HO$_2$ to be collected for a period of 30 min on a D$_2$O matrix at 77 K before detection. Both techniques directly measure HO$_2$ but their applicability to atmospheric observations is limited, due to either instrument needs or low time resolution.

More recent methods such as peroxy radical chemical amplification (PERCA) (Cantrrell and Stedman, 1982; Cantrrell et al., 1984; Liu et al., 2009; Horstjann et al., 2014), chemical ionization mass spectrometry (CIMS) (Hanke et al., 2002; Edwards et al., 2003; Hornbrook et al., 2011; Kim et al., 2013; Wolfe et al., 2014), and laser induced fluorescence (LIF) (Stevens et al., 1994; Brune et al., 1995; Griffith et al., 2013; Walker et al., 2015) provide lower detection limits at high temporal resolution. However, these techniques do not measure HO$_2$ directly. Instead, the aforementioned techniques require that HO$_2$ be titrated with NO, which may introduce additional complexity, primarily from reactions of NO with RO$_2$. The PERCA technique, for example, exploits the 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. The production of NO$_2$ molecules is proportional to the contact time between the added reagents and the sample gas. Because multiple NO$_2$ molecules are produced from each HO$_2$, the signal is effectively amplified. The NO$_2$ has then traditionally been detected using luminol, though some recent measurements employ cavity ring-down spectroscopy (Liu et al., 2009; Horstjann et al., 2014). If organic peroxy radicals are present, the addition of NO to the sample gas results in additional production of HO$_2$; therefore the technique allows for the measurement of HO$_2$ + RO$_2$. As of yet, speciation of HO$_2$ from other peroxy radicals has not been successful, though previous attempts have been made (Miyazaki et al., 2010).

Chemical ionization techniques such as RO$_2$ Chemical Conversion/CIMS (ROxMAMS) (Hanke et al., 2002) and Peroxy radical CIMS (PerCIMS) (Edwards et al., 2003; Hornbrook et al., 2011; Kim et al., 2013; Wolfe et al., 2014) also rely on addition of NO to the sample gas. The OH produced from HO$_2$ titration subsequently reacts with SO$_2$ which is added to the inlet to produce H$_2$SO$_4$. The H$_2$SO$_4$ is then ionized by nitrate ions (NO$_3^-$) to produce a stable HSO$_4^-$ product ion for detection. Because NO is added, PerCIMS suffers from positive artifacts from the contribution of the RO$_2$ + NO reaction to the measured HO$_2$ concentration. Previous attempts to limit the contribution of the RO$_2$ + NO reaction have been made. For example, 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 the conversion of some peroxy radicals to ~ 15%. However, the effectiveness of the oxygen dilution modulation scheme depends largely on the chemical structure of the hydrocarbons in the sample. Unsaturated hydrocarbons, such as isoprene, have additional pathways to the formation of HO$_2$ which are not suppressed by the oxygen dilution modulation scheme.

Unlike CIMS techniques and chemical amplification, the laser induced fluorescence technique does not require multiple conversion steps. It only requires the titration of HO$_2$ to OH, which is subsequently detected using laser excitation at 308 nm. The relative simplicity of the technique allows for more effective control of reaction time, which can be used to minimize RO$_2$ + NO reactions. Nevertheless, LIF instruments have previously been shown to be susceptible to similar artifacts, with magnitudes dependent on the effective reaction time allowed after NO addition before detection and on peroxy radical precursor composition of the sample gas (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, a direct fast time resolution measurement of HO$_2$ would benefit efforts aiming to measure and model HO$_2$ in order 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 measured to modeled HO$_2$ ratios are highly variable (Stone et al., 2012). In this work, we evaluated the potential of various chemical ionization schemes and propose the Br$^-$ ionization of HO$_2$ to form a Br$^-$(HO$_2$) adduct as a direct method for 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 instrument performance. Important measurement considerations and future improvements are also discussed.

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 HR-ToF-CIMS consists of an atmospheric pressure interface with five differentially pumped stages, utilizing two scroll pumps and a multi-stage turbomolecular pump. The instrument design has been described in detail by Bertram et al. (2011). Figure 1 shows a schematic diagram of the HR-ToF-CIMS. HO$_2$ is measured by introducing 2 standard L min$^{-1}$ of sample into the ion–molecule reaction region through a 0.5 mm orifice and mixed with Br$^-$ reagent produced by passing 10 scm of a 0.2 % CF$_3$Br / N$_2$ mixture carried by ~ 2 standard L min$^{-1}$ N$_2$ gas (99.999 %, Airgas) through a cylindrical 10 mCi $^{210}$Po alpha radiation source. The ion–molecule reaction region (IMR) has a residence time of 0.07 s and is operated at a pressure of 100 mbar. The contents of the IMR were sub-sampled through a 0.3 mm critical orifice leading to the instrument’s ion optics. HO$_2$ present...
3 HO$_2$ generation and calibration procedure

HO$_2$ were generated for the evaluation of chemical ionization schemes and instrument calibrations 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). Air was humidified by passing the gas stream through glass bubblers and diluted in dry air from a pure air generator (AADCO 747-14) to vary the relative humidity of the gas. The gas stream was then introduced into a black anodized aluminum square flow tube (15.6 mm × 15.6 mm × 520 mm) and exposed to UV radiation through a small slit. HO$_2$ concentrations were calculated using Eq. (1),

$$\Delta[H_2O] = \phi \sigma I [H_2O] \Delta t,$$

where $\phi$, $\sigma$, $I$, and $\Delta t$ represent the quantum yield, water absorption cross-section, UV lamp photon flux at 184.9 nm, and irradiation time, respectively. The quantum yield was assumed to be unity and a value of $7.22 \times 10^{-20}$ cm$^2$ was used for the water absorption cross section (Creasey et al., 2000). The lamp photon flux was measured using a Hamamatsu Phototube (Hamamatsu Photonics), and found to be $2.6 \times 10^{13}$ 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$_2$O gas analyzer. The irradiation time was calculated based on the flow velocity which was measured using a Dwyer pitot tube and a magnehelic pressure sensor. Flow velocities varied between 400 and 800 cm s$^{-1}$ ($Re > 4000$) to promote plug flow conditions. The slit allowing light into the tube was located such that the distance before irradiation after entry into the tube was 10 times the hydraulic diameter, allowing the flow profile to fully develop before exposure to UV light. Plug flow conditions were confirmed by measuring the flow velocity both at the center line and near the wall of the tube, showing no measurable differences. The water vapor mixing ratios varied between 0.66 and 8.20 ppt. The time after irradiation before introduction into the instrument was minimized ($\tau \sim 60 \text{ ms}$) to avoid additional HO$_2$ generation from OH oxidation of 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. Addition of 40 ppm of C$_3$F$_6$ as an OH scavenger had no effect on the HO$_2$ signal intensity, confirming the lack of contribution from OH oxidation to HO$_2$ production. The HO$_2$ concentration was kept low (2–45 ppt) to calibrate for the HO$_2$ levels observed during ambient sampling and to avoid non-linearity in the calibration curve due to depletion of HO$_2$ through HO$_2$ radical-radical recombi-
nation. At the HO$_2$ mixing ratios employed, less than 1 % of HO$_2$ are estimated to be lost to recombination. The overall calibration uncertainty is 18 % (1σ). The contribution of the different parameters to the overall uncertainty is given in Table S1 in the Supplement. A conservative estimate of 20 % is used in this work.

4 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$_2$. HO$_2$ were generated using the procedure in Sect. 3. HO$_2$ mixing ratios were typically in excess of 300 ppt for initial reagent ion evaluation, and varied by varying the gas humidity and velocity. NO was added in excess (2–4 ppm) to obtain the instrument background. NO was also added in small concentrations and in increasing increments to roughly test the kinetics suggested by the HO$_2$ signal response to additions of varying concentrations of NO, as additional confirmation that the analyte being observed corresponded to HO$_2$. Tests were conducted primarily at room temperature (293 K). The humidity of the gas stream was determined by the amount of water vapor added to produce HO$_2$. No additional sources of water vapor were present, nor was water directly added to the IMR. The reagent ions evaluated 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 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$_2$F$^-$ 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$_2$F$^-$ (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$_3$I mixtures, respectively. Full mass spectra obtained using the quadrupole CIMS identified Cl$^-$ (HCl), Cl$^-$ (HNO$_2$), and Cl$^-$ (CF$_3$COOH) as prominent ions. However, the Cl$^-$ (HNO$_2$) 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 with 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 addition 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 m/z 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 an increase in a peak (m/z 159.9896) not associated with HO$_2$ that we could not identify. The addition of NO$_2$ did not affect the high-resolution I$^-(\text{HO}_2)$ signal but is expected to be a significant artifact for instruments of low resolving power.

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 from NO$_2$ or O$_3$, making this an ideal scheme for measurements of HO$_2$. To evaluate potential positive artifacts as observed using iodide, NO$_2$ was added to the N$_2$ gas sample and measured using the bromide reagent, but no increase in the Br$^-$ (HO$_2$) (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$^-$ a potential 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$_3$COO$^-$ signal which arise from impurities in PFA Teflon™. Iodide ionization was attempted once more during ambient sampling, which will be discussed in Sect. 5.3.

Br$^-$ ionization: sensitivity, selectivity, humidity, and temperature dependence

The instrument sensitivity using Br$^-$ reagent was calibrated following the procedure in Sect. 3. Figure 2 shows HO$_2$ calibration curves for $^{79}$Br$^-$ (HO$_2$) at m/z 112. The figure shows two separate calibrations performed on two different occasions to illustrate reproducibility. The curves are linear with slopes of 4.95 ± 1.00 and 5.26 ± 1.05 which represent the instrument sensitivity in cps ppt$^{-1}$ for a $^{79}$Br$^-$ ion count of 10$^6$ cps. Intercepts of 27 ± 5 and 30 ± 3 are observed for the calibration curves which are not explained by errors in any of the parameters used to calculate the expected HO$_2$ concentrations in Eq. (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
possibility of other potential artifacts. Large concentrations of NO were added, which did not elicit a response. Hydrogen peroxide and formaldehyde were sampled with the instrument to assess the signal response is due to ion–molecule reaction with Br$^-$ or unidentified wall reactions within the experimental chamber. Regardless, these responses are insignificant under most atmospheric and laboratory experimental conditions. Furthermore, if the resulting signal increase is due to reactions inside the IMR, the contribution of these species can be removed from the measurement by obtaining appropriate instrument backgrounds, such as by using additions of NO. Such additions would remove HO$_2$ in the sample, but not remove H$_2$O$_2$ or HCHO. The small contributions to the signal at m/z 112 would be present in the background and therefore removed from the measurement.

Another important consideration for this technique is the effect of temperature and humidity on cluster stability, which was explored during laboratory characterizations. The effect of varying water vapor mixing ratios in the sample gas on sensitivity is shown in Fig. 3. At relative humidities in the sample below 10%, the sensitivity appears to have a strong, negative water dependence. However, when the humidity in the sample gas is higher than 10%, the sensitivity is invariant with increasing relative humidity, which simplifies ambient sampling, as no humidity-dependent correction is required. The temperature dependence was also explored, where an IMR temperature increase from 20 to 40°C resulted in a 20% decrease in instrument sensitivity. The relatively strong negative temperature dependence suggests that Br$^-$(HO$_2$) is a weak cluster. This highlights the importance of temperature control and performing calibrations at the sampling temperature.

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 (9–25 June 2015) in Atlanta at an urban 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, b). The
Figure 4. Hourly median diurnal profiles of HO$_2$, NO, O$_3$ and UV index in Atlanta. The sampling period was during 9 June 2015 21:14:00 to 11 June 2015 13:28:00, and 15 June 2015 01:52:00 to 25 June 2015 01:32:00 LT.

5.1 Bromide-CIMS measurements of HO$_2$

Figure 4 shows the diurnal profiles of HO$_2$, as well as the diurnal profiles of the UV radiation index, NO, and O$_3$ concentrations. The difference in the time between peak actinic flux and peak HO$_2$ concentration is at least partially 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 2 and 3 p.m. with a mixing ratio of $\sim$ 5 ppt, comparable to previous studies in other urban regions (Emmerson et al., 2005; Kanaya et al., 2007; Dusanter et al., 2009). The 3$\sigma$ limit of detection was calculated to be 0.7 ppt for a 1 min 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$_2$ in early evening may partially be explained by non-photolytic HO$_2$ production, e.g., 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.

The mass spectrum for a 24 h period of ambient observations is shown in Fig. 5 and compared to a laboratory spectrum generated during HO$_2$ calibration. Few additional peaks are present in ambient spectrum, suggesting that Br$^-$ ionization is selective at the mass-to-charge values shown in the figure. Further, the majority of the additional peaks have signal intensities much lower than the intensity of the HO$_2$ signal at $m/z$ 112, which makes it unlikely that the species at the additional peaks and their respective isotopes will affect the signal at $m/z$ 112.

HNO$_3$ and NO$_2$ measurements were used to infer HO$_2$ concentration for comparison with the measured HO$_2$ concentrations. The HNO$_3$ and HO$_2$ are assumed to be in thermal equilibrium for the calculation. Details regarding the calculation are discussed in the Supplement. Their respective diurnal profiles are shown in Fig. S3. The profiles agree well temporally but not quantitatively, differing by a factor of 5 during the afternoon. A more complete discussion regarding the comparison is presented in the Supplement.

5.2 Instrument background determinations

Measurement backgrounds were conducted by the addition of NO to the sample gas, as mentioned previously. To evaluate the accuracy of the instrument background, a metal wool scrubber was utilized for comparison to the NO addition. The scrubber was first tested to ensure complete scrubbing of sample HO$_2$ by generation of additional HO$_2$ in ambient air with a mercury lamp. Though HO$_2$ was generated, none was observed when the scrubber was placed before the instrument, demonstrating that the scrubber was effectively removing all HO$_2$ in the sample gas.
It was observed that the two methods of obtaining the instrument background did not agree, with the NO addition providing a lower background signal than the metal wool scrubber. 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 $\sim$ 4 ppt of HO$_2$ generated inside the instrument. The similarity suggests that HO$_2$ generation is independent of sample composition. The HO$_2$ is likely produced from ion-molecule reactions of trace gases in the N$_2$ used for ion generation. The HO$_2$ mixing ratios were corrected by subtraction of an additional, constant 4 ppt contribution from internal HO$_2$ generation.

Based on the observations made in this work, future instrument backgrounds can be conducted in alternative ways to eliminate the need for post-correction. For example, a physical scrubber may be used as has been done here to avoid removal of internally generated HO$_2$ from the background signal. Alternatively, the NO addition concentration and contact time can be optimized such that the HO$_2$ + NO reaction is efficient in the sample line before the instrument, where the pressure is approximately atmospheric, but inefficient inside the IMR, where the pressure is at least a factor of 10 lower. The addition of NO under optimal conditions would then only titrate HO$_2$ efficiently in the sample line, but would not allow significant NO reaction with internally generated HO$_2$.

### 5.3 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 (25 July 2015 06:00 p.m. to 27 July 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 pattern, nor was the signal effectively suppressed by NO additions. Instead, NO additions caused $m/z$ 160 to increase. 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. The resolving power of the instrument during the sampling period was $\sim$ 3000 and the high-resolution time series of the major peaks at nominal $m/z$ 160 appear to be mostly independent of each other, which suggests that resolution is not a limiting factor. Additionally, a peak ($m/z$ 159.990 Th) which may pertain to the NO$_2$ related artifact observed during earlier laboratory characterizations was present (Fig. 6). 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\textsubscript{2}. This is not the case for Br\textsuperscript{−}. Figure 6 shows the mass spectra of Br\textsuperscript{−} and I\textsuperscript{−} at the mass-to-charge ratios where the HO\textsubscript{2} clusters are observed. The Br\textsuperscript{−} spectrum shows that the Br\textsuperscript{−}(HO\textsubscript{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\textsubscript{2} with Br\textsuperscript{−} does not require high-resolution capability.

6 Conclusions and future work

HO\textsubscript{2} is an important contributor to photochemistry in the atmosphere. In this work, we investigated the feasibility of a direct chemical ionization measurement of HO\textsubscript{2}. We evaluated a number of negative reagent ions (O\textsuperscript{2−}, SF\textsubscript{6}−, Cl\textsuperscript{−}, I\textsuperscript{−}, and Br\textsuperscript{−}) using a HR-ToF-CIMS and found that detection of HO\textsubscript{2} using charge exchange ionization is not feasible in the real atmosphere. However, ionization of HO\textsubscript{2} via clustering was found to be a promising mechanism for the direct measurement of atmospheric HO\textsubscript{2}. Among the reagent ions evaluated, Br\textsuperscript{−} was found to be the best candidate for the measurement of HO\textsubscript{2}, providing improved selectivity over I\textsuperscript{−}. The HO\textsubscript{2} sensitivities as measured at m/z 160 and m/z 112 using iodide and bromide, respectively, were found to be similar, giving Br\textsuperscript{−} a potential advantage in sensitivity, as an isotopically pure CF\textsubscript{3}I/Br mixture should nearly double the sensitivity at m/z 112. Using Br\textsuperscript{−} also allows for the measurement of HO\textsubscript{2} at a lower m/z which may decrease the likelihood of measurement interferences and reduce ambiguity in peak identification, as a smaller number of possible chemical formulas for ion products are possible. Furthermore, Br has a high electron affinity, which makes the production of small charged ions from ionization and collisional dissociation unlikely.

Ambient measurements were conducted in Atlanta in June 2015 to demonstrate the performance and capability of the instrument. The sensitivity using Br\textsuperscript{−} (5.1 ± 1.00 cps ppt\textsuperscript{−1} per 10\textsuperscript{6} 79Br ion counts) was sufficient for ground-based measurements as the observed baselines were relatively low. Furthermore, the absolute sensitivity for HO\textsubscript{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\textsubscript{2} generation. The measured HO\textsubscript{2} diurnal profile behaves in a manner consistent with the NO\textsubscript{3} and HNO\textsubscript{3} abundance, though there exist no previous measurements for HO\textsubscript{2} in Atlanta available for a more quantitative comparison. Future work will focus on optimizing the instrument sensitivity to HO\textsubscript{2}, conducting instrument intercomparisons, and further exploring Br\textsuperscript{−} ionization for the measurement of other atmospherically important species.

7 Data availability

The data presented in this paper are available upon request from the corresponding author.

The Supplement related to this article is available online at doi:10.5194/amt-9-3851-2016-supplement.

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