Supplement of Atmos. Meas. Tech., 9, 3851–3861, 2016
http://www.atmos-meas-tech.net/9/3851/2016/
doi:10.5194/amt-9-3851-2016-supplement

Supplement of

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

Javier Sanchez et al.

Correspondence to: Nga L. Ng (ng@chbe.gatech.edu)

Table S1: HO_2 measurement uncertainties for each parameter in the HO_2 calculation from Eq. 1. S_{HO2} refers to the HO_2 signal fluctuation in the CIMS using 1 minute time resolution data.

Parameter	**Uncertainty (1σ %)**
$\sigma_{\text{water,184.9 nm}}$	3
I	17
$[H_2O]$	1.5
Δt	3
S_{HO2}	3
Total calibration uncertainty	**18**

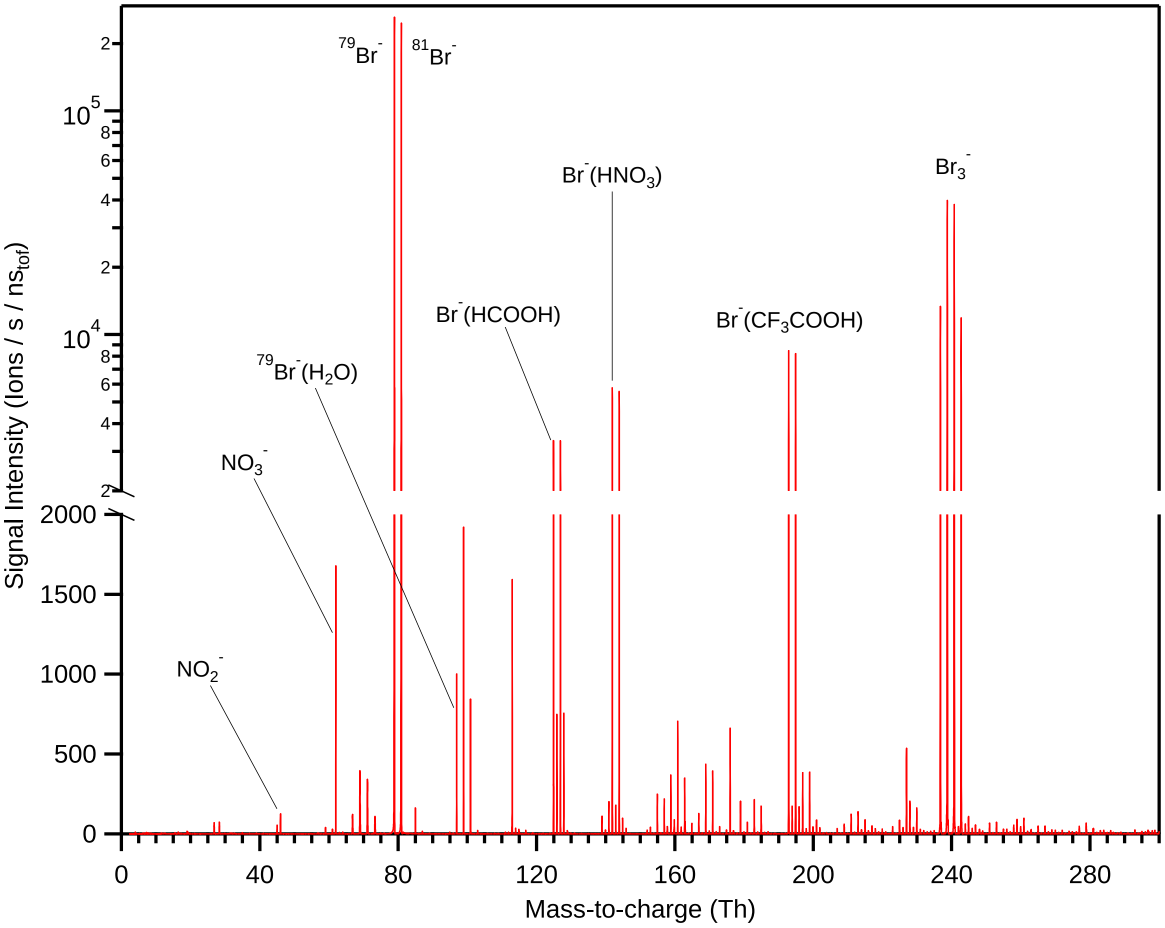

Figure S1: Full Br^- ionization mass spectrum up to *m/z* 300. Large, commonly detected peaks are labeled. The y-axis displays the signal intensity in ions/second normalized by time-of-flight of species. Integration over the time-of-flight axis is required to determine signal intensity.

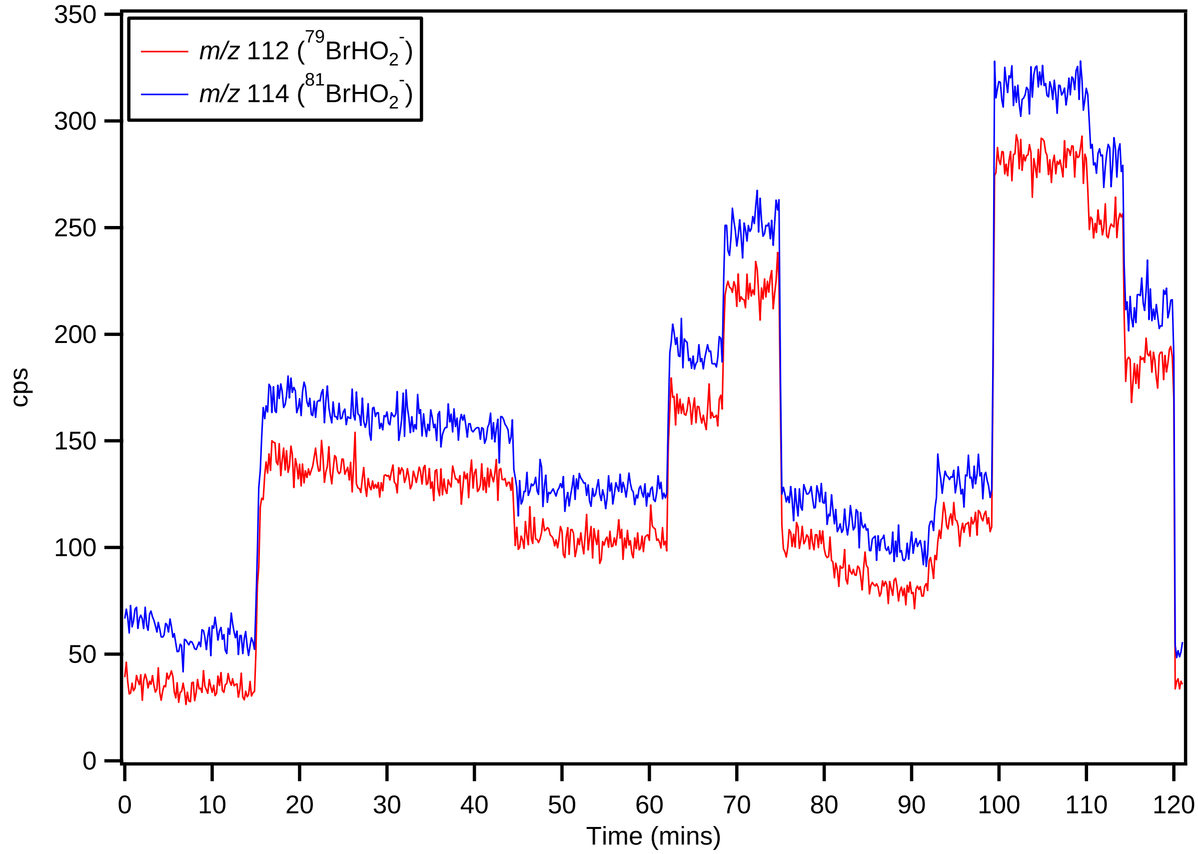

Figure S2: Time series of laboratory calibration of HO_2 at both mass-to-charges where HO_2 is observed. Points are averaged to 10 seconds to better display instrument response to changes in generated HO_2. At time zero, no HO_2 is being generated in the sample line. The mercury lamp is turned on at 15 minutes, resulting in an increase in signal. The small decrease in signal between 20 and 40 minutes is due to decreasing relative humidity in the sample line due to cooling in the bubbler from water evaporation. The lowest point above the background (~90 minutes) corresponds to 2.6 ppt of HO_2. The higher background associated with *m/z* 114 is due to contribution from the isotope of a trifluoroacetic acid (*m/z* 113) contamination associated with Teflon^{TM} tubing.

HNO_4 measurement calculation to infer HO_2 abundance and comparison with $Br^-(HO_2)$ measurements

During the ambient sampling period, HNO_4 measurements were made using a quadrupole CIMS with I^- reagent. The $I^-(HNO_4)$ cluster was measured at *m/z* 206. The HNO_4 background was obtained by passing the gas sample through a charcoal scrubber periodically. The HNO_4 was calibrated by passing a small flow of UHP (99.999%) N_2 through a U-tube containing a small amount of synthesized HNO_4. The gas was then diluted to obtain varying HNO_4 concentrations. HNO_4 was quantified by thermal decomposition to NO_2 and subsequent measurement using a Cavity Attenuated Phase-Shift NO_2 monitor (Aerodyne Inc.).

HO_2 concentrations were also inferred via HNO_4 and NO_2 measurements based on the equilibrium, $HO_2+NO_2 \leftarrow\rightarrow HNO_4$ (Eq. S1).

$$[\mathrm{HO_2}] = \frac{[\mathrm{HNO_4}]}{K(T)[\mathrm{NO_2}]}, \qquad \text{(S1)}$$

where the equilibrium constant $K(T)$ is a function of temperature alone (Burkholder et al. (2015). $K(T)$ in Eq. (S1) has 30% uncertainty in this temperature range (Burkholder et al., 2015). The uncertainty of the HO_2NO_2 measurement was 16%, resulting in an overall uncertainty of 34% in the inferred HO_2 concentration. The precision of the NO_2 measurement is <100 ppt for a 10 s average time, and thus the NO_2 measurement did not contribute significantly to the uncertainty in the inferred HO_2. During the period over which observations were made, the temperature was > 27°C and the lifetime of HNO_4 was less than 20 s. The validity of the equilibrium assumption made in Eq. S1 at the sampling site is determined by the time scale of fluctuations of NO and NO_2, which can be rapid given the site's proximity to an interstate. For the purpose of the comparison in Fig. S3, the effects of deviations from equilibrium are expected to be small, given the use of hourly median values. A detailed analysis of the inference of HO_2 via HNO_4 will be found in Chen et al. (2016, in preparation).

The HO_2 inferred from HNO_4 measurements was compared to the HO_2 measured using Br^- ionization. The results of that comparison are shown in Fig. S3. The two measurements peak around the same time of day but the HO_2 mixing ratios suggested by both differ by at least a factor of 5 during the afternoon. This is likely due to a combination of factors, including a potential 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. The use of HNO_4 measurements to infer HO_2 has yet to be validated. The discrepancy between both methods of obtaining HO_2 should be the subject of future work.

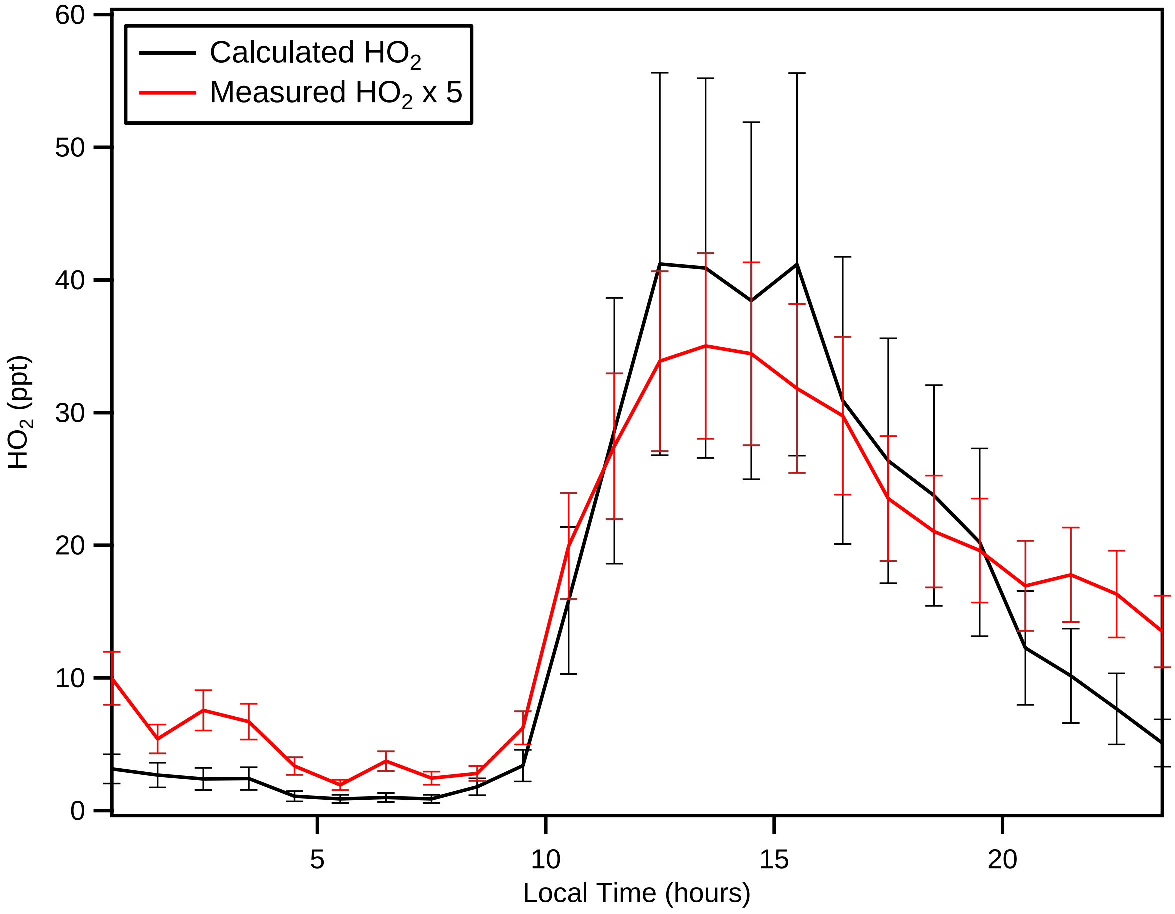

Figure S3: Comparison of HO_2 diurnal profiles (6/15/2015 to 6/18/2015) for measured HO_2 and HO_2 calculated assuming equilibrium between HO_2 and HNO_4. The measured HO_2 signal has been corrected by subtracting the contribution from internal generation of HO_2. The uncertainty in the measured HO_2 is attributed to the combined uncertainties from the calibration parameters in Eqn. 1. The uncertainty in calculated HO_2 only takes into account uncertainties in the equilibrium constant and the HNO_4 calibration.

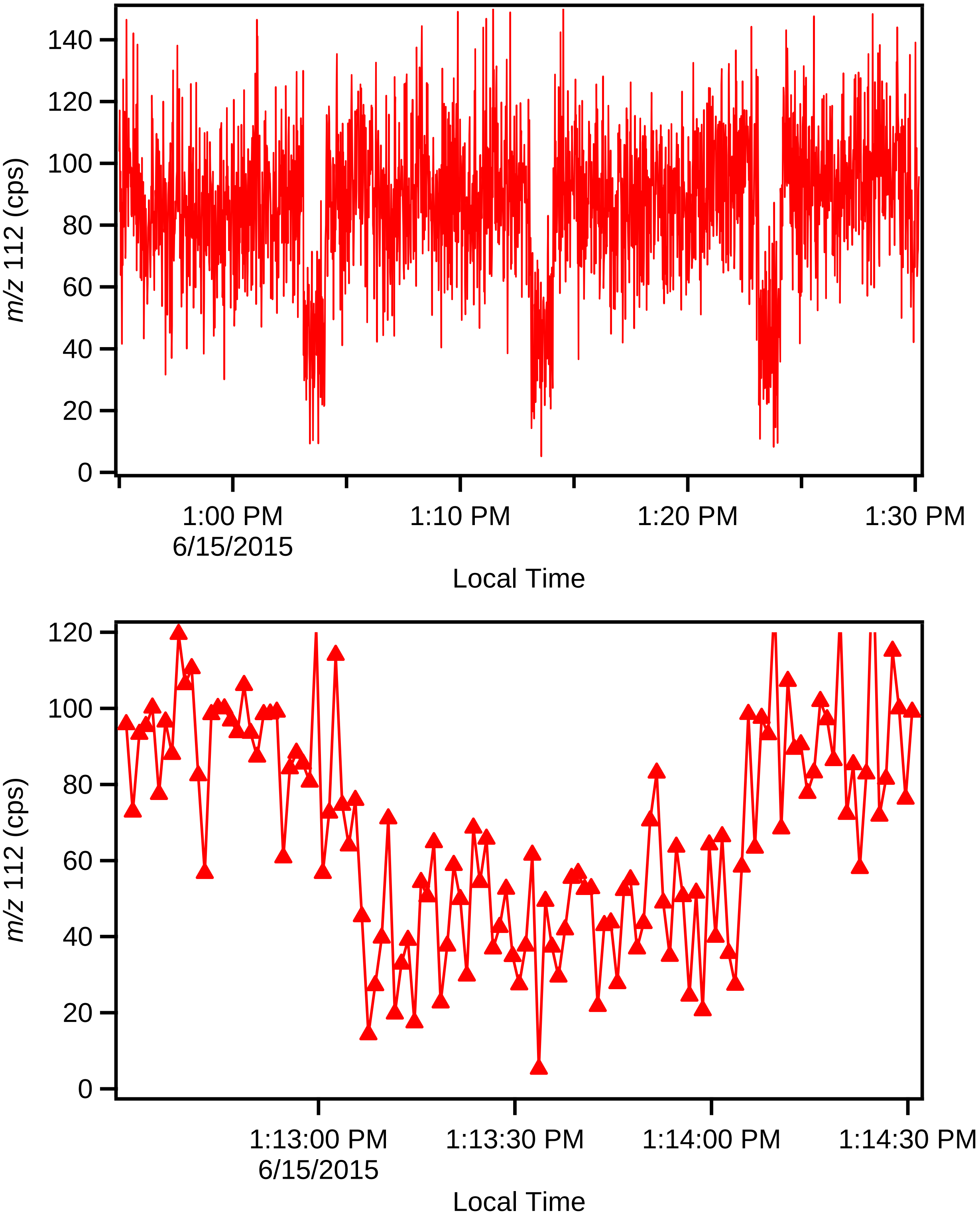

Figure S4: Raw *m/z* 112 time series data, 1 second time resolution. Three background periods using NO addition are shown in the top panel. The middle background period is shown more closely in the bottom panel. Each marker is a 1 second data point. The response time associated with the NO background is only a few seconds.

References

Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18,"JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, 2015.

Chen, D., Huey, L. G., Tanner, D. J., Li, J., Ng, N. L., and Wang, Y. H.: Inferring hydroperoxyl radical (HO_2) in an urban site via the measurement of pernitric acid (HO_2NO_2) using chemical ionization mass spectrometry (CIMS), in prepration, to be submitted to Atmos. Meas. Tech., 2016.