A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions ($\text{H}_3\text{O}^+$ ToF-CIMS) for measurements of volatile organic compounds in the atmosphere

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Abstract

Proton transfer reactions between hydronium ions (H$_3$O$^+$) and volatile organic compounds (VOCs) provide a fast and high sensitive measurement technique for VOCs, leading to extensive use of proton-transfer-reaction mass spectrometry (PTR-MS) in atmospheric research. Based on the same ionization approach, we describe the development of a high-resolution (HR) time of flight chemical ionization mass spectrometer (ToF-CIMS) utilizing H$_3$O$^+$ as the reagent ions. The new H$_3$O$^+$ ToF-CIMS has sensitivities of 100-1000 cps/ppb (ion counts per second per part-per-billion mixing ratio of VOC) and detection limits of 20-600 ppt at 3$\sigma$ for a 1-second integration time for simultaneous measurements of many VOC species of atmospheric relevance. Compared with similar instruments with quadrupole mass spectrometer, e.g. proton-transfer-reaction mass spectrometers, the ToF analyzer with mass resolution (m/$\Delta$m) of up to 6000 not only increases measurement frequency of the instrument, but also expands the number of measurable species. The humidity dependence of the instrument was characterized for various VOC species and the behaviors for different species can be explained by compound-specific properties that affect the ion chemistry. The new H$_3$O$^+$ ToF-CIMS was successfully deployed on the NOAA WP-3D research aircraft for the SONGNEX campaign in spring of 2015. The measured mixing ratios of several aromatics from the H$_3$O$^+$ ToF-CIMS agreed within ±10% with independent gas chromatography (GC) measurements from whole air samples. Initial results from the SONGNEX measurements demonstrate that the H$_3$O$^+$ ToF-CIMS dataset will be valuable for the identification and characterization of emissions from various sources, investigation of secondary formation of many photochemical organic products and therefore the chemical evolution of gas-phase organic carbon in the atmosphere.
1. Introduction

Volatile organic compounds (VOCs) are ubiquitous in the atmosphere. The oxidation of VOCs contributes to formation of ozone (Atkinson, 2000) and secondary organic aerosol (SOA) (Hallquist et al., 2009). Accurate measurements of VOCs in the atmosphere are essential to understand their sources, chemical transformations and hence their effects on ozone and SOA formation (Isaksen et al., 2009). Measurements of VOCs require techniques with high time resolution to effectively capture their high variability in the atmosphere, especially for measurements performed on mobile platforms.

Proton transfer reaction mass spectrometry (PTR-MS) has been an important scientific tool for VOC measurements, associated with high sensitivity and fast time response (de Gouw and Warneke, 2007; Lindinger et al., 1998; Blake et al., 2009). The first generation of PTR-MS instruments used quadrupole mass spectrometers (QMS) for the detection of reagent and product ions. For atmospheric measurements, PTR-QMS instruments are usually used in selected-ion mode, in which the mass filter steps through several pre-selected masses consecutively each with a dwell time of 0.1-1 s (Warneke et al., 2015). The measurement frequency for each species is thus determined by the total cycle length, which is usually on the order of several seconds to 1 minute dependent on user settings. The datasets produced from PTR-QMS are usually disjunct and the information for masses beyond the selected ones is not available. The time resolution of PTR-QMS is generally sufficient for ground-based measurements targeting VOC mixing ratios, but not ideal for aircraft measurements or eddy covariance flux measurements of more than a few species. In recent years, other mass analyzer, e.g. ion traps (Warneke et al., 2005; Mielke et al., 2008; Steeghs et al., 2007) and time of flight (ToF) mass spectrometers (Blake et al., 2004; Ennis et al., 2005; Tanimoto et al., 2007), were used in PTR-MS to overcome some of these inherent drawbacks in PTR-QMS.

PTR-MS instruments that use time-of-flight mass spectrometers (PTR-TOF) were made commercially available in 2009 by Ionicon Analytik (Jordan et al., 2009). The Ionicon PTR-TOF, equipped with Tofwerk orthogonal acceleration reflectron TOF-MS (HTOF), had both much higher sensitivities (10-50 cps/ppbv) and better mass resolution ($m/\Delta m=\infty$) than earlier PTR-TOF instruments (<5 cps/ppbv and $m/\Delta m=100-1200$) (Jordan et al., 2009). Recently, a newer version of the Ionicon PTR-TOF equipped with a
quadrupole ion guide (PTR-QiTOF) was developed and is more sensitive (by a factor of 
~25) than the previous version of Ionicon PTR-TOF that uses an electrostatic ion lens
system (Sulzer et al., 2014). The performance of these PTR-TOF instruments surpasses
those of PTR-QMS in several ways due to the ability of the ToF to obtain whole mass
spectra and their high mass resolution. The high mass resolution of the ToF analyzer
facilitates separation of isobaric isomers (Graus et al., 2010; Sulzer et al., 2014), which
increases the number of measurable VOC species and reduces the possible chemical
interferences (Warneke et al., 2015). PTR-TOF has been used successfully in several
field campaigns at ground sites to measure concentrations and fluxes of a large suite of
VOC species (Park et al., 2013; Müller et al., 2010; Kaser et al., 2013; Holzinger et al.,
2013). Recently, an aircraft-deployable PTR-TOF with mass resolution up to ~1000 was
developed and successfully deployed on the NASA P-3B research aircraft during the
DISCOVER-AQ campaign (Müller et al., 2014a). The deployment of this PTR-TOF has
demonstrated many advantages over PTR-QMS for aircraft measurements, such as much
higher time resolution and hence better spatial resolution, and separation of several
isobaric masses in the lower mass ranges (Müller et al., 2014a).

In this study, a high-resolution ToF-CIMS utilizing hydronium ions (H$_3$O$^+$) similarly
to PTR-MS was developed based on the commercial Aerodyne ToF-CIMS (Lee et al.,
2014). This instrument contains two quadrupole ion guides to transport ions from the drift
tube reaction region to the time-of-flight mass analyzer. The quadrupole ion guides, as
demonstrated in the PTR-QiTOF recently (Sulzer et al., 2014), provide better
transmission efficiency for the reagent and product ions than the conventional ion lens
system. The new instrument was deployed onboard the NOAA WP-3D research aircraft
during the SONGNEX campaign in spring of 2015. Here, we will present development
and characterization of the instrument and its performance during the SONGNEX
campaign.

2. $\text{H}_3\text{O}^+$ TOF-CIMS instrument description

A commercial Aerodyne chemical ionization mass spectrometer (CIMS) (Lee et al.,
2014) was used to construct the airborne H$_3$O$^+$ ToF-CIMS (Figure 1). Briefly, the
Aerodyne ToF-CIMS consists of (1) an ion-molecule reaction (IMR) chamber, (2) a
small segmented radio frequency (RF) only quadrupole ion guide that is used as
collisional dissociation chamber (SSQ), (3) a second big segmented RF-only quadrupole (BSQ), (4) a series of DC optics that further focus and accelerate the primary beam (PB), and (5) a high-resolution ToF detector (HTOF, Tofwerk AG, Switzerland) (Bertram et al., 2011). In the new H$_2$O$^+$ ToF-CIMS, the IMR chamber was replaced by a drift tube (Figure 1), which provides a homogenous and controllable electric field for ion-molecule reactions. The drift tube is comprised of stainless steel rings separated by Teflon rings for both vacuum sealing and electronic insulation (de Gouw and Warneke, 2007). A hollow cathode discharge ion source was connected in front of the drift tube to produce high purity hydronium ions by introducing a flow of 5 mL min$^{-1}$ of water vapor. The detailed description for both drift tube and ion source can be found in previous review papers (de Gouw and Warneke, 2007; Blake et al., 2009). In addition to the 3-stage split-flow turbo pump (Pfeiffer SplitFlow 310) used for the high vacuum of BSQ, PB and TOF, another turbo pump (Pfeiffer TMH-071-P) was installed to draw air from the SSQ and water vapor from the ion source. A butterfly exhaust throttle valve (MKS T3Bi) was used to control the pumping rate of the newly installed turbo pump (Figure 1), and the pressure of the SSQ can be adjusted by the opening percentage of the valve. In practice, the pressure of drift tube is also actively controlled (see below) and SSQ pressure only needs to be adjusted sporadically.

The newly built H$_2$O$^+$ ToF-CIMS was deployed on the NOAA WP-3D aircraft in March-April, 2015 as part of the Shale Oil and Natural Gas Nexus (SONGNEX) campaign. During SONGNEX, a total of 19 flights were carried out mainly over oil and gas production basins in the western United States. For the detailed flight strategies, the readers are referred to the SONGNEX website (www.esrl.noaa.gov/csd/projects/songnex).

A heated Teflon tube (40 °C) mounted inside a winglet on a window plate was used to transport air into the instrument (Figure S1). Pressure at the downstream end of the inlet was regulated to 180 mbar using a pressure controller. A PEEK capillary was placed between the pressure controller and drift tube to further reduce the pressure from 180 mbar to the maintained pressure in the drift tube (2.40±0.01 mbar). During SONGNEX, the 11 cm long drift tube had a drift voltage of 710 V and was heated to 50 °C, which resulted in an E/N ratio (electric field to number density) of 120 Td (1 Td= 10$^{-17}$ V cm$^2$).
inside the drift tube. The flow of the inlet varied from ~500 mL min\(^{-1}\) at sea level to ~100 mL min\(^{-1}\) at 6.5 km of altitude. Background signals of the instrument were determined by passing ambient air for 90 s every 30-40 min through a Platinum catalytic converter heated to 350 °C. In-flight calibrations were performed by adding a small flow (0.5-3.0 mL min\(^{-1}\)) of a ten-component gas standard (see the list in Table 1) to the inlet flow automatically for 90 s every 1-2 hours (Figure S1). Calibrations were conducted by adding the gas standard flow to either clean air from the catalytic converter or ambient air during SONGNEX. A diffusion cell introduced a small amount of 1,3,5-trichlorobenzene (C\(_6\)H\(_3\)Cl\(_3\)) into the instrument continuously to facilitate ToF mass calibration at the high ends of the m/z range. Laboratory experiments show that 1,3,5-trichlorobenzene mainly generates C\(_6\)H\(_3\)Cl\(_3\)H\(^+\) (m/z 180.9373, 98.5%) in the instrument, with small contributions from C\(_6\)H\(_3\)Cl\(_2\)H\(^+\) (m/z 179.9295, 1.0%) and C\(_6\)H\(_3\)Cl\(_2\)H\(^+\) (m/z 145.9685, 0.4%). The signals of C\(_6\)H\(_3\)Cl\(_3\)H\(^+\) ion were around 2000 cps during the SONGNEX campaign.

The axial voltage gradients for SSQ and BSQ were tuned using the Thuner software (Tofwerk AG) by maximizing signals of the protonated product ions of several VOC species (acetone, benzene and isoprene), minimizing VOC signals from charge transfer reactions with O\(_2\)\(^+\), and maximizing mass resolution of the TOF analyzer before the campaign. In addition, the effects of turning the RF amplitudes of the SSQ and BSQ were explored manually (see below). The voltage of micro-channel plate (MCP) detector for TOF are determined and set before takeoff for each individual flight by maintaining the single ion signal (SIS) at around 1.8 mV·ns, which effectively prevents mass discrimination as the result of MCP aging (Müller et al., 2014b). The extraction frequency of the TOF was set at 25 kHz, which enables to measure masses up to m/z 500. During SONGNEX, mass spectra were averaged and stored to 10 Hz and were further averaged afterward to 1 Hz for the analysis shown in this paper.

ToF data were processed using the Tofware software package (v2.5.1) (www.tofwerk.com/tofware) developed by Tofwerk and Aerodyne Research Inc. (www.aerodyne.com). The detailed procedures of the ToF data processing have been presented in a previous publication (Stark et al., 2015). Post-measurement mass calibrations were conducted using 6-7 isolated masses, including m/z 19.0178 (H\(_2\)O\(^+\)), m/z 29.9974 (NO\(^-\)), m/z 31.9893 (O\(_2\)\(^+\)), m/z 37.0284 (H\(_2\)O\(^+\)(H\(_2\)O)), m/z 55.0390
(H$_3$O$^+$)(H$_2$O)$_2$), m/z 125.9610 (FeH$_5$O$_4$H$^+$) and m/z 180.9373 (C$_6$H$_3$Cl$_3$H$^+$). Mass calibration of the ToF was accurate within 5-10 ppm for various masses, similar to the results reported for another Aerodyne ToF-CIMS instrument (Lee et al., 2014).

Instrument functions (peak shape, peak width and baseline) were derived for each individual flight based on the algorithms shown in Stark et al. (2015). High-resolution peak fitting to the mass spectra were performed using a user defined peak list with masses up to m/z 181.

In the orthogonal extraction region of the TOF analyzer, ions of different masses have the same energy but different velocities, and are therefore extracted at different duty cycles (Chernushevich et al., 2001). The Tofware software corrects for this effect using the equation of $I_{corr} = I_{raw} \times \frac{55}{m/z}$ to a reference mass of m/z 55. In this study, all of the signals are reported as the ToF duty cycle corrected signals ($I_{corr}$), unless otherwise noted.

3. H$_3$O$^+$ TOF-CIMS instrument performance

3.1 Quadrupole ion guides

In addition to hydronium ions (H$_3$O$^+$), water clusters are also present in the instrument, including protonated water dimers (H$_3$O$^+$)(H$_2$O)) and protonated water trimers (H$_3$O$^+$)(H$_2$O)$_2$). In standard PTR-MS operation, the product ion signals are normalized to the reagent ion count rates to account for drifts in the ion source. Because the reagent ions in the H$_3$O$^+$ ToF-CIMS are so strongly dependent on humidity, the measured cluster ion distribution needs to be understood in detail as it affects the normalization procedure and therefore the measured mixing ratios. As the drift tube in H$_3$O$^+$ ToF-CIMS is identical to those in PTR-MS, the cluster distribution and their humidity dependence in the drift tube are expected to be similar as in PTR-MS, which has been understood well and described in detail in de Gouw and Warneke (2007). However, the cluster distribution can be altered in the quadrupole ion guides, because the electric field inside the ion guides is not always the same as that in the drift tube. Thus, the reagent ions and VOC signals as a function of various settings of the quadruple ion guides are investigated here.
The signals of the reagent ions as a function of the pressure inside the SSQ are shown in Figure 2. As the SSQ pressure increases from 1.0 mbar to 1.5 mbar, the intensities of all reagent ions increase, indicative of better ion transmission through the SSQ at higher pressures. When the SSQ pressure is higher than 1.5 mbar, the \( \text{H}_3\text{O}^+ \) signal starts to decline slightly and water clusters continue to increase, implying that the reagent ions shift to larger clusters at these SSQ pressures. The ratios of \( \text{H}_3\text{O}^+(\text{H}_2\text{O})/\text{H}_3\text{O}^+ \) \( (R_{37/19}) \) increase with the SSQ pressure throughout the range studied here. At higher SSQ pressure, the effective de-clustering ability or \( E/N \) ratio is reduced. The \( \text{H}_3\text{O}^+(\text{H}_2\text{O})_2 \) ions account for small a fraction of the reagent ions throughout the explored range of SSQ pressures. The signals of protonated benzene and acetone at constant mixing ratios (2.5 ppb) both increase with higher SSQ pressure, although the increase of benzene signals is small when SSQ pressures go beyond 1.5 mbar. The protonated VOC signals correlate better with \( \text{H}_3\text{O}^+ \) than with \( \text{H}_3\text{O}^+(\text{H}_2\text{O}) \), suggesting that \( \text{H}_3\text{O}^+ \) ions are the dominant participant in proton-transfer reactions, even though \( \text{H}_3\text{O}^+ \) ions are measured at comparable levels as \( \text{H}_3\text{O}^+(\text{H}_2\text{O}) \) at high SSQ pressures. Along with this observation, the observed slight reduction of \( \text{H}_3\text{O}^+ \) and disproportionally larger enhancement of \( \text{H}_3\text{O}^+(\text{H}_2\text{O}) \) with SSQ pressures above 1.5 mbar imply that the transmission of \( \text{H}_3\text{O}^+ \) in the SSQ is significantly lower than that of \( \text{H}_3\text{O}^+(\text{H}_2\text{O}) \) (and other higher \( m/z \)). Choosing the optimum SSQ pressure therefore represents a trade-off between higher intensities of the reagent (and VOC) ions and lower signals of water clusters. We have selected to run the instrument with the SSQ pressure at 1.30±0.01 mbar during the SONGNEX campaign.

In addition to the SSQ pressure, the signals of reagent ions and VOC product ions were also explored as a function of RF amplitudes for both SSQ and BSQ (Figure S2 and Figure S3). From these experiments, the main findings are: (1) as expected, lower RF amplitudes in the BSQ lead to better transmission for light ions but worse ion focusing (Chernushevich et al., 2001). (2) Ion chemistry needs to be taken into account in the SSQ, for example \( \text{H}_3\text{O}^+ \) declines and \( \text{H}_3\text{O}^+(\text{H}_2\text{O}) \) increases when RF amplitudes decrease from 80 V to 40 V. (3) Variations of VOC signals generally follow the reagent ions, but they are influenced more by poorer focusing at low RF amplitudes, especially for heavier VOC masses. (4) \( \text{O}_2^+ \) signals and charge transfer products of aromatics increase quickly.
when RF amplitudes of the SSQ are higher than 80 V, possibly due to discharge in the SSQ (TOF-CIMS manual indicates that discharge happens with >200 V). Based on these results, the RF amplitudes of the SSQ and BSQ were set to 50 V and 350 V, respectively.

3.2 Transmission of reagent ions and their humidity dependence

The humidity of the sampled air affects the distribution of the reagent ions in PTR-MS (de Gouw and Warneke, 2007). Figure 3A shows the reagent ion signals versus water vapor mixing ratios (w) of the sampled air from a laboratory experiment. As expected, the H$_3$O$^+$(H$_2$O) signals increase as the air gets more humidified. The signals of H$_3$O$^+(H_2O)_2$ were small, but increase quickly with humidity. However, there is also an increase of H$_3$O$^+$ signals with humidity. Compared to dry air with w=0 g/kg, the H$_3$O$^+$ signals are 52% higher under the condition with w=22.4 g/kg equivalent to a relative humidity (RH) of 90% at 25 °C. This behavior is in marked contrast to the reported dependence of the reagent ions on humidity in a conventional PTR-MS using ion lenses to transfer ions (de Gouw and Warneke, 2007): in these instruments, H$_3$O$^+$ decreases and H$_3$O$^+(H_2O)$ increases with rising humidity and the total intensities of the two reagent ions are relatively stable with humidity with the remaining difference explainable from the difference in detection efficiency between H$_3$O$^+$ and H$_3$O$^+(H_2O)$.

The distribution of H$_3$O$^+$ and H$_3$O$^+(H_2O)$ ions exiting the SSQ is determined by the distribution of these same ions entering the SSQ as well as the fragmentation and clustering processes that modify the distribution in the SSQ. At the SSQ pressure used, an individual ion entering the SSQ undergoes many collisions that can add or subtract a ligand molecule. As a result, the transmission efficiency of an reagent ion in the SSQ reflects the averaged transmission efficiencies of ions with m/z 19 and m/z 37 weighed by the time the ion spends as H$_3$O$^+$ vs. H$_3$O$^+(H_2O)$. This issue is qualitatively similar to the measured mobilities of H$_3$O$^+$ and H$_3$O$^+(H_2O)$ observed in the drift tube of PTR-MS (Warneke et al., 2001). The larger H$_3$O$^+$ signals at higher humidity in the H$_3$O$^+$ ToF-CIMS are the result of the low transmission efficiency of H$_3$O$^+$ ions compared to other heavier masses, which has been inferred from the dependence of the reagent ions with SSQ pressures above. The low transmission of H$_3$O$^+$ ions is related to the low-mass cut-off of the RF-only quadrupoles (Chernushevich et al., 2001). The strong increase in H$_3$O$^+$ signal intensity with humidity reflects the fact that while ions may be detected as H$_3$O$^+$,
they spent a larger fraction of time as H$_3$O$^+$($H_2$$O$) in the SSQ at higher humidity and are therefore transferred with a higher average transmission efficiency.

The transmission efficiency of H$_3$O$^+$ ions relative to H$_3$O'($H_2$$O$) is quantified using additional laboratory experiments. Methanol and acetonitrile were introduced into the instrument at such high concentrations that significant fractions of the reagent ions were depleted (Figure S4). Methanol and acetonitrile are used, because their product ion masses (m/z 33 and m/z 42) bracket the mass of H$_3$O$^+$(H$_2$$O$) ions. We observed more product ions of both methanol (CH$_3$OH$^+$, m/z 33.0335) and acetonitrile (C$_2$H$_3$NH$^+$, m/z 42.0338) than the summed depletion of H$_3$O$^+$ and H$_2$O'(H$_2$$O$). As the transmission factor of H$_3$O'(H$_2$$O$) ions should be in between protonated methanol and acetonitrile ions, the ratios between H$_3$O$^+$ changes and the changes of the sum of product ions and H$_3$O'(H$_2$$O$) ions in each depletion experiment reflect the ratios of the transmission efficiency between H$_3$O$^+$ and H$_3$O'(H$_2$$O$) ($T_{H_3O^+/T_{H_3O^+}}$). From the scatterplots in Figure S4, the $T_{H_3O^+/T_{H_3O^+}}$ ratios are determined to be in the range of 0.21-0.35 and 0.14-0.25 from the experiments with methanol and acetonitrile, respectively (Figure S5). The discrepancies between the estimates from methanol and acetonitrile may come from the differences between the transmission factors of m/z 33 and m/z 42 (Figure S6), and/or small amount of methanol forming methanol-water clusters (see section 3.3). The determined $T_{H_3O^+/T_{H_3O^+}}$ ratios are larger at higher water vapor mixing ratios (Figure 3B, also in Figure S5), in accordance with the expectation of a higher effective transmission efficiency of H$_3$O$^+$ ions with increasing humidity discusses above.

The relationship of $T_{H_3O^+/T_{H_3O^+}}$ versus water vapor mixing ratios shown in Figure 3B can be used to correct the measured H$_3$O$^+$ signals to the same transmission efficiency as H$_3$O'(H$_2$$O$) (Figure 3C). The corrected H$_3$O$^+$ signals exhibit slightly lower signals at higher humidity, which is more similar to the relationship observed in the PTR-MS drift tube (de Gouw and Warneke, 2007). The summed signals of the corrected H$_3$O$^+$ and measured H$_3$O'(H$_2$$O$) are also shown in Figure 3C. We see higher total reagent ion signals at increasing humidity. It is clear that H$_3$O$^+$ ions dominate the reagent ions in the drift tube throughout the explored humidity range, even though the measured H$_3$O$^+$ signals are lower than H$_3$O'(H$_2$$O$) ions at high humidity levels. At a high humidity level
(RH=90% at 25 °C, w=22.4 g/kg), H$_3$O$^+$ (H$_2$O) ions account for 24-30% of the total reagent ions. Taken together, both the signals of the reagent ions and their transmission efficiency in the instrument exhibit non-linear relationships with humidity. The total reagent ion signals can be derived from the determined $T_{H_3O^+}/T_{H_3O^+(H_2O)}$, but it is associated with significant uncertainties (Figure 3C). A simple equation to derive a parameter with little humidity dependence from reagent ion signals seems to be difficult. Thus, the product ion signals will be normalized to H$_3$O$^+$ signals of $10^6$ cps to account for drifts in the ion source. Normalization to H$_3$O$^+$ signals does not involve any mathematical computation of the reagent ions, which may introduce extra uncertainty.

The ratios of H$_3$O$^+$ (H$_2$O) ions to H$_3$O$^+$ ions ($R_{37/19}$) can be used as a proxy for humidity in PTR-MS (de Gouw et al., 2003a). The dependence of $R_{37/19}$ with water vapor mixing ratios of the sampled air is shown in Figure 3D. We see higher $R_{37/19}$ ratios with increasing humidity from both laboratory experiments and ambient measurements during the SONGNEX, suggesting that $R_{37/19}$ is also a good internal humidity indicator for the instrument. The agreement between laboratory experiments and ambient data is good, considering that the humidity sensors used for laboratory experiments were not cross-calibrated with the sensors on the NOAA WP-3D. The correlation coefficients from laboratory experiments and SONGNEX ambient data are 0.98 and 0.99, respectively, both indicative of tight linear relationship of the data points. The intercept in Figure 3D is the result of excess water vapor entering the drift tube from the ion source. Based on the linear fit to SONGNEX data points in Figure 3D, the $R_{37/19}$ ratio in the instrument is 1.4 at a humidity level of RH=90% at 25 °C (or w=22.4 g/kg), which will be used to characterize the instrument response and compare with dry conditions in this study.

3.3 The humidity dependence of VOC sensitivities

3.3.1 Species without significant dehydration and hydration

A series of laboratory experiments were performed to describe instrument sensitivities of various VOC species as a function of humidity. Figure 4 shows the results for acetone and benzene from one of the experiments. Constant mixing ratios (8.0 ppb in Figure 4) of acetone and benzene were introduced into the instruments and the
background subtracted raw signals of protonated product ions of the two compounds were observed at various humidities. As described in the previous section, \( R_{37/19} \) is used as the indicator of humidity. Protonated acetone signals increase with rising humidity, whereas protonated benzene signals decline under humidified conditions. The signals of protonated acetone and protonated benzene at the humidity level of \( R_{37/19} = 1.4 \), equivalent to RH=90% at 25 °C, are 111% and 32% of those under dry condition, respectively. The humidity dependencies of these two species are similar to that reported for conventional PTR-MS in many previous studies (Warneke et al., 2001; de Gouw et al., 2003a).

The normalized signals of acetone and benzene from the humidity experiments are shown in Figure 4B. As illustrated in the previous section, \( \text{H}_3\text{O}^+ \) signals are 52% higher at \( R_{37/19} = 1.4 \) relative to dry condition. The increase of \( \text{H}_3\text{O}^+ \) signals with humidity is apparently larger than the increase of protonated acetone, which in turn leads to a reduction of the normalized protonated acetone signals with increasing humidity. Because of the low transmission of \( \text{H}_3\text{O}^+ \) ions and clustering/de-clustering effects as described earlier, the normalization to reagent ions leads to a different humidity dependence of the normalized signals in the \( \text{H}_3\text{O}^+ \) ToF-CIMS compared to that in the conventional PTR-MS.

The normalized signals at varying humidity levels relative to that at dry condition for acetone, benzene and other VOC species are determined. After attempts using several different fit functions to describe the data points, a double exponential function was found to achieve the best representation of the data. The fitted humidity curves for acetone, benzene and other VOC species are compiled in Figure 5. Generally, a stronger humidity dependence was observed for hydrocarbons than for OVOCs. Comparing the results of the aromatics (benzene, toluene, o-xylene, methylstyrene, 1,2,4-trimethylbenzene and p-cymene), we see less humidity dependence for heavier aromatics. The same trend is also observed for ketones (acetone, MEK, pentanone and hexanone). The heavier species in the two compound series tend to have higher proton affinities (PA) (Hunter and Lias, 1998), suggesting that proton affinities of the species play a role in the humidity dependence.
The fractions of normalized signals at $R_{37/19}=1.4$ relative to dry condition $(f_{37/19}=1A)$ were determined and plotted as a function of proton affinities of the species in Figure 5C. A positive correlation between the determined fractions and proton affinities of VOC species is generally observed. This is expected, as a higher proton affinity for a VOC species has several implications: (1) the reaction with $H_2O^+(H_2O)$ ions is exothermic when the proton affinity exceeds that of water dimer ($801$ kJ/mol); and (2) the reaction more readily becomes exothermic through either direct proton transfer or other routes (Midey et al., 2002). The data points in Figure 5C are color-coded using the permanent dipole moment ($\mu_D$) of the neutrals, which has been shown to affect the efficiency of ligand switching reactions between VOC species and water clusters (Spanel and Smith, 1995). It is clear that species with $\mu_D<1$ D are more strongly humidity dependent than the species with $\mu_D>1$ D, which implies that ligand switching reactions are important in the instrument as the result of substantial amounts of $H_2O^+(H_2O)$ ions.

Based on proton affinity and permanent dipole moment, the species shown in Figure 5C can be divided into four groups: group I with PA>$801$ kJ/mol and $\mu_D>1$ D (e.g. acetone); group II with PA<$801$ kJ/mol and $\mu_D>1$ D (e.g. acetaldehyde); group III with PA>$801$ kJ/mol and $\mu_D<1$ D (e.g. isoprene); group IV with PA<$801$ kJ/mol and $\mu_D<1$ D (e.g. benzene). Species in group I (high PA and $\mu_D$) can undergo proton transfer with $H_2O^+(H_2O)$ and $H_3O^+$ at similar rate constants, whereas the reactions with $H_2O^+(H_2O)$ are either not happening or inefficient for species in group IV (low PA and $\mu_D$). For species in group II (low PA, high $\mu_D$) and III (high PA, low $\mu_D$), ligand switching and direct proton transfer reaction with $H_3O^+(H_2O)$ can occur in the instrument, respectively.

The inverse of $H_2O^+$ signal relative to dry conditions ($\frac{1}{m_{19}}$) was included in Figure 5 (A and B) as a reference. If the humidity dependence for a VOC species follows this reference line, the raw signal of the VOC actually has no humidity dependence and the lower normalized signals at higher humidity levels are solely the result of normalization to higher $H_3O^+$ signals. Species above this reference line are associated with higher raw signals at higher humidity, and vice versa. As discussed in section 3.2, the increase of $H_3O^+$ signals with rising humidity is caused by a higher effective transmission of ions detected as $H_3O^+$ (Figure 3B). Thus, the upper limit of the humidity dependence curve should be a flat unity line in Figure 5 (A and B) (see exceptions in section 3.3.2). Many
heavier OVOC masses were observed during SONGNEX, but their humidity dependence was not explored. As higher proton affinities are expected for these heavier OVOC species, the humidity dependence curves for these heavier OVOCs should lie in the shaded area filled by patterns in Figure 5 (A and B).

3.3.2 Species with significant dehydration and hydration

Product ions of the species explored for humidity dependence in the previous section (3.3.1) are associated with minor dehydration following the proton transfer reaction. Dehydration happens when the product ion of a VOC species fragments by losing one or more water molecules. Propanols and higher alcohols are known to mainly yield dehydration product ions in PTR-MS (Spanel and Smith, 1997; Blake et al., 2009; Warneke et al., 1996). For example, isopropanol (C₃H₇OH, PA=795.4 kJ/mol) is mainly detected as C₃H₇⁺ (m/z 43.0542), rather than C₃H₆OH⁺ (m/z 61.0648) in H₂O⁺ ToF-CIMS (Figure 6A). We see higher C₃H₆OH⁺/C₃H₇⁺ ratios with increasing humidity in the instrument. The measured humidity dependence of C₃H₇⁺ ions is similar to that of acetaldehyde (and other OVOCs), whereas more C₃H₆OH⁺ ions are detected with increasing humidity and the normalized signal of C₃H₆OH⁺ ions at \( R_{37/19} \) = 1.4 is 1.7 times of in dry air. Similar to i-propanol, a positive dependence of protonated ethanol on humidity is also observed (Figure 6B), as ethanol fragments significantly by losing a water molecule as well (Baasandorj et al., 2015).

In addition to dehydration, hydrated product ions in the form of MH⁺(H₂O) (where M is the formula of VOC species) are observed, including acetaldehyde, acetone, methanol and acetic acid (Figure 7A). The ratios of hydration ions to protonated molecular ions (MH⁺(H₂O)/MH⁺) are observed to increase with humidity for these compounds. Among the species investigated, formic acid (HCOOH, PA=741.8 kJ/mol) and isocyanic acid (HNCO, PA=753.1 kJ/mol) are clustering the most, with MH⁺(H₂O)/MH⁺ ratios of 0.34 and 1.2 at \( R_{37/19} \) = 1.4, respectively. The protonated ions of the two compounds both decrease quickly with humidity, and the normalized signals at \( R_{37/19} = 1.4 \) are both only approximate 2% of those at dry conditions. The signals of hydration ions cannot account for the difference between the humidity dependent curves of these two compounds and the region other OVOCs occupy in Figure 5. The reason for the strong humidity dependence of the two compounds is not known, but it is possibly
due to enhanced loss of ions after hydration. A similar enhanced loss of ions at higher humidity was observed for formic acid in a PTR-QMS at a low E/N ratio (85 Td), but not at higher E/N ratios (Baasandorj et al., 2015). Baasandorj et al. (2015) (see Figure 5f in their paper) showed that, at the low E/N ratio (85 Td), protonated ions of formic acid decrease by 12 ncps/ppb and hydration ions only increase by 6 ncps/ppb going from RH=18% to RH=88%. The enhanced loss of isocyanic acid at higher humidity might be related to its hydrolysis, which is reported to be accelerated by water dimer and trimer (Raspoet et al., 1998).

The examples of isopropanol, formic acid and isocyanic acid suggest that the humidity dependence can be affected by dehydration and hydration processes of the product ions. The abundance of water molecules affects the equilibrium ratios of the respective ion pairs. In contrast, there are some species associated with significant fragmentation without water molecule as a neutral product, e.g., monoterpenes and p-cymene, which exhibit similar humidity dependence as other VOCs (Figure 5C).

Therefore, special attention should be paid to the humidity dependence of the species associated with either significant fragmentation by losing water molecule or significant molecule-water clusters.

### 3.4 Mass resolving power and separation of isobaric masses

The mass resolving power (m/Δm) was derived from the observed linear relationship between the full-width half maximum (FWHM) of several isolated mass peaks and their m/z using Tofware (Stark et al., 2015). The typical m/Δm for the H$_3$O$^+$ ToF-CIMS during the SONGNEX campaign is shown in Figure S7. The m/Δm in the range of m/z 30 - 200 (where most VOCs were detected), are 3900-5900 with higher resolution for heavier masses. These mass resolutions are sufficient to separate many isobaric ions residing at the same nominal masses. Figure 8 shows the separation of C8 aromatics (C$_8$H$_{10}$H$^+$, m/z 107.0855) from benzaldehyde (C$_7$H$_6$OH$^+$, m/z 107.0491) for m/z 107 during a flight leg (18:15-18:45 UTC) over the Permian Basin in Texas, US. The two mass spectra in A and B are 30 s averages centered around 18:25:00 and 18:35:10, respectively. The two time windows had either benzaldehyde or C8 aromatics as the higher peak between the two. The time series of benzaldehyde and C8 aromatics determined from the mass spectral fits for this 30-min period correlated well with acetone.
(R=0.87) and benzene (R=0.94), respectively. This is consistent with the expectation that benzaldehyde was mainly from secondary formation and C8 aromatics were dominated by primary emissions from oil and gas activities. The signals at m/z 107 are usually assigned to C8 aromatics in PTR-QMS studies (de Gouw and Warneke, 2007). Although the possible interference from benzaldehyde to C8 aromatics has been known, it usually constitutes a small fraction of the total signal at nominal mass 107 (Warneke et al., 2003).

The example shown in Figure 8 indicates that benzaldehyde, in some environments, can contribute significantly to signals at nominal mass 107.

Based on results in previous studies (Stark et al., 2015; Graus et al., 2010), the mass resolving power of the ToF analyzer presented in this study can separate many of the isobaric masses in the mass range of m/z<200 by utilizing the high-resolution peak fitting algorithms. The separation of isobaric ions has several advantages over the nominal mass data of PTR-QMS: (1) reduce chemical interferences, e.g. the interference of benzaldehyde to C8 aromatics at nominal m/z 107 as shown above; (2) decrease background signals for several compounds of interest, e.g. for methanol (Müller et al., 2014a) and acetaldehyde, the instrument backgrounds of which have interferences from O$_2$H$^+$ and CO$_2$H$^+$ at the same nominal masses, respectively; (3) increase the number of species that can be measured. In general, 10-20 compounds are usually measurable by the PTR-QMS explicitly without significant interference depending on the origin of the air masses (de Gouw and Warneke, 2007). During the SONGNEX campaign, a total of 1055 peaks between m/z 12 and m/z 181 were identified and assigned to signals in the mass spectra of H$_3$O$^+$ ToF-CIMS. Not all of these mass signals can be used for VOC quantification. Many masses (1) are associated with large errors from high-resolution peak fittings as the result of a much larger peak nearby and/or poor separation from another peak; or (2) have no significant enhancement over instrument background. Over 260 masses had periods (at least 1 min) with signal to background ratios larger than three during the flight over the Permian Basin on April 23, 2015. Although not all of these masses are attributable to specific compounds, chemical formulas of the masses give more detailed information on the chemical composition than just the nominal m/z.

Detailed interpretation of the mass spectra in various air masses during the SONGNEX campaign will be presented in a separate publication (Koss et al., in prep).
3.5 Background correction, in-flight calibration and detection limits

The humidity dependence curves illustrated in Figure 5 were used to correct the normalized signals of various VOC species from measurements made during SONGNEX.

After that, background signals were averaged for each measurement cycle and interpolated to the periods between background measurements. Two features in ambient measurements were considered in the interpolation of background signals. First, we observed continuously decrease of background signals for some ions during the flights (Figure S8B). The decrease of background signals cannot be avoided during aircraft measurements, as the instrument only had 2-3 hours start-up time in the morning of each flight day and the instrument backgrounds usually become lower as the instrument runs.

Second, background signals for many ions are dependent on humidity in the air, even after the correction for the humidity dependence of their sensitivities (Figure S8D). This is also of particular importance for aircraft measurements, as a rapid change of humidity is encountered during aircraft ascents and descents (de Gouw and Warneke, 2007).

Exponential decay function was used to describe the continuous decline of background signals, whereas humidity dependence of background signals was described using linear relationships with one of the humidity indicators (R_{37/19}, \text{H}_3\text{O}^+(\text{H}_2\text{O})_2/\text{H}_3\text{O}^+, \text{O}_2^+ signals and \text{CO}_2^+ signals). Both effects were important for some ions and they were taken into account by consecutive implementation of the procedures (Figure S8C). For other ions, a simple linear interpolation was adopted (Figure S8E). The variations of instrument backgrounds with instrument running time and humidity may also be critical for other PTR-MS and CIMS instruments, especially for aircraft deployments and in some circumstances when meteorological conditions change quickly during ground measurements. The procedures shown here should be easy to incorporate into these measurements if necessary.

The measurements of each in-flight calibration are averaged in the same way as the background measurements. The results for benzene, isoprene, acetaldehyde and acetone during the SONGNEX campaign are shown in Figure 9. Each of the four species represents one of the four groups of compounds described in section 3.3. The calibration results for the four species show tight linear correlations between corrected normalized signals and calculated mixing ratios from the gas standard ($R>0.995$), indicating stable
instrument performance from flight to flight during the SONGNEX campaign. No clear
dependence of sensitivities on \( R_{37/19} \) is observed, demonstrating that the effects of
humidity on the sensitivities are properly accounted for by the procedures described
above. The measured sensitivities for various VOC species are shown in Table 1, which
lists sensitivities under dry conditions. The sensitivities for most VOC species of interest
are better than 400 cps/ppb, with several species higher than 800 cps/ppb. The lower
sensitivity for methanol is consistent with previous studies (Warneke et al., 2015),
whereas lower sensitivities for isoprene and \( \alpha \)-pinene are due to the fragmentation of their
product ions.

The counting statistics of the ions follow a Poisson distribution, i.e. the 1-\( \sigma \) error of
counting \( N \) ions is \( \sqrt{N} \). Recent studies showed that the high-resolution peak fitting to the
TOF mass spectra can add significant additional noise to the fitted peak intensities of the
masses (Cubison and Jimenez, 2015; Corbin et al., 2015). Figure 10 shows standard
deviations of the background signals versus the background signals themselves from the
individual zeroing periods for the masses listed in Table 1 during one SONGNEX flight
(April 27, 2015). Note that the signals shown in Figure 10 were not corrected for the ToF
duty cycle, so they represent the actual ion signals detected by the MCP. Real variations
of background signals due to instrument drift may contribute some to the standard
deviations of background signals. Thus, data points in Figure 10 are best viewed as the
upper limits of the errors from counting statistics. Most of the data are observed in the
region between \( \sqrt{N} \) and \( 2\times\sqrt{N} \), suggesting that high-resolution peak fitting can increase
the errors in the ion signals by as much as a factor of 2 for the VOC masses in Table 1.

The signal to noise ratio (S/N) of the species \( X \) from a CIMS instrument can be
expressed by (Bertram et al., 2011):

\[
\frac{S}{N} = \frac{\mathcal{C}_f [X]t}{\alpha \times \sqrt{\mathcal{C}_f [X]t + 2Bt}}
\]  \hspace{1cm} (1)

Here, \([X]\) is the mixing ratios of the species (ppb), \( \mathcal{C}_f \) is the sensitivity of the species
(cps/ppb) and \( B \) is the background count (cps), both of which are values without
corrections for the ToF duty cycle. \( t \) is the sampling time (s). \( \alpha \) is the scaling factor of the
errors in ion signals relative to Poissonian statistics, and used to account for the
additional errors from HR peak fitting. \( \alpha \) for each species is determined from Figure 10
(see Table 1 for values). We define the detection limit as the mixing ratio with a S/N ratio of 3. The calculated 1-s detection limits for various species are listed in Table 1. The 1-s detection limits are better than 100 ppt for most species. Higher detection limits for acetaldehyde, acetic acid, isoprene, methanol and ethanol are the result of higher background counts for the former two species and lower sensitivities for the latter three species, respectively.

Figure 11 compares sensitivities and detection limits of methanol, acetone and benzene between the NOAA PTR-QMS from several previous campaigns (Warneke et al., 2011) and the new H$_3$O$^+$ ToF-CIMS during SONGNEX. As discussed in Warneke et al. (2011), the performance of the NOAA PTR-QMS improved gradually as a result of many instrumental developments, which led to higher sensitivities and lower detection limits. As shown in Figure 11, the sensitivity of acetone in the new H$_3$O$^+$ ToF-CIMS is similar to that of PTR-QMS in the recent campaigns (CalNex and UBWOS 2013), whereas sensitivities of methanol and acetone are somewhat lower than the PTR-QMS. The performance of a commercial PTR-TOF (PTR-TOF 8000, Ionicon Analytik) during the UBWOS 2013 (Warneke et al., 2015) is also included in Figure 11. We observed much higher sensitivities for our H$_3$O$^+$ ToF-CIMS than the PTR-TOF used in UBWOS 2013. The large difference in the sensitivities between the PTR-TOF 8000 and H$_3$O$^+$ ToF-CIMS is mainly attributed to the difference between ion lenses used in the PTR-TOF to transfer ions from the drift tube to the mass analyzer and the quadrupole ion guides used in H$_3$O$^+$ TOF-CIMS. A large enhancement in sensitivities of a PTR-TOF by using quadrupole ion guides was recently also demonstrated in a PTR-QiTOf instrument from Ionicon Analytik (Sulzer et al., 2014), which achieved a benzene sensitivity up to 2900 cps/ppb.

As discussed in the introduction, the operation of a QMS and a TOF-MS is different. The TOF instruments acquire full mass spectra every second (or faster), whereas PTR-QMS is usually operated in selected-ion mode with 1-sec measurement for each of the selected masses every ~15 seconds. So if the total counts measured in each 15-second period are calculated (the middle panel in Figure 11), the overall signal to noise of the ToF instruments will compares very favorably to the PTR-QMS.
Consistent with the sensitivities, 1-s detection limits of H$_3$O$^+$ ToF-CIMS are close to those in PTR-QMS and better than the PTR-TOF used during the UBWOS 2013. As with sensitivities, the detection limits of TOF instruments compare more favorably to QMS if measured data is averaged to the total cycle length of a PTR-QMS to scan the selected masses for their dwell time. We note that the detection limits for methanol, acetone and benzene in the PTR-QiTOF were not reported in Sulzer et al. (2014), and hence a comparison with H$_3$O$^+$ ToF-CIMS is not possible at this point.

3.6 Inter-comparisons with GC-MS

In addition to H$_3$O$^+$ ToF-CIMS for VOC measurements, whole air samples were collected into canisters in-flight and were analyzed post-flight by GC-MS (iWAS) during the SONGNEX campaign. A total of 72 samples were obtained for most flights. The fill time for each canister was 3-15 s dependent on aircraft altitude. A brief description of the iWAS system was provided in recent publications (de Gouw et al., 2015; Warneke et al., 2016). A few compounds were measured by both H$_3$O$^+$ ToF-CIMS and the iWAS system, including benzene, toluene and C8 aromatics. For C8 aromatics, the H$_3$O$^+$ ToF-CIMS measured the total mixing ratios of the isomers, whereas the iWAS system was able to measure mixing ratios for the individual isomers (o-xylene, m/p-xylene and ethylbenzene).

Figure 12 compares measured results for benzene, toluene and C8 aromatics between H$_3$O$^+$ ToF-CIMS and iWAS. The agreement between the two instruments is good for all three aromatic species, with slopes in the range of 0.89-1.1 and correlation coefficients ($R$) larger than 0.9. We note that there are a few data points with larger disagreement, which are the result of imperfect time alignment of the two measurements during large transient concentration spikes downwind from point sources.

3.7 Applications to ambient measurements

As mentioned above, the H$_3$O$^+$ ToF-CIMS was deployed onboard the NOAA WP-3D during the SONGNEX campaign. Figure 13 shows measurement results from a portion of a flight on April 13, 2015 over the Denver-Julesburg Basin, which is an active oil and gas extraction region. Mixing ratios of benzene and toluene were elevated over and downwind from the oil/gas field. Several concentration spikes of the two aromatics were observed and attributed to large point sources related to oil and gas activities. Urban
emissions may also contribute to the mixing ratios of benzene and toluene, when the NOAA WP-3D flew over the cities (Loveland, Fort Collins and Greeley) in the area. As shown in Figure 13, variations of benzene and toluene mixing ratios below 100 ppt still tracked each other well, illustrating the low detection limits of the two compounds in the H$_3$O$^+$ ToF-CIMS. As the emissions of aromatics and other VOCs from motor vehicles are declining in both U.S. and European cities (Warneke et al., 2012; Derwent et al., 2014), the need for techniques (e.g. our H$_3$O$^+$ ToF-CIMS) that can measure these compounds rapidly and accurately with low detection limits is increasing.

Concentration peaks of acetonitrile were detected several times in this period, when the aircraft sampled plumes from agricultural burns in the area (de Gouw et al., 2003b). The concentration peaks of acetonitrile were pretty narrow, especially the one at 21:34 UTC (see the inserted graph in Figure 13B). These small fire plumes can be easily missed if a PTR-QMS had been applied for the detection of acetonitrile, as PTR-QMS has a duty cycle of only a few percent for each individual mass, as shown in the inserted plot in 13B. Along with acetonitrile, furan and furfural were also observed in these biomass burning plumes. Furan is a known emission from biomass burning and has been detected in the atmosphere mainly using PTR-MS (de Gouw and Warneke, 2007; Karl et al., 2007). In PTR-QMS, furan cannot be distinguished from isoprene. Its aldehyde derivatives, furfurals, were only measured in a recent laboratory experiment of biomass burning emissions (Stockwell et al., 2015) and in a forest fire plume in the US (Müller et al., 2015) both by PTR-TOF.

The third class of compounds shown in Figure 13 is acetaldehyde and acetone. Time series of the two OVOCs were similar to those of benzene and toluene with elevated mixing ratios over and downwind from the oil and gas wells, but they lacked the concentration spikes observed for the aromatics, consistent with secondary formation as their main sources. Acetaldehyde and acetone were also enhanced in the biomass burning plumes.

As a final example, acetic acid and ethanol were observed in both oil/gas and biomass burning plumes. Additional peaks of acetic acid and ethanol were detected shortly before and after 21:00 UTC. These enhanced mixing ratios were believed to be the result of emissions from agricultural facilities in this area. Weld County, the main...
flight area shown in Figure 13, is home to over half million beef and dairy cattle in over 100 feedlots facilities. Emissions of acetic acid and ethanol from dairy operations have been reported recently in the Central Valley of California (Gentner et al., 2014).

Figure 13 demonstrates that four different groups of VOC species exhibited with distinctly different time series and spatial distributions, as the result of their different sources. The examples in Figure 13 illustrate that the high time resolution dataset from H$_3$O$^+$ ToF-CIMS provides important information on characterizations of various air masses in the atmosphere. Along with unique tracers (e.g. acetonitrile for biomass burning), rich information on the chemical signatures will help to identify and separate the contributions of different sources to air mass components in the atmosphere. Measurements of secondary products, in conjunction with primary emissions will be valuable to constrain chemical evolution of gas-phase organic carbon in the atmosphere.

4. Conclusions

In this study, an aircraft-deployable H$_3$O$^+$ ToF-CIMS instrument was developed based on a commercial Aerodyne ToF-CIMS. We characterize the humidity dependence of reagent ions and instrument sensitivities for various VOC species. The new H$_3$O$^+$ ToF-CIMS has sensitivities in the range of 100-1000 cps/ppbv for many VOCs of interest and the 1-s detection limits are in the range of 20-500 ppt depending on product ion masses and their instrument backgrounds. The instrument was deployed onboard the NOAA WP-3D research aircraft as part of the SONGNEX campaign in March-April of 2015. The measured mixing ratios for several aromatics from the H$_3$O$^+$ ToF-CIMS agreed very well with independent GC measurements from whole air samples. Some initial results from the instrument demonstrate that the H$_3$O$^+$ ToF-CIMS dataset will be extremely valuable for the characterization of VOC emissions and photochemistry in the atmosphere.

We showed that the low transmission of H$_3$O$^+$ ions and secondary ion chemistry inside the SSQ complicates signal normalization and interpretation of the humidity dependence of VOC sensitivities. Further development by removal of the SSQ may ameliorate this issue and is being considered. We also anticipate a further increase in sensitivities from these modifications, as shown in a recent publication (Sulzer et al., 2014). We show that many instrument settings, including SSQ pressure, RF voltages in quadrupoles and the axial voltage gradients along the quadrupoles, affect both reagent
ions and VOC signals significantly in our instrument. Some of these effects were
explored or seen in other Aerodyne TOF-CIMS instruments as well (Zheng et al.,
2015; Lopez-Hilfiker et al., 2015). The next generation of PTR-MS (PTR-QiTOF) that
uses quadrupole ion guides for ion transmission may also be affected by some of
secondary ion chemistry in the quadrupole. Instruments using different ion chemistry are
expected to behave differently with these settings. Therefore, characterization of each
individual instrument for these variations and calibrations using authentic standards are
essential for generating high quality measurement data with these sophisticated CIMS
instruments.

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### Table 1. Sensitivities and detection limits of H$_3$O$^+$ ToF-CIMS for various VOCs

<table>
<thead>
<tr>
<th>VOC species</th>
<th>Ion Formula</th>
<th>Sensitivity$^1$</th>
<th>Background, cps$^2$</th>
<th>α value$^3$</th>
<th>l-s detection limit, ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ncp/ppt</td>
<td>cps/ppb$^2$</td>
<td></td>
<td></td>
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<tr>
<td>Methanol$^*$</td>
<td>CH$_3$OH$^+$</td>
<td>81</td>
<td>158</td>
<td>128</td>
<td>1.34</td>
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<tr>
<td>Acetonitrile$^*$</td>
<td>C$_2$H$_3$NH$^+$</td>
<td>376</td>
<td>822</td>
<td>26</td>
<td>1.33</td>
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<td>Acetaldehyde$^*$</td>
<td>C$_2$H$_4$OH$^+$</td>
<td>289</td>
<td>654</td>
<td>499</td>
<td>1.36</td>
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<tr>
<td>Acetone$^*$</td>
<td>C$_3$H$_6$OH$^+$</td>
<td>354</td>
<td>916</td>
<td>261</td>
<td>1.28</td>
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<tr>
<td>Acetic acid</td>
<td>C$_2$H$_4$O$_2$H$^+$</td>
<td>209</td>
<td>551</td>
<td>660</td>
<td>1.40</td>
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<td>Furan</td>
<td>C$_4$H$_4$OH$^+$</td>
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<td>470</td>
<td>11</td>
<td>1.26</td>
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<td>Isoprene$^*$</td>
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<td>206</td>
<td>26</td>
<td>1.21</td>
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<tr>
<td>MVK</td>
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<td>454</td>
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<td>C$_6$H$_5$H$^+$</td>
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<td>579</td>
<td>6</td>
<td>1.39</td>
</tr>
<tr>
<td>o-xylene$^*$</td>
<td>C$_6$H$_9$OH$^+$</td>
<td>193</td>
<td>673</td>
<td>4</td>
<td>1.49</td>
</tr>
<tr>
<td>1,2,4-TMB$^*$</td>
<td>C$_9$H$_9$H$^+$</td>
<td>185</td>
<td>686</td>
<td>3</td>
<td>1.69</td>
</tr>
<tr>
<td>α-pinene$^*$</td>
<td>C$_10$H$_7$H$^+$</td>
<td>67</td>
<td>263</td>
<td>2</td>
<td>1.24</td>
</tr>
</tbody>
</table>

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$^1$ Sensitivity under dry condition;  
$^2$ Calculations using H$_3$O$^+$ signal at the typical level of 2.5×10$^6$ cps during the SONGNEX campaign. The signals or sensitivities are not corrected for the ToF duty cycle (see text).  
$^3$ α is the scaling factor of the errors in ion signals relative to Poissonian statistics (Equation 1).  
$^*$ Stars indicate that the compounds were calibrated in-flight using the ten-component gas standard.
Figure 1. Schematic drawing of the H$_3$O$^+$ ToF-CIMS. HC: hollow-cathode discharge; IC: intermediate chamber; SSQ: small segmented quadrupole; BSQ: big segmented quadrupole; PB: primary beam; MCP: microchannel plate detector.
Figure 2. (A) Signals of reagent ions and $H_3O^+ (H_2O)/H_3O^+$ ratio ($R_{37/19}$) as a function of SSQ pressure. (B) Signals of protonated benzene and acetone at constant mixing ratios of 2.5 ppb as a function of SSQ pressure. The light blue vertical dashed lines indicate the SSQ pressure (1.30 mbar) used during the SONGNEX campaign.
Figure 3. (A) Reagent ion signals as a function of water vapor mixing ratios in the instrument. (B) Inferred transmission ratios between H$_3$O$^+$ and H$_3$O$^+(H_2O)$ ions ($T_{H_3O^+}/T_{H_3O^+(H_2O)}$) as a function of water vapor mixing ratios. (C) The H$_3$O$^+$ signals and total signals of the two reagent ions that are corrected to the transmission factor of H$_3$O$^+(H_2O)$ ions as a function of water vapor mixing ratios. The measured H$_3$O$^+(H_2O)$ signals are also shown. The shaded areas in (B) and (C) indicate the possible ranges of the parameters, which are bounded by estimates from the depletion experiments of methanol and acetonitrile, respectively. (D) H$_3$O$^+(H_2O)/H$_3$O$^+ (R_{37/19})$ as a function of water vapor mixing ratios during SONGNEX and from laboratory experiments. The black line is the linear fit to all of the SONGNEX data.
Figure 4. Normalization and humidity dependence of acetone and benzene detection from a laboratory experiment. (A) Background subtracted raw signals of protonated acetone and benzene with mixing ratios of 8.0 ppb as the function of $R_{37/19}$. The signals of $H_3O^+$ and $H_3O^+ (H_2O)$ are also shown for reference. (B) Signals of protonated acetone and benzene normalized to the $H_3O^+$ signal as a function of $R_{37/19}$. 
Figure 5. Derived humidity dependence curves for the normalized signals relative to dry condition as a function of $R_{37/19}$ ratios for oxygenates (A) and hydrocarbons (B), respectively. The humidity dependent curves of benzene and acetone are shown in both panels.
(A) and (B). The thick gray lines indicate the reciprocal of the $\text{H}_3\text{O}^+$ signal relative to dry conditions ($\frac{1}{m_{19}}$). Vertical dashed lines in A and B indicate the level of $R_{37/19}$ under dry condition. (C) Normalized signals at $R_{37/19}=1.4$ (equivalent to RH=90% at 25 °C) relative to dry condition for different VOC species as a function of their proton affinities. Data points are color-coded using the permanent dipole moment of the species. The two purple vertical dashed lines are proton affinities of water and water dimer, respectively. The two black dashed lines indicate the linear fits to the species with permanent dipole moment larger than 1 ($y=-1.30+2.52\times10^{-3}\times\text{PA}$) and lower than 1 ($y=-1.38+2.29\times10^{-3}\times\text{PA}$), respectively.
Figure 6. (A) Normalized signals relative to dry condition for protonated and dehydrated ions of isopropanol as a function of $R_{37/19}$ ratios. The vertical dashed line indicates the level of $R_{37/19}$ under dry condition. (B) Normalized signals relative to dry condition for protonated ion of ethanol as a function of $R_{37/19}$ ratios.
Figure 7. (A) The ratios of hydrated ions to protonated ions for several OVOC species as a function of $R_{37/19}$ ratios. (B and C) Normalized signals relative to dry condition for protonated and hydrated ions of formic acid (HCOOH, B) and isocyanic acid (HNCO, C) as a function of $R_{37/19}$ ratios. The ratios of hydrated ions to protonated ions for formic acid and isocyanic acid versus $R_{37/19}$ ratios are also shown in (B) and (C), respectively. Vertical dashed lines in each panel indicate the level of $R_{37/19}$ under dry condition.
Figure 8. Separation of benzaldehyde and C8 aromatics from the nominal mass at m/z 980 in a period (18:15-18:45 UTC) during the flight over the Permian Basin on April 23, 2015. (A and B) HR peak fittings of mass spectra at m/z 107 at 18:25 and 18:37, respectively. (C) Time series of benzaldehyde and C8 aromatics during the period. Flight altitude of the NOAA WP-3D aircraft is included in C.
Figure 9. Inflight calibration results of benzene (A), isoprene (B), acetaldehyde (C) and acetone (D) during the SONGNEX campaign. Signals for the species have been humidity corrected. Data points are color-coded using $R_{37/19}$ ratios. The total times (N) when gas standard was introduced into the instrument during SONGNEX and correlation coefficients (R) are shown in the textbox.
Figure 10. Scatterplot of the standard deviations of background signals versus the measured background signals from a flight on April 27, 2015 during SONGNEX. In this graph, the signals are not corrected for the ToF duty cycle to better reflect the counting statistics of the ToF detector. The two dashed lines are $\sqrt{N}$ and $2\sqrt{N}$, respectively.
Figure 1. Comparison of the sensitivities (A), total ion counts from measurements in a period of 15 s (B) and 1-s detection limits (C) of methanol, acetone and benzene for the NOAA PTR-QMS (Warneke et al., 2011), a PTR-TOF during UBWOS 2013 (Warneke et al., 2015), the PTR-QiTOF in Sulzer et al. (2014) and the $\text{H}_3\text{O}^+$ ToF-CIMS presented here during SONGNEX. In (B), we assume that the PTR-QMS was operated at the typical cycle length of 15 s with 1-s dwell time for the three compounds as have been the norm during our aircraft measurements. Note that the detection limits (DL) of methanol in panel C are drawn on the right axis.
Figure 12. Comparison of measured mixing ratios of benzene, toluene and C8 aromatics between the H$_3$O$^+$ ToF-CIMS and iWAS (Lerner, in prep) during the SONGNEX campaign.
Figure 13. VOC measurements by the H$_3$O$^+$ ToF-CIMS for the characterization of air masses and atmospheric photochemistry during a part of the flight (20:50-22:00 UTC) on April 13, 2015 over the Denver-Julesburg basin. Time series of various VOC species from oil/gas or urban emissions (A), biomass burning (B), secondary formation (C) and agricultural emissions (D) are shown. The inserted plot in B highlights acetonitrile around 21:34 UTC, where the black dots indicate re-sampled acetonitrile data every 15 s, reflecting measurement results if a PTR-QMS had been deployed onboard the NOAA WP-3D. Flight tracks color-coded using mixing ratios of benzene (E), acetonitrile (F), acetaldehyde (G) and acetic acid (H) are shown in the right panels. Urban regions and locations of oil and gas wells are indicated in the right panels. The arrow in E indicates wind direction in the boundary layer during this period.