We thank the reviewer for the helpful comments on the manuscript. Our point-to-point responses to each comment are as follows (reviewer comments are in black, and author responses are in blue).

The authors describe a characterization study on a new ion source which is tailored for field-deployable time-of-flight mass spectrometers, which are widely used by the atmospheric science community. The procedure of electrospraying methanolic salt solutions of alkali metals and ammonium for positive ion generation is described as a major advantage compared to radioactive source materials, which are subject to certain restrictions and regulations. Gas-phase measurements are demonstrated for a limited number (three) of standards, and ion-source flow and humidity dependencies are investigated. The application of the source with four different cluster ion systems (Li^+, Na^+, K^+ and NH_4^+) is demonstrated using α-pinene ozonolysis as a surrogate system for ambient SOA.

While the manuscript certainly falls into the scope of AMT, I have some major objections that need to be addressed before publication.

1) The manuscript does not provide a sound argument why the presented technique is an alternative to already existing techniques, such as e.g. proton-transfer reaction (PTR) technology. While the argument of providing a non-radioactive way of charge generation is certainly valid, the authors only indirectly mention (by the citation of e.g. Veres 2008 and Yuan 2016) that a common way to generate ions for atmospheric measurements is the use of hollow cathodes or corona discharge.

A certainly novel characteristic of the described technique is the sampling with an orthogonal high flow rate at atmospheric pressure across the inlet capillary, which likely reduces sampling losses of highly oxidized, low-volatile compounds. The presented design enables the authors to measure oxidized monomers and dimers of α-pinene oxidation in the gas phase that are usually not accessible with common PTR inlets. However, Breitenlechner et al. (2017) recently have shown that PTR ionization using charged water clusters as reagent ions is sensitive towards monomeric and dimeric α-pinene oxidation products in the gas phase at ppqv levels. This demonstrates that the gas inlet design is crucial for successfully measuring highly oxidized compounds in the gas phase. Breitenlechner et al. demonstrated that the whole volatility spectrum of VOCs, SVOCs, LVOCs and ELVOCs can be covered by PTR and thus it is questionable that one needs multiple complementary ionization schemes (as stated in l. 80).

Response: We appreciate the reviewer's point, and have added a reference to the new PTR-3 to the introduction as it is showing an impressive sensitivity to a wide range of organic compounds. Our experience has been that each reagent ion chemistry has advantages and disadvantages

depending upon the analytical goal. Adduct ionization can lead to humidity dependencies or ion-induced dimers (as discussed herein), while reactive charge transfer methods such as PTR can lead to water loss from alcohols or nitric acid loss from nitrates and thus changes in the spectrum compared to the sample as discussed in Blake et al. (2009).

One of the major characteristic of the CIMS techniques including PTR technology is their high selectivity. The volatility and polarity spectra of the targeted species largely depend on the selection of reagent ions. Although a specific reagent ion may sensitively detect species spanning a wide spectrum of volatility or polarity, it may not be able to cover all of the species presented within the spectrum. For example, as presented in this study, the Na^+ reagent ion is sensitive to the species covering the volatility spectrum of VOCs, SVOCs, LVOCs, and ELVOCs, as well as the polarity spectrum of less oxygenated and highly oxygenated species. However, some species such as the very small species (CH_2O_2, CH_2O_3, and $C_2H_2O_3$) and certain highly oxygenated species detected by I^- and NO_3^- are not detected or sensitively detected by Na^+, presumably because of the low sensitivity to these specific species.

Moreover, this comment seems only relevant to organic compounds, but there is continued interest in a suite of inorganic vapors for atmospheric chemistry including halogens, reactive nitrogen oxides, and reduced nitrogen species which may be detected well by some ionization methods and not others. Therefore, multiple complementary ionization schemes are needed to obtain a comprehensive view of a complex chemical system such as that found in the atmosphere.

The electrospray chemical ionization (ESCI) source presented in this work provides an alternative to radioactive sources and allows the production of reagent ions (e.g., Li^+, Na^+, K^+ and NH_4^+) that are largely unavailable in current CIMS techniques, including ionization methods that utilize hollow cathodes or corona discharge methods. Thus, the work provides a new alternative form of ionization with a good deal of flexibility to study ionization of compounds by adduct formation across a range of binding enthalpies.

2) The authors state that the main advantage of CIMS is the inherently quantitative character when applying the kinetic theory of gases. To estimate the upper limit ionization efficiency it is a prerequisite that the flows in the IMR region are laminar in order to calculate the interaction time between ions and neutrals. Any flow disturbance or pressure fluctuation in the ionization region can result in turbulent mixing in which secondary ion interactions can become dominant. Therefore the authors evaluated the design with CFD simulations (not shown) and found that under the investigated conditions flows are in the laminar regime.

However, when using electrospray as a source and sampling ambient air of different humidity, ions do appear solvated by alcohol or water clusters (e.g. Horning,1974; Garvey, 1994). This implies that the ion mobility of the charged clusters in the IMR is different from the values stated for unsolvated NO_3^- and Na^+ stated in line 145 and thus the interaction time between ion clusters and gas phase analytes is unknown. The fact that water vapour concentration changes the cluster

size distribution (ion source residence time) and thus affects the sensitivity should be added to the discussion in l. 274 ff.

Furthermore, it can also not be excluded that secondary reactions occur in the ion transfer optics hindering the estimation of ionization efficiency.

Response: We agree that the reagent ions can be solvated by methanol or water clusters in the IMR. Because of the lack of information on the ion mobility of the solvated reagent ions, the reaction time between these reagent ions and gas phase analytes in the IMR is currently unknown. However, given that the ion mobility of solvated ions is generally smaller than unsolvated reagent ions, the actual ion-molecule interaction time in the IMR is expected to be longer than that estimated for the unsolvated ions.

We have modified the statement around line 145 (changes underlined):

"Under laminar flow conditions, the reaction time between reagent ions and sampled trace gases in the IMR is mainly determined by the electric field-induced drift velocity of the reagent ions. For instance, for two reagent ions used in this study, NO_3^- and Na^+, the ion molecule reaction time (i.e., ion drift time) in the IMR is estimated to be 0.5-1 ms and 0.4-0.7 ms, respectively, with an ion mobility of 2.37 $cm^2 s^{-1} V^{-1}$ for NO_3^- (Ellis et al., 1978) and 3.4 $cm^2 s^{-1} V^{-1}$ for Na^+ (Bohringer et al., 1987) under typical operation conditions (2-4 kV across the IMR). However, when using electrospray as a source and sampling ambient air of different humidity, the reagent ions can be solvated by methanol or water clusters (Horning et al., 1974; Garvey et al., 1994). As the ion mobility of solvated reagent ions is likely smaller than the values for unsolvated reagent ions, the ion-molecule reaction time between solvated reagent ions and gas phase analytes in the IMR is expected to be longer than that estimated for the unsolvated ions."

We have also modified the paragraph in lines 274-281 (changes underlined):

"The presence of water vapor can affect sensitivities, either by competing for I^- ions, thus lowering the sensitivity, or by accommodating excess energy from the collision to stabilize the Iodide-molecule clusters, thereby increasing the sensitivity (Lee et al., 2014; Iyer et al., 2016). Water vapor may also affect sensitivities by changing the size distribution of reagent ion clusters and thus their residence time (ion-molecule reaction time) in the IMR. Moreover, water vapor can affect the transmission of soluble gases through sample tubing. It is difficult to evaluate the effect of changing cluster size distribution as the information regarding the distribution and ion mobility of the reagent ion clusters is currently unavailable. In the current configuration of the ESCIMS, it is also difficult to isolate the sample transfer effect experimentally as done previously in low-pressure IMR regions by using separate delivery lines for calibrants and water vapor. Thus, our results shown here reflect a combination of ionization efficiency, cluster distribution, and sample transfer aspects."

The secondary reactions in the ion transfer optics cannot be ruled out, but they are usually assumed to be negligible for estimating the maximum sensitivities.

3) The list of reagent ions in CIMS (l. 69) does not mention protonated ethanol for selective measurements of gas phase NH_3, DMSO and VOCs (Nowak, 2002). In addition to this, I wonder what would be seen with the described system when using only methanol instead of a methanolic solution of the described salts. In theory methanol has a slightly smaller proton affinity than ethanol (7.9 vs 8.2 eV) and one might observe ionization by proton transfer reactions from methanol electrospray itself (via the reagent ion clusters $(CH3OH)_nH^+$).

Furthermore, are proton transfer reactions observed when using NH_4^+ as reagent ion?

Response: Thanks for catching this oversight. We have modified the sentence in line 69 (changes underlined):

"The reagent ions used mainly include I^-, NO_3^-, acetate, CF_3O^-, and SF_6^- for negative ion CIMS, and H_3O^+, NO^+, protonated ethanol, and benzene cation for positive ion CIMS."

We have not tried using only methanol as the electrospray liquid. However, we did not see evidence of protonated methanol clusters when electrospraying a methanolic solution of the described salts. Our comparisons of spectra also do not provide any obvious evidence for proton transfer reactions when using NH_4^+ as the reagent ion for the a-pinene ozonolysis system.

We have also added the following statement after line 170:

"No evidence of protonated methanol clustering was observed when electrospraying a methanolic solution of the described salts except at the extreme voltage differences between the lens and entrance capillary where it was likely a discharge developed. Although the reagent ion is likely solvated by methanol initially, the sensitivity of the ionization to various trace gases did not appear to be significantly affected in the present study."

4) Electrospray ionization has previously been reported in an extraction mode, in which online measurements of aerosols (Gu, 2010) and especially a-pinene SOA (Doezema, 2012; Gallimore, 2013) has successfully been demonstrated. The apparent question related to these publications and the reported application to chamber studies of a-pinene SOA is: How can the authors rule out that the observed signal does not emerge from aerosol particles? This is not discussed in the manuscript but might have fundamental consequences on the interpretation made in chapter 3.4. The figure that needs to be shown is that the gas phase concentration is independent of SOA mass.

Response: In the present study, the ESCI source is coupled to an orthogonal continuous-flow atmospheric pressure IMR region. Under typical sample flow and ion source flow conditions, the mixed flow in the IMR remains laminar, and the sample flow acts to carry the unevaporated

droplets entering the IMR away from the effective ionization region, thus largely isolating the electrospray plume from incoming samples, making the ESCI source a chemical ionization source rather than extractive or secondary electrospray ionization (EESI or SESI).

The evidence of the ESCI source being a chemical ionization source and not EESI or SESI can be provided by monitoring the signal ratio of $NO_3^-/I(HNO_3)^-$ when sampling gas phase HNO_3 in the iodide mode. If the direct interaction between electrospray plume and incoming sample flow is important, HNO_3 dissolved in charged droplets can dissociate forming H^+ and NO_3^-, leading to the generation of NO_3^- ions in the negative ion mode. Therefore, a large signal ratio of $NO_3^-/I(HNO_3)^-$ is expected. Figure R1 shows the signal ratio of $NO_3^-/I(HNO_3)^-$ as a function of gas phase HNO_3 concentration under dry and wet conditions observed in the iodide mode. The signal ratios of $NO_3^-/I(HNO_3)^-$ are significantly smaller than 0.01 at various HNO_3 concentrations, suggesting the direct interaction of electrospray plume with incoming samples is not important in the ESCI source.
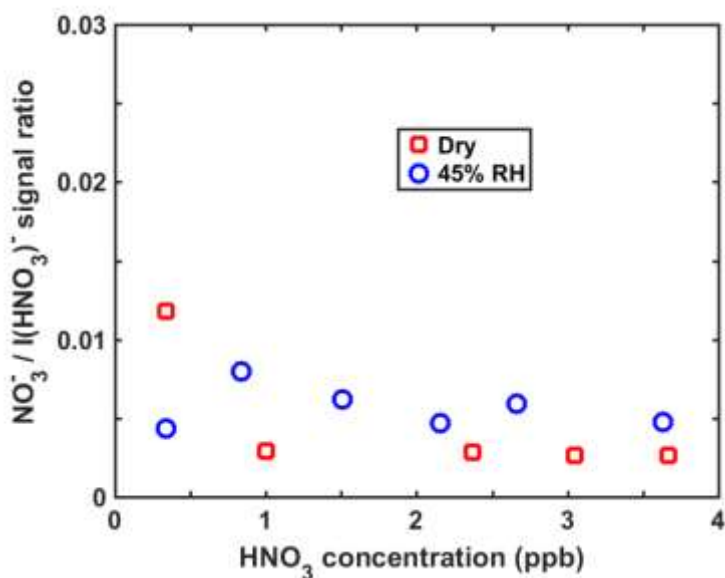
Figure R1 Signal ratio of $NO_3^-/I(HNO_3)^-$ as a function of HNO_3 concentration under dry and wet conditions observed using iodide as the reagent ion.

We have added Figure R1 and following paragraph after line 146.

"Under typical operating conditions, the sample flow likely transports any unevaporated droplets away from the effective ionization region in the IMR, thus largely isolating the electrospray plume from the incoming samples, making the ESCI source a chemical ionization source rather than secondary or extractive electrospray ionization (SESI or EESI) source. The evidence of the ESCI source being a chemical ionization source and not SESI or EESI is provided by monitoring the signal ratio of $NO_3^-/I(HNO_3)^-$ when sampling gas phase HNO_3 in the iodide mode. If the direct interaction between electrospray plume and incoming sample flow is important, HNO_3

dissolved in charged droplets can dissociate forming H^+ and NO_3^-, leading to the generation of NO_3^- ions in the negative ion mode. Therefore, a large signal ratio of $NO_3^-/I(HNO_3)^-$ is expected. Figure 2 shows the signal ratio of $NO_3^-/I(HNO_3)^-$ as a function of gas phase HNO_3 concentration under dry and wet conditions observed in the iodide mode. The signal ratios of $NO_3^-/I(HNO_3)^-$ are significantly smaller than 0.01 at various HNO_3 concentrations, suggesting the direct interaction of electrospray plume with incoming samples is not important in the ESCI source."

5) Chapter 3.4.3: While the work by Lopez-Hilfiker et al. (2016) was conducted at IMR pressure 70 Torr, the reported work samples from an atmospheric pressure IMR. Thus, I assume that the pressure in the transfer ion optics reported in this work is significantly higher than in the work by Lopez-Hilfiker et al. (2016). How does the pressure in the transfer quadrupoles affect the declustering?

Response: In the present work, a stainless steel capillary tube (20 mm long, 0.13 mm ID) acts as the atmospheric pressure interface between the IMR and the vacuum chamber of the MS, and effectively drops the pressure from 1 atm in the IMR to about 1.5 Torr in the first quadrupole of the MS. The pressure in the transfer ion optics in the present study is very similar to that in the work by Lopez-Hilfiker et al. (2016). Thus, the deculstering results obtained in the two studies can be compared.

We have modified the sentences in lines 131-133 (changes underlined):

"The SS capillary projects 3.5 mm into the IMR and acts as the atmospheric pressure interface between the IMR and the vacuum chamber of a commercial HRToF-MS (Tofwerk AG, Thun, Switzerland), effectively dropping the atmospheric pressure in the IMR to 1.5 Torr in the first quadrupole of the MS."

6) The conclusion that the observed dimers are covalently bound molecules instead of non-covalently bound clusters cannot be made, since the authors do not show that ion cluster dimers show a different declustering profile in the Li-mode. Furthermore, the fact that gas-phase dimers are covalently bound molecules was already reported by Kirkby et al. (2016), contrary to the statement in l. 438 ff.

Response: See our response to reviewer 1. We have modified the conclusion that the dimer ions have adduct energies with Li^+ that approach covalent bonds. As the behavior and formation mechanism of dimers is out of the scope of characterizing and showing the promise of ESCI source in the present study, we have deleted the discussions about the dimers in lines 436-444.

Minor comments:

l. 88: $NH4^+$ is not a metal cation- Li^+ is missing.

Response: We have revised "certain reagent ions such as metal cations (e.g., Na^+, K^+, and NH_4^+)" as "certain reagent ions such as metal cations (e.g., Li^+, Na^+, and K^+) and NH_4^+".

l. 92 - 93: Why is it expected that metal cations are less selective toward HOMs? Furthermore, it is not possible to infer carbon oxidation state from the molecular composition. E.g. an hydroperoxide and an alcohol functional group lead to the same carbon oxidation state but different avg. OSC. Also a carbonyl group is a higher carbon oxidation state than a hydroperoxide.

Response: It is more that the metal cations are more sensitive to less oxygenated compounds than are I^- and NO_3^-. Compared to I^- and NO_3^-, which are significantly more sensitive to highly oxygenated organic compounds than to less oxygenated ones, the metal cations such as Li^+, Na^+, and K^+ are less selective because in our system they can sensitively detect both less oxygenated (e.g, compounds containing only carbonyl groups) and highly oxygenated multi-functional organic species. We are now careful to specify that by carbon oxidation state we mean average oxidation state of carbon in the molecule.

To clarify these points, we have modified the sentences in lines 91-96 (changed underlined):

"Compared to I^-, NO_3^-, and acetate, which are significantly more sensitive to highly oxygenated organic compounds than less oxygenated ones (Aljawhary et al., 2013; Lee et al., 2014, Hyttinen et al., 2015; Iyer et al., 2016, Berndt et al., 2016), these metal cations are expected to be less selective toward oxygenated organic compounds and can be used to sensitively detect both less oxygenated (e.g, compounds containing only carbonyl groups) and highly oxygenated multi-functional organic species (Gao et al., 2010; Nguyen et al., 2010; Nizkorodov et al., 2011; Laskin et al., 2012; Witkowski and Gierczak, 2013; Zhao et al., 2015; Tu et al., 2016; Zhao et al., 2016; Zhang et al., 2017)"

l. 133: What is the sample flow of the MS?

Response: The sample flow of MS is about 300 sccm. We have added this to the revised manuscript.

l. 143: Na+ superscript.

Response: We have revised this.

l. 217: What is the driving force of evaporation? Temperature or dilution into a solvent-free sample flow?

Response: The driving force of evaporation includes both the addition of a flow of ultra-high purity N_2 to the evaporate tube and the dilution into a solvent-free sample flow. However, as the sample flow can quickly carry the unevporated droplets out of the effective ionization region, the

evaporation of these droplets would not be a major contributor to the total ion signal (see the reply to Major Comments #4).

Although we did not investigate the temperature effect on evaporation, we believe that a higher temperature (e.g., a heated ion source flow) can further improve the evaporation and is worth considering in the further development and characterization of the ESCI source.

l. 246: Why is the ion molecule reaction time in ESCIMS shorter than in low-pressure CIMS?

Response: The ion-molecule reaction time in ESCIMS is determined by the electrical-induced ion drift velocity of the reagent ions. The lower limit is equal to the residence time of unsolvated reagent ions and is, for example, 0.5-1 ms for NO_3^- and 0.4-0.7 ms for Na^+ when there is 2-4 kV across the IMR. In contrast, the ion-molecule reaction time in low-pressure CIMS is determined by the flow conditions in the IMR and is typically 30 to 100 ms (Lopez-Hilfiker et al., 2016; Bertram et al., 2011; Lee et al., 2014).

l. 307: The background signals in Figure 5a are lower than those written.

Response: Thank you for pointing this out. The y-axes in all mass spectrum figures including Figure 5 actually represents the signal density, i.e., d(Signal)/d(m/Q), and the ion signal is equal to the integration of the peak area. We have revised the y-axes label "Signal (cps)" as "d(Signal)/d(m/Q) (cps)" in all the mass spectrum figures. .

l. 327: misspelling: reagent

Response: We have revised this.

l. 424: misspelling: reagent

Response: We have revised this.

l. 429: Why are the declustering scans for the monomers not shown?

Response: Scans for the monomers are discussed in the text, but for example purposes, the differences in the behaviors resulting from the reagent ions Li^+, Na^+, K^+, and NH_4^+ were simply cleaner and clearer using the dimers. These ions have more uncertainty regarding their source and structure and thus provide a scientifically more interesting example. As noted above, in the case of Li^+, these dimer ions are very strongly bound and would therefore provide a good test case for quantum chemical modeling of the binding energies of a covalent dimer compared to two monomers surrounding the ion. Thus, we wish to highlight the dimer ions here as monomer ion declustering behaviors for Iodide are shown in this study and discussed in detail in Lopez-Hilfiker et al. (2016).

Figure 8: What is the peak-width of the measured signals in y-direction? Some of the dimers have a very large positive mass defect (>0.2 at m/z < 300). What is the elemental composition of these signals?

Response: The peak-width at half height is 0.03 at m/z 127 and 0.07 at m/z 381. The dimers with a mass defect > 0.2 and m/z < 300 have low O:C and high H:C ratios. Their molecular formulae include $C_{15}H_{28-30}O_2$, $C_{16}H_{30-32}O_{2-3}$, $C_{17}H_{28-30}O_{2-4}$, $C_{18}H_{28-32}O_3$, etc.