Review on: **"An electrospray chemical ionization source for real-time measurement of atmospheric organic and inorganic vapors"** by Zhao et al.

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 NH4+) 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).

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 NO3- 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.

3) The list of reagent ions in CIMS (l. 69) does not mention protonated ethanol for selective measurements of gas phase NH3, 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 NH4+ as reagent ion?

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.
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?
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.

Minor comments:

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

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. OS_C. Also a carbonyl group is a higher carbon oxidation state than a hydroperoxide.

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

l. 143: Na+ superscript.

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

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

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

l. 327: misspelling: reagent

l. 424: misspelling: reagent

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

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?

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