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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measurement of formic acid, acetic acid and hydroxyacetaldehyde, hydrogen peroxide, and methyl peroxide in air by chemical ionization mass spectrometry: airborne method development" *by* Victoria Treadaway et al.

Anonymous Referee #1

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This study details the detection and quantification of a selection of important atmospheric molecules using a multi-reagent ion chemical ionization mass spectrometer (CIMS). The multi-reagent ion system reported here blends CO2 in air and CH3I in N2, with the primary reagent ions being O2-, CO2(O2)-, and I-. This is different from previously implemented multi-reagent ion systems, as the two reagent gases are added simultaneously and tuned such that I-, O2-, and CO2(O2)- ion cluster chemistries are operable. The multi-reagent system was successfully deployed in ambient air-borne and laboratory measurements. This novel twin-reagent CIMS technique is likely to be in-

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teresting to researchers working with CIMS instruments to detect important gas-phase atmospheric molecules. The less selectivity of O2- (and CO2(O2)-) CIMS coupled with the better understood I- CIMS has potential to improve the current understanding of atmospheric gas-phase chemistry. I recommend publication of the manuscript after some relatively minor issues (detailed below) are addressed.

âĂć Line 145: What is the reaction time between the sample gas and the reagent ions inside the ion-sample reaction cell?

âĂć Line 153: “This pressure was stated to provide the maximum yield of cluster ions and peak sensitivity. . .” Just checking, was this stated by the RXN cell manufacturer?

âĂć Line 165: Maybe mention the optimized mixing ratios of CO2 and pure air used for HP and MHP signals in addition to the reference to the O’Sullivan paper?

âĂć Figure 2: The figure presently does not provide a lot of information. What was the averaging time used to obtain the spectrum? Would a longer averaging time provide a less noisy spectrum with the relevant peaks clearly defined? I suppose the log scale was used to show the lower signals of I-(HP), I-(HFo), and I-(MHP) in the same figure. Maybe having a linear scale (so the highest peaks can be clearly shown), and a zoomed-in inset of these lower signals would make a better figure?

âĂć Trivial comment: Figure 4 has no a) and b) labels although it is referenced as such in the text.

âĂć Paragraph starting from line 399: Do you see an increase in signals of (H2O)nI- clusters (where n is 2,3,4. . .) at above 1000 ppm water vapor mixing ratio? It could be that, at higher degrees of hydration of the I- anion, (HAc)I- formation becomes unfavorable (probably due to a steric hindrance to (HAc)I- formation, i.e. the multiple water molecules attached to I- make the formation of I-(HAc) difficult), causing a decrease in sensitivity. On the other hand, I-(HFo) formation might become more favorable when multiple water molecules are attached to I- (HFo being a smaller molecule might be ad-

ditionally stabilized by a sequential evaporation of multiple water molecules), explaining the increase in I-(HFo) sensitivity at higher water vapor mixing ratios you report. In any case, the possible detection of water dimers, trimers, tetramers clustered to I- at high water vapor concentration should probably be commented upon.

âĂć Continuing on the same theme, I would think that the binding strength of (H2O)I- cluster is weaker than the (HAc)I- cluster, so a ligand-exchange reaction between HAc and water, which is reaction 4 in your manuscript, is likely not the reason for the decrease in (HAc)I- signal at higher water vapor concentrations.

âĂć Line 402: “indicated the switching reaction equilibrium for HAc (4) behaved like that for HFo. . .”. I might have misunderstood, but don’t you observe an increase in the sensitivity of (HFo)I- with an increase in water vapor mixing ratio? Does that then not imply that (HFo)I-, unlike HAc, is not affected by a possible ligand exchange reaction with water (reaction 4)?

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