

Review of Atmos. Meas. Tech. Discuss., 8, 10121-10157, 2015

This is a very interesting paper that demonstrates the applicability of benzene cluster cations to several important and hard to measure atmospheric species such as DMS. The paper is well written, well referenced, and concise. This paper represents a clear advance in measurement technology. I highly recommend publication but suggest that the authors address the following comments.

- 1) Page 10126, lines 6-10. The density of states of the benzene cation cluster is stated to be important to allow soft ionization. I am not sure I buy this argument. For example, you could have a cluster with a high density of states transfer a proton to an alcohol. The alcohol will still probably eliminate water and form a fragment ion. In this case the density of states of the reactant cluster ion is not critical issue. This statement should be modified or deleted or reference provided if left in the paper.
- 2) Page 10127, line 19. "significantly longer than the time scale of ion-molecule reactions to reach equilibrium". The time scale to reach equilibrium for an ion-molecule reaction depends on the energetics of the reaction as well as the concentrations of reactant. So this statement is a little broad. Perhaps a better statement would be something like "significantly longer than the time scale for most weakly bound clusters (e.g. water or benzene) to reach equilibrium."
- 3) Page 10128 line 16 – probably should be changed to a continuous dynode electron multiplier i.e delete the "and".
- 4) R4 is written as $N_2 + \alpha^{2+} \rightarrow N_2^+ + \alpha^+$, I think the reaction is probably better represented as:
 $N_2 + \alpha^{2+} \rightarrow N_2^+ + \alpha^{2+} + e^-$. This reaction also explains why negative ions can be made efficiently with a polonium source.
- 5) Page 10134, line 2. "due to the proton affinity of eucalyptol" This statement indicates that the proton affinity of eucalyptol is especially high? Is this the case? If so it should be stated and compared to the other species that don't have a proton transfer channel. Another possibility is that this species may be more hydrophilic than the other VOC studied which may favor a channel that leads to a hydrated, protonated ion.
- 6) Page 10134, line 21. The laboratory studies of the benzene-water clusters are interesting. However, if they are truly are a single benzene molecule with multiple waters I doubt they apply since it is almost certain that there are multiple benzene molecules in the ion clusters in this work. So I am not so sure that the conclusion that greater than three waters leads to effectively protonated water clusters. I would also suggest that this observation is inconsistent with the charge transfer chemistry that is primarily observed in this work. So I am not sure this discussion is applicable and the differences between the two experiments should be at least mentioned.
- 7) Page 10136, line 17. I am not sure what "choked flow conditions" mean.

- 8) In general the very strong water dependence on the α -pinene relative to DMS and isoprene is very interesting and very important to point out. I wonder if the α -pinene cation is more hydrophilic than the cations of DMS and isoprene? i.e. the reaction rate at higher water levels is driven by the solvation of the product cation. This might be an avenue worth exploring at some point to sort out which molecules are likely to have a strong water sensitivity.
- 9) The correlation between the CIMS measurement of DMS with the API measurement is very encouraging and a great first step. However, I was surprised that the data was compared on an hourly basis. Is this the time scale of the API measurement? If not it would be much more interesting to compare faster time scale data. For example, the authors state that the two sampling locations on the ship are effectively equivalent as there is good correlation between the two measurements. I think this statement is only true for an hour average which might not indicate that the two sampling environments are identical on short time scales (e.g. you might measure different DMS fluxes using eddy covariance). At the very least the choice of the time scale for the averaging needs to be discussed and the conclusions drawn tempered by the time scale of the comparison.
- 10) In the caption for Figure 11 it is stated that a slight humidity dependence is apparent. This is not obvious to me. I agree that some of the points most below the correlation line are at high humidity (blue circles). However, many of the points well above the line are at moderate humidities (i.e. yellow circles). So I think a little more analysis could be done to support this statement. For example looking at the ratio as a function of humidity or filtering the data as a function of humidity to give a better quantitative result to support this claim. Also the time scale of the data analyzed in this plot should be considered i.e. is this one hour data? Is water highly variable during this period?