

Response to two anonymous referee comments on Kim et al., *Revisiting benzene cluster cations for the chemical ionization of dimethyl sulfide and select volatile organic compounds*

We have organized the following response to include: (1) original comment/question from the referees, (2) our response to each comment/question (in blue), and (3) the change to be made in manuscript.

Referee #1

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.

Our statement regarding the density of states of benzene being responsible for the soft ionization is speculative and perhaps overstated. The reviewer is correct that alcohols (such as MBO) are shown to dehydrate using this ion chemistry, as the energy barrier for dehydration is very small, thus requiring an exceptionally soft ionization processes and minimal collisions post ionization. A more correct approach to this question is a quantum mechanical calculation of the reaction coordinate. The advantages of using a reagent ion with a high density of states likely comes into play when considering whether a weakly bound adduct can be stabilized.

In the revised manuscript this section will read: *The high density of states of C₆H₆ and (C₆H₆)₂ may also permit the efficient formation of weakly bound ion-neutral clusters, as collisional energy from ion-molecule reactions can be readily absorbed. However, the extent to which this is important is governed by the energetics of the specific ion-molecule reaction.*

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.”

Again, we agree that this statement should be tempered and agree with the authors suggested revision.

In the revised manuscript this section will read: *Reaction times are estimated to be on the order of 100 ms, 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”.

Agreed.

In the revised manuscript this section will read: *... continuous dynode electron multiplier ...*

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.

Agreed.

In the revised manuscript R4 will read: $N_2 + \alpha^{2+} \rightarrow N_2^+ + \alpha^{2+} + e^-$

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.

The reviewer is correct that this specific statement is not qualified and is speculative without a detailed comparison of proton affinities for the range of compounds. It is possible that the protonation channel is related to the hydrophilicity of eucalyptol.

In the revised manuscript this section will read: *“In the case of eucalyptol, a secondary ionization reaction was evident at the M-H⁺ channel.”*

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.

We think that the laboratory experiments of Ibrahim et al and Miyazaki et al. are interesting (as does the referee) and worthy of discussion and citation. However, we agree with the referee that the conditions of the Ibrahim and Miyazaki experiments may not translate to the conditions here and have revised the text to make that clear.

We have modified the statement as: *It is likely that the sensitivity dependence we observe in these experiments is related to the aforementioned laboratory studies and depends on the location of the charge (benzene vs. water) and the size of the benzene-water cluster (n), both of which are related to q. However, in our experiments it is almost certain that the reagent ion contains more than one C₆H₆ molecule limiting the direct comparison between the two studies. In what follows, we show that standard additions under a range of atmospheric values for q are required for accurate measurements of mixing ratios in the atmosphere.*

7) Page 10136, line 17. I am not sure what “choked flow conditions” mean.

Choked flow refers to a restricted flow condition controlled by the critical orifice in the custom glass manifold described by Ellis, et al. (2010). Under choked flow conditions, the sample flow rate is insensitive to downstream pressure fluctuations (i.e. pumping efficiency).

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.

This is an interesting comment and suggestion. This is certainly something we will explore further in the future.

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.

Since both instruments were deployed for eddy covariance measurements, concentration measurements were made at sampling rates of $>10\text{Hz}$. In the revised manuscript we will show the comparison of the 1-10 sec averages. We note however that DMS flux measurements between the two instruments (beyond the scope of this paper) displayed an R^2 better than 0.70.

The revised manuscript will have a revised Figure 11 that highlights either 1 or 10s averages.

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?

As noted above, we will remake Figure 11 with 1-10s data to address the referees concerns. However, we also note that the range in absolute humidity that was sampled was quite narrow and upon inspection of the dependence of the sensitivity on absolute humidity (as shown in Figure 9), DMS appears to be largely insensitive to Q between $3-8\text{ g kg}^{-1}$.

The revised manuscript will have a revised Figure 11 that highlights either 1 or 10s averages.

Referee #2:

Overall, this is a useful, well-written and relevant paper on benzene cation cluster CIMS, and is appropriate for publication in AMT after minor revisions. The paper describes laboratory experiments of DMS and select VOC calibrations, and shows a detailed intercomparison of DMS measurements during the HiWinGS study. The authors use comparison of two different CIMS with different setups and thus different electric fields to gain insight on ionization mechanisms. The authors propose charge transfer and ligand switch as mechanisms for different types of VOCs. The one component that is missing from this paper is an understanding of the water interference / impact of humidity on sensitivity. The observation of strong water sensitivity (Figure 10) perhaps suggests that a ligand switch with benzene-water clusters is very efficient for α -pinene, although as the authors note, no benzene-water clusters were observed. It is puzzling that the molecule that likely undergoes a charge transfer is more water sensitive than the molecules that clearly undergo ligand-exchange mechanisms. As much of the paper is focused on understanding the mechanisms of benzene CIMS, it would be useful for the authors to hypothesize a reason(s) for these observations.

It is true that at this time we do not have a detailed understanding of the physics and chemistry of the ion-molecule reaction that gives rise to the observed water dependence. In this manuscript we have taken the approach to characterize the dependence empirically and conduct standard additions in the field to capture this effect. We also highlight that the water dependence is unique to each analyte. A detailed investigation, involving quantum mechanical calculations is currently underway, but beyond the scope of this paper. Several hypotheses could be suggested for the water dependence, but we feel that this is conjecture at this stage and would like to reserve that discussion for a follow-up manuscript that addresses the question properly. This begins with a more detailed understanding of what the reagent ion cluster is under the operating conditions of the CI-ToFMS and the transition states that the ion-molecule adduct under goes en route to the observed product ions.

Detailed comments:

The first paragraph in Introduction emphasizes sesquiterpene contributions to biogenic SOA, but the paper does not rigorously discuss a sesquiterpene measurement - instead, it would make more sense to reframe the Introduction to place more emphasis on DMS and its relationship to marine SOA.

This is a fair point. We have extended the introduction to provide a few additional statements regarding DMS.

We have added the following statements to the introduction (10124 line 10): *The following paper focuses on the development of a chemical ionization procedure for targeting marine trace gas emissions (e.g., DMS, isoprene, monoterpenes) that, following oxidation, may have consequent impacts on aerosol particle mass loadings and size distributions.*

p 10127, line18-20: states "reaction times... are significantly longer than the timescale for ion-molecule reactions to reach equilibrium". Is there a reference for this? What are the timescales for ion-molecules reactions to reach equilibrium?

Please see the response to a similar comment in our responses to referee #1.

p10128, section 2.1.2: what is the residence time in the ion-molecule reaction chamber (same design, but higher pressure, suggesting a shorter residence time)?

While the pressure is slightly higher in the CI-QMS instrument (100 mbar compared to 70 mbar in the CI-ToFMS instrument) the residence time in the IMR is also on the order of 100 ms as the QMS was operated under slightly different inlet flow conditions.

p.10134, lines 3-4: eucalyptol is detected as M-H⁺ due to a proton transfer - but from what? Is that proton transfer from benzene⁺ reagent, or from the protonated water clusters?

Please see the response to a similar comment in our responses to referee #1.