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Comment

## ***Interactive comment on “Revisiting benzene cluster cations for the chemical ionization of dimethyl sulfide and select volatile organic compounds” by M. J. Kim et al.***

### **Anonymous Referee #2**

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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 sen-

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sitivity (Figure 10) perhaps suggests that a ligand switch with benzene-water clusters is very efficient for  $\alpha$ -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.

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.

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?

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)?

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

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