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Interactive comment on "Measured solid state and sub-cooled liquid vapour pressures of nitroaromatics using Knudsen effusion mass spectrometry" *by* Petroc D. Shelley et al.

Anonymous Referee #2

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Saturation vapor pressure (Psat) is essential for understanding and modeling of OA formation. Due the complexity of ambient OA, it is not feasible to measure the Psat and GCMs are frequently used for predicting Psat. However, GCMs can strongly overestimate the Psat due to a range of factors (e.g. underrepresentation of long-chain hydrocarbons and specific functional groups, a lack of data for the impact of intramolecular bonding). Although aromatic nitrates are important atmospheric compounds that contribute to OA formation, quality Psat data for them are not available. In this study, the authors provide Psat and thermodynamic data for 20 functionalized aromatic nitrates, including Nitro-phenols, Nitro-benzaldehydes, Nitrobenzoic acids. They performed a systematic investigation on how H bond effect, steric effects, dipole moments, and

crystallographic packing density affect the Psat. Moreover, the performance of GCMs is evaluated using the measured data set. The data presented in the manuscript are useful and give an insight into the impact of functional group positioning which is missing, or only available in a limited capacity, for the currently available GCMs. While this study can be a good contribution to atmospheric science, the presentation of the results can be improved. Thus, I recommend a major revision. Major Comments 1. Line 224-260 First of all, the authors spend a lot of effort in introducing some general information about inductive, resonance, and H-bond effects. I don't think it is appropriate to put all of this background information in the Results section. This information could be moved to the Theory section or even supporting information. Second, methoxy-phenols are not compounds of interest measured by this study. This study already included a lot of chemical compounds. I believe the authors can use the studied species to illustrate the relationship between H-bond energy and partial charge of the phenolic carbon. Moreover, figure 3 does not contain much useful information, and table 4 should be changed accordingly. 2. Line 270-348: Here, the authors present a lot of results to illustrate how the H-bond effect, steric effects, dipole moments, and crystallographic packing densities affect the Psat. It is challenging to follow the description and interpretations based only on the text. I think a summary table including key parameters involved (e.g. partial charge on phenolic C, dipole moments, crystallographic packing densities) will be beneficial. Additionally, some correlation figures (e.g. partial charge vs Psat, dipole moment vs Psat, crystallographic packing vs Psat) or visual images could be useful for the discussion and for readers to follow. 3. The author evaluated the Psat data predicted by the GCM comprehensively. Could the authors make a summary table to show the features of each GCM method, the performance of the prediction (the difference as compared to measurements), and short explanation of why the predictions differ from measurements. Furthermore, could the authors make a summary to say which prediction method may provide best result for a type of compound? This will help the researchers to get a more reasonable result when use GCMs doe predicting Psat for new compounds. Specific comments 1. Line 37-38. The sentence regarding

SOA formation mechanism is not rigorous. Gas phase photochemical reactions do not produce SOA directly. Another step of gas-to-particle conversion is needed. Moreover, 2. Line 112-123: The discussion on the PEG has been presented by Krieger et al. (2018) already. It is not necessary to show it here again. Moreover, the author stated that "KEMS was able to determine Psat of PEG-4 to PEG-7, through good agreement with the other techniques". Why the author used PEG3 here for calibration if only measurements for PEG-4 to PEG-7 have good agreement? 3. Line 124-125 This sentence seems to be redundant. 4. Line 214-217 Why the measurement temperature range needs to be listed here and why only listed for 5 compounds? 5. Line 268-269: I suggest to take the first sentence to the previous paragraph. 6. Line 381-382. Why the authors still used EVAPORATION to estimate the Psat of studied compounds and used SIMPLO for fluoro-aromatics? It is stated clearly that "A common misuse of GCMs occurs when a GCM is applied to a compound containing functionality not included in the training set, e.g. using EVAPORATION (Compernolle et al., 2011) with aromatic compounds or using SIMPOL (Pankow and Asher, 2008) with compounds containing halogens." (lines 194-196) 7. Line 422, A full stop is needed after "by Dang et al. (2019)" 8. Section 4.5: Details of EDB measurements regarding physical state determination and Psat estimation should be moved to section 2.3. 9. section title "Result" should be replaced by "Result and Discussion". 10. The reference style should be checked throughout. For example, Line 51-52 "Barley and McFiggans (Barley and McFiggans, 2010) and O'Meara et al. (O 'meara et al., 2014)" should be changed to "Barley and McFiggans (2010) and O'Meara et al. (2014)". 11. There is not much information in table 12. These numbers are listed in the text and displayed in Figure 9 already. 12. PL sat sometimes are in Bold in the text (e.g. on Page 17). 13. I think table 5,6,7 can be merged into 1 table, also table 8,9,10. These two sets of tables show similar information. 14. The quality of Figure 4 is poor.

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