Comment on acp-2022-113
Anonymous Referee #3

Referee comment on "Radical chemistry in the Pearl River Delta: observations and modeling of OH and HO2 radicals in Shenzhen 2018" by Xinping Yang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-113-RC3, 2022

This paper presents measurements of OH and HO2 radicals during the during the STORM campaign in the Pearl River Delta and compare their measurements to model predictions. The authors conclude that the model underestimates the measured OH concentration but can reproduce the measured HO2 concentrations. The authors propose that the "X" mechanism can explain the discrepancy, similar to that proposed in previous studies. The proposed mechanism involves an unmeasured species "X" that converts RO2 to HO2 and HO2 to OH similar to NO. The authors conclude that a mixing ratio of "X" equivalent to 0.1 ppb of NO is needed to bring the measured OH concentrations into agreement with the measurements.

However, it is not clear that their measurements support their conclusion that the model significantly underestimates the measured concentrations, as it appears that the model agrees with the measurements to within the uncertainty of the technique. This is in contrast to the previous measurements highlighted in the paper, where the discrepancy between models and measurements were found to be much greater, such as the factor of 3-5 found by Hofzumahaus et al. (2009). While the addition of the X mechanism does improve the agreement with the measurements, there is no discussion as to why the measurements reported here are in better agreement with the model compared to the previous measurements discussed in the paper. The paper would benefit from an expanded discussion of the measurement-model agreement taking the uncertainties associate with both into account. In addition, the paper would benefit from an expanded discussion of a comparison of their results with the previous measurements mentioned in the manuscript, especially the difference between their measurements and those at the Backgarden and Heshan sites in the PRD (Hofzumahaus et al., 2009; Tan et al., 2019). Such a discussion could provide more information about the source of the model-measurement discrepancies at all these sites.

The measurements of OH and HO2 appear to be high quality and are of interest to the atmospheric chemistry community. In addition to addressing the major comment
described above, I believe the paper would be publishable after the authors also address the following in a revised manuscript.

- The authors state that the base model agrees with the measurements to within the uncertainties of the measurements and the model (line 177), but then states that the model underestimates the measurements after 10 am when NO decreases. However, based on the information provided in Figure 3a, it appears that the model still agrees with the measurements to within the combined uncertainty of both the model and the measurements. This should be clarified. Addition of uncertainty estimates in Figure 3 would help to illustrate the agreement.

- Similarly, the base model predictions at low NO shown in Figure 5, although lower than the median measurements, appear to be within the combined uncertainty of model and measurements. The authors should quantify the discrepancy between the measurements and the model at each NO bin and reassess whether there is significant disagreement at low NO.

- The analysis of the OH measurements assumes that there are no interferences associated with the LIF-FAGE measurements. However, there is no discussion of whether the authors tested for unknown interferences with their measurements through a chemical modulation technique similar to that described in Tan et al. (2019). This should be addressed, as a significant interference would suggest that the model overestimation of OH could be more significant.

- I assume that the higher NO flow that was used in the HO2 measurements was required to increase the signal to allow for adjusting the laser wavelength given the failure of the reference cell. Were these measurements included in the data? While the authors claim that the NO concentrations were still low enough to minimize RO2 conversion to OH, did the authors perform calibrations of some RO2 conversion efficiencies to confirm this? What HO2 to OH conversion efficiencies did these two NO flows correspond to? Providing more details on the potential for RO2 interferences with the HO2 measurements would improve the reader’s confidence in the measurements.

- The authors should clarify that the rate of ozone production shown in equation 2 (line 322) represents the gross instantaneous rate of ozone production rather than the net rate of ozone production, as it does not take into account any NO2 formed that does not lead to O3 production through the formation of HNO3 from the OH + NO2 reaction. In contrast Tan et al. (2017) appear to use the net rate of ozone production in their analysis of the chemistry at the Wangdu site. As a result, the comparison of the rate of ozone production between the sites shown in Figure 7c may not be an appropriate comparison. This should be clarified.