Referee 1

We thank the referee for their helpful comments. Each comment in turn is shown below followed by our response in bold, and followed by any changes to the manuscript in red.

In this study the authors used an aerosol flow tube reactor connected to a photofragmentation laser induced fluorescence detection set-up to evaluate the heterogeneous chemistry of NO2 with irradiated TiO2 aerosols. The uptake coefficients of NO2 were determined for NO2 mixing ratios ranging between 34 and 400 ppb. The HONO production was determined as well at different relative humidities (RH), the highest being at 25 % RH. The performed kinetic box model suggested HONO production by heterogeneous reaction of NO2 with TiO2 aerosol surface involving two NO2 molecules, and a HONO loss which is dependent on the initial NO2 mixing ratio. Additional experiments have shown that HONO is also formed upon irradiation of mixed nitrate/TiO2 aerosols in the absence of NO2. This is an interesting study following the continuation of a number of previous studies focused on this topic. The experiments are well performed and the kinetic box model was used to support the experimental results. I would suggest publication of this study in Atmospheric Chemistry and Physics as it can be of broad interest for the atmospheric chemistry community.

1. The photo-fragmentation laser induced fluorescence detection apparatus seems promising tool for online measurements of HONO in ambient air. However, the only reference about this instrument is the thesis of Boustead (2019) which is not easily accessible. I wonder if this instrument was previously used in an intercomparison campaign against other well established instruments for real time HONO measurements (e.g. DOAS, LOPAP).

We are not aware of any previous intercomparison campaigns that have used this technique. In the revised manuscript we will include a reference to Liao et al., (2006) and also Wang et al. (2020) who have used the photo-fragmentation LIF method for HONO detected during fieldwork. An electronic copy of the PhD thesis of Boustead is available online from the University of Leeds.

We have revised the manuscript on page 4 using the following text:

"The experimental setup used in this investigation is described in detail in (Boustead, 2019), as well as similar systems having been used to measure HONO in the field (Liao et al., (2006), Wang et al., (2020)), and therefore only a brief description of the setup is given here."

2. The authors observed HONO formation upon irradiation of mixed nitrate/TiO2 aerosols and pure nitrate aerosols but they did not mention in the manuscript whether or not HONO is formed only upon irradiation of TiO2 aerosols in absence of NO2. These tests should be carried out as control experiments.

There is no significant production of HONO from TiO_2 aerosol surfaces without the presence of NO_2. We have added the following text:

Pg 9 ln 229. "Additional experiments showed no significant production of HONO on TiO_2 aerosol surfaces without the presence of NO_2".

3. The authors mentioned that the aqueous solutions ready to be dispersed in the air, were obtained by dissolving 5 g of TiO2, but they did not mention the quantity of dissolved ammonium nitrate in the solution. How relevant is this amount of TiO2 dissolved in water?

5g of TiO_2 and 5g of ammonium nitrate were dissolved into 500ml milli-Q water, as stated in the manuscript on page 30, line 625. The mass of TiO_2 dissolved in water allows some control over the maximum TiO_2 which can be atomised into the aerosol phase but does not affect the size distribution of aerosols produced. We get finer control of this by using the HEPA filter.

4. Another very important point is that many papers related to NO2 heterogeneous chemistry on TiO2 as a HONO source are not cited and discussed. For example, Gandolfo et al (Appl. Catal. B: Environ., 2015, 166-167, 84-90; Appl. Catal. B: Environ., 2017, 209, 429-436) have shown that the

disproportionation reaction of NO2, which has been also suggested as a night-time source of HONO in the atmosphere, can be photocatalytically enhanced in the presence of TiO2 which is in agreement with the statement in this study that two NO2 molecules forming HONO are required to reproduce the experimental trend of the uptake coefficients and observed HONO concentrations. Furthermore, a similar profile of the observed dependence of HONO mixing ratios with the RH was also observed by Gandolfo et al. (2015) by detecting a maximum of HONO at 30 % RH as was measured in this study. Increase of HONO with RH on building surface containing TiO2 was also observed by Langridge et al (Atmospheric Environment 43 (2009) 5128-5131).

We thank the referee for pointing out those papers. Our paper is focussed on HONO production from the surfaces of suspended TiO_2 and other aerosols and so the citations were more aimed towards these types of studies. Previous studies of surface interactions of NO_2 to form HONO were only considered when investigating the mechanism of dimer formation. However, we should have cited these studies by Gandolfo, as they are related to the RH dependence studies within our paper. We have included the Gandolfo et al. references in the revised manuscript and also the Langridge et al. paper. These papers are cited as followed in the revised manuscript:

Page 20, Line 435. "An increase in HONO as a function of RH has also been observed on TiO_2-containing surfaces (Gandolfo et al., (2015), Gandolfo et al., (2017), Langridge et al., (2009)) with a similar profile for the observed RH dependence of HONO was observed by Gandolfo et al., (2015) from photocatalytic paint surfaces with a maximum in HONO mixing ratio found at 30 % RH."

References:

Gandolfo, A., Bartolomei, V., Gomez Alvarez, E., Tlili, S., Gligorovski, S., Kleffmann, J., and Wortham, H.: The effectiveness of indoor photocatalytic paints on NOx and HONO levels, App. Catal. B: Environ., 166-167, https://doi.org/10.1016/j.apcatb.2014.11.011, 2015

Gandolfo, A., Rouyer, L., Wortham, H., and Gligorovski., D.: The influence of wall temperature on NO_2 removal and HONO levels released by indoor photocatalytic paints, App. Catal. B: Environ., 209, https://doi.org/j.apcatb.2017.03.021, 2017

Langridge, J. M., Gustafsson, R. J., Griffiths, P. T., Cox, R. A., Lambert, R. M., and Jones, R. L.: Solar driven nitrous acid formation on building material surfaces containing titanium dioxide: A concern for air quality in urban areas?, Atmos. Environ., 43, https://doi.org/10.1016/j.atmosenv.2009.06.046, 2009

Liao, W., Hecobian A., Mastromarino, J., and Tan, D.: Development of a photo-fragmentation/laser-induced fluorescence measurement of atmospheric nitrous acid, Atmos. Environ., 40, https://doi.org/10.1016/j/atmosenv.2005.07.001, 2006

Wang, C., Bottorff, B., Reidy, E., Rosales, C. M. F., Collins, D. B., Novoselac, A., Farmer, D. K., Vance, M. E., Stevens, P. S., and Abbatt, J. P. D.: Cooking, Bleach Cleaning, and Air Conditioning Strongly Impact Levels of HONO in a House, Environ. Sci. Technol., 54, https://doi.org/10.1021/acs.est.0c05356, 2020