Comments by Referees are in blue. Our replies are in black. Changes to the manuscript are highlighted in red both in here and in the revised manuscript.

**Reply to Ref #2:**

Summary. Due to its high refractive index, $TiO_2$ has been considered as a geoengineering material that could be deliberately injected into the upper atmosphere for the purpose of scattering incoming solar radiation. However, the consequences of this added aerosol mass on heterogeneous reactions that impact ozone levels in the stratosphere are unknown. Tang et al. present a combined experimental and modeling studied aimed at understanding the effects of injected $TiO_2$ particles on stratospheric chemistry, with a focus on heterogeneous hydrolysis of chlorine nitrate ($ClONO_2$), a process known to activate Cl and lead to stratospheric ozone depletion. Tang at al. use an aerosol flow tube technique with chemiluminescence detection of $ClONO_2$ (and associated aerosol sizing / number measurements) to study the loss of $ClONO_2$ on $TiO_2$ particles. For comparison, losses onto $SiO_2$ aerosols are also studied, in addition to the adsorption of $ClONO_2$ to the flow tube walls. Ambient temperature uptake coefficients for $ClONO_2$ are reported over a limited relative humidity range.

It is clear to this reviewer that a lot of hard work that went into making these measurements; they are not easy. Generating a flow of $ClONO_2$ that is free of impurities, the constant supply of uniformly sized aerosols that is required, and the method of indirectly detecting $ClONO_2$ via catalytic decomposition followed by chemiluminescence detection are complex and present multiple challenges. The methods appear to be appropriately chosen and the experiments executed in the best possible way. The main weakness in the experiments is that wall uptake was so high that in some cases, wall losses masked uptake onto the aerosol particles; this likely contributed to the limited scope of the data presented.

A unique aspect of the work is its use of modeling to evaluate the impact of the measured $ClONO_2$ uptake coefficients on a hypothetical event where $TiO_2$ or sulfate aerosols are injected into the stratosphere. A vertically resolved global chemistry-climate model (UKCA) indicated that less ozone destruction occurred as a result of reactions of $ClONO_2$ and $N_2O_5$ on injected $TiO_2$ particles vs. on aerosols formed from the Mt. Pinatubo eruption (under conditions where both injection events had the same solar radiation scattering). My comments are listed below.

**Author reply:** We would like to thank Ref #2 for his/her positive comments on our manuscript. All the comments have been properly addressed in the revised version, as detailed below.

1. General Comments. The description of $ClONO_2$ generation and detection is detailed in the methods section, but at times it is difficult to reconcile with Figure 1. I recommend that more detail be added to Figure 1 to show the aerosol cyclone mentioned, two diffusion driers, and the reactor that converts $ClONO_2$ to NO, etc. In addition, it would benefit the reader, especially when reading section 2.1.3, to include a diagram of the $ClONO_2$ detection scheme.

**Author reply:** In the revised manuscript the following changes have been made:

1) As request, in our revised manuscript we have updated Figure 1 to include the cyclone and how we mixed a NO flow with the sampled $ClONO_2$ flow. It should be pointed out that diffusion dryers were included in our initial figure.

2) Scheme 1 has been added in the revised manuscript to explain our $ClONO_2$ detection scheme (page 37). Accordingly a sentence has been added in Section 2.1.3 (page 10, line 227-228): "The scheme used in our work to detect $ClONO_2$ is shown in Scheme 1 and explained in detail below."

2. I feel that the rationale for choosing the $ClONO_2$ uptake coefficients used in the model was not made sufficiently clear. Uptake coefficients for both $N_2O_5$ and $ClONO_2$ hydrolysis on stratospheric $TiO_2$ particles are set to 0.0015. The $N_2O_5$ value of 0.0015 is taken from the group's prior work (Tang et al. 2014d). It is not clear why the authors assume the uptake coefficient for $ClONO_2$ is the same as that of $N_2O_5$. The values for gamma($ClONO_2$) listed in Table 2 for $TiO_2$ are 0.001, so I am assuming that given the error in the measurements the authors are just assuming that the uptake coefficients are the same within error for the two processes?

**Author reply:** The referee is correct. In our revised manuscript we have added one sentence to make this clearer (page 16, line 365-367): "Considering errors in measurements, this value agrees with experimental $\gamma(ClONO_2)$, which was determined to be ~$1.2\times10^{-3}$ in our work as shown in Table 2."

3. I feel that the $TiO_2$ uptake coefficient for $ClONO_2$ may be underestimated, meaning the ozone loss predicted by the model may be underestimated. The studies here were conducted at room temperature and lower temperatures expected for the stratosphere could result in higher gamma-values. The authors discuss this near line 549 and argue that the measured room temperature gamma-values may be within a factor of 2 or 3 of those at lower temperatures. More important may be the concentration effect. A concentration dependence of the uptake coefficient for the reaction of $ClONO_2$ on $TiO_2$ surfaces is an important consideration that should be addressed in a revised manuscript. One would expect significant surface saturation at the high concentrations (hundreds of ppb) used in this study. This effect would result in correspondingly low uptake coefficients. $ClONO_2$ levels in the stratosphere are 2-3 orders of magnitude lower than the concentrations used in this study. Therefore, it is likely that the uptake coefficients under atmospheric conditions of lower $ClONO_2$ concentrations would be higher than those reported. Related to this, I feel it is important to list specific $ClONO_2$ concentrations used in each experiment listed in Table 1 and 2.

**Author reply:** We agree that low stratospheric temperatures will affect the measured $\gamma$ values. This is addressed in our reply to Ref 1 (point 6). We agree with the referee that the dependence of $\gamma(ClONO_2)$ on $ClONO_2$ concentrations could be significant. We have made the following changes in the revised manuscript:

1) In Section 4.2 we have added the following sentences to address the possible effect of $ClONO_2$ concentration on $\gamma(ClONO_2)$ (page 19, line 438-441): "It should be pointed out that our measurements were carried out with $ClONO_2$ mixing ratios of several hundred ppbv, significantly higher than those found in the lower stratosphere. Therefore, our measurements could underestimate $\gamma(ClONO_2)$ under stratospheric conditions."

2) In captions of Tables 1 and 2, we have included initial $ClONO_2$ mixing ratios used in our work. Because $ClONO_2$ concentrations in each experiments were very similar, we do not list them individually.

4. How relevant is it to consider adsorption to a $TiO_2$ surface, which at room temperature and at 7-33 % relative humidity would contain a monolayer (or less) of adsorbed water? In the stratosphere, I would think that injected $TiO_2$ particles would be rapidly coated in NAT, HCl, $H_2SO_4$, etc. If that is true, should not the model be treating the $TiO_2$ as simply a seed particle? Or does it already? In that case, would it not be more accurate to assume that the uptake coefficients would be those for $ClONO_2$ uptake onto PSC components, which could be one or two orders of magnitude higher than what was measured in this work on $TiO_2$?

**Author reply:** The referee has raised a critical question on stratospheric particle injection. We agree that if a material (e.g., $TiO_2$ considered in our work) was injected into the stratosphere, it may be coated by $H_2SO_4$, NAT, water ice, and etc. However, assessing these microphysical aerosol processes is beyond the scope of the modelling experiments performed here. In Section 6, we have added the following sentences to emphasize this issue (page 27, page 636-640): "In this work we have only considered heterogeneous chemistry of fresh $TiO_2$ particles. If injected into the stratosphere, $TiO_2$ particles would likely be coated with $H_2SO_4$, NAT, water ice, etc., and heterogeneous reactivity of coated $TiO_2$ particles could be very different from fresh particles. This important issue should be addressed by further laboratory and modeling studies."

5. Lastly, I am aware of the meaning of the word "nudged" in the context of atmospheric models. However it is ambiguous and could be misinterpreted by a non-scientist who could think "nudging" a model means to coax it into giving you the results you want to see (thinking of "Climategate here). I would encourage the authors to consider replacing a phrase like, ": : :simulations were nudged: : :" with something more accurate; for example, ": : :initial conditions were set to: : :"

**Author reply:** We thank the reviewer for their comment. As the reviewer states, nudging is a technical term that deserves better definition in the text. We have amended the text to give a fuller definition of what is meant by the term nudging in the text and supplied appropriate references as well (page 14-15, line 329-335). However, as it is a technical term which describes part of the model set-up used in this study, we feel it is necessary to include this term in our discussion.

Specific Comments:

line 279: replace "spectroscopy" with "spectrometry."

**Author reply:** Corrected.

line 540-542: It is not clear to me how the presented “measurements suggest that the uptake coefficient onto $TiO_2$ is smaller than that for sulphate below ~215K.” This comment is related to the discussion above regarding the relevance of treating $TiO_2$ as pure $TiO_2$ surface or one that coated and has surface properties more in line with a PSC.

**Author reply:** In the revised manuscript we have change “onto TiO2” to “onto fresh $TiO_2$”. We have also provided a few sentence in Section 6 to discuss the relevance of coating on $TiO_2$, see our reply to comment 4.