Reply to reviewer 1
(Authors reply is in blue)

The paper reports solid experimental work, is well written, avoids unnecessary length and conveys a clear message. However, it defers the reporting of reaction (photo) products to a later stage which is unfortunate because the discussion of the products belongs into the same paper dealing with the uptake kinetics (it is not clear whether this fragmentation will ultimately lead to a higher "h" factor compared to more compact reporting!).

In fact, at the end of this kinetic study we already had preliminary information on the reaction products (as mentioned in the manuscript). Considering that the individual yields of the gas phase products were found to be strongly dependent on the experimental conditions such as relative humidity, temperature and concentration of oxygen it was obvious that a separate extensive and detailed study of the reaction products was needed.

- The analysis of the rate law for NO_2 uptake rests on the assumption that the MS signal as a function of gas-phase residence time follows a first-order decay based on results given in Figure 3. However, the authors report signal decays only over a factor of five which is insufficient for claiming first-order decay kinetics. A factor of 50 to 100 would be more appropriate to bolster such a claim.

The signal decays usually observed in flow tube studies range from 10-20% to a factor 10, i.e. the signal decay by a factor of five (80% consumption) reported in the manuscript is not the worst case for flow tube technique. The signal decays over a factor 50 to 100 seem to be difficult to reach, especially if one considers that heterogeneous reactions of atmospheric relevance are usually studied with initial concentration of the gas reactant as low as possible, i.e. not far from the detection limit.

In addition, I applaud the efforts of the authors to change the flow velocity and thus the gas residence time (Figure 3, squares vs. triangles). However, it is not clear that one may compare results at two residence times separated by roughly a factor of ten in case the uptake is NOT first order. In my experience the uptake kinetics of gases on solids is rarely first order, and the authors must evaluate whether or not first-order decays are a reasonably close approximation to the effective rate law for uptake. In other words: Is the heterogeneous rate constant independent of the gas-flow velocity? I support the author's efforts which is seldom undertaken aiming at extending the useful dynamic range of fast laminar flow tubes. However, this comes at the "price" of performing overlapping studies in which the same rate constant is measured at two different flow velocities in the laminar flow tube. If the k-values are different at these differing flow velocities, then by how much?

Yes, the same rate constant was measured with different flow velocities. For example, it is clear that the data presented in Figure 4 (initial k' drops by a factor of 50) could not be measured with the same flow velocity. In these experiments the flow velocity was progressively decreased with time in order to provide measurable decays of NO_2 upon decrease of the rate constant. Naturally, the results obtained for k' with different flow velocities were compared each time when the latter was changed. Specifically, the k'-values measured with flow velocities differing by a factor of 9 were similar in the range of stated experimental uncertainty. We never discuss this issue in our papers, considering that independence of k' of the gas-flow velocity in the reactor is a basic condition for the flow tube kinetic studies.

- Figures 2, 3 and 4 are plotted without giving the inherent uncertainties of these single measurements. Uncertainties should be a part of any reporting of scientific results.

Corresponding uncertainties are added

- The linear mass dependence of "gamma" displayed in Figure 5 and discussed on pg. 27868 is by no means proof that the relevant surface area for the TiO_2/NO_2 interaction corresponds to the BET surface area. Adsorbed nanometric TiO_2 occurs as an agglomerate rather than a multitude of layers of primary particles of 10-50 nm diameter (20 nm average). The linear mass dependence must in this case be interpreted as displaying the effect of increasing surface coverage of TiO_2 agglomerates on "gamma". It is especially unrealistic to claim that "gamma"0 corresponds to instantaneous interaction of NO_2 with the total internal and external sample surface because it takes some time for NO_2 to explore the total surface. I would like to propose a compromise in that the authors list both values based on the geometric and BET value with the expectation that the "true" value lies in-between. In this case it must be clearly indicated which effective surface area has been used to convert the heterogeneous rate constant k to an uptake coefficient.

The use of the BET surface area for the calculation of the uptake coefficient in the present study is based on the data of Figure 5. Our interpretation of the linear mass dependence (considering that the coating was visible to the naked eye and we have never observed any uncovered area on the support tube) is not original and is widely used throughout the literature.
Considering the results of Figure 5 it seems impossible to express the NO_2 uptake data in terms of geometric surface area (uptake coefficient would increase with the mass of sample). However, an upper limit of γ_0 can be estimated. Thus, applying the geometric (projected) surface area to the data observed with the smallest mass of TiO_2 used in these experiments (m = 0.08 mg cm^{-1}, k'_0 = 12.7 s^{-1}) one gets the value of 1.9×10^{-3} for the uptake coefficient which is an upper limit of γ_0. This estimation is added in the text.

- Regarding the "gamma" value under "dark" conditions given by the authors (pg. 27868, line 25) I would like to remark that Setyan et al. (PCCP 2009, 11, 6205) have not observed any uptake of NO_2 on three different types of TiO_2, among which on TiO_2 P25 used by the present authors. This is the only uptake study undertaken at this time that uses a method other than a laminar flow tube. The "gamma"0 value reported by the present authors has to multiplied by roughly a factor of 50 in order to yield "gamma"0 = 3 x 10(-4) based on the geometric surface. This value should have been easily observed by Setyan et al. in their work at a NO_2 gas residence time of 40 s in a Knudsen flow reactor. The factor of 50 used above has been established by using an average loading of 0.3 mg/cm leading to a total mass of 12 mg by estimating a total TiO_2-coated area of 120 cm2 in the present work. In this context the question of a missing reference experiment comes up which the authors should report in this context.

Thanks for this remark. Indeed, Setyan et al. have not observed any NO_2 uptake on TiO_2 P25. Unfortunately they do not give any estimation of the upper limit of the uptake coefficient. However, simple calculations show that the value of γ from the present study would lead to initial drop of NO_2 signal at least by a factor of 1.5 under their experimental conditions. The reason for the lower NO_2 uptake to TiO_2 surface in the study of Setyan et al. compared with the present one, could be the mode of preparation of solid samples. Remind that in the present

work TiO_2 samples were heated under pumping prior to uptake measurements. The reference and comment are added in the manuscript.

- The NO_2 saturation behavior displayed in Figure 6 and discussed on pg. 27870, bottom, is consistent with both Langmuir-Hinshelwood AND Eley-Rideal surface chemistry and cannot be used to distinguish between these two mechanisms. The distinction between both mechanisms is not trivial and cannot be performed by monitoring the saturation behavior, notwithstanding claims to the contrary.

We agree with the reviewer that the distinction between both mechanisms is not trivial and we do not try to make it in this work. It was just stated that usually, in the literature, this behaviour is associated with a Langmuir-Hinshelwood mechanism. In any case, we remove this phrase from the manuscript to avoid any ambiguity.

- The seemingly good agreement with Underwood et al., 1999, of "gamma"0(dark) pointed out on pg. 27870, line 16, may be fortuitous as the Grassian group uses residual gas MS and not molecular beam sampling in all their work. Therefore, these latter results are influenced by the background conditions in the MS chamber at any given time and which may lead to uncertainties of a factor of several (up to ten) for "gamma".

In our opinion, nothing in the paper of Underwood et al. indicates that the background signals were not properly taken into account. In addition, the stability of the initial NO_2 signal (when sample compartment is closed) during around 2 hours in their experiments seems to indicate that the background signal was more or less stable or negligible compared with that of NO_2 coming from the reactive cell.

- I do not understand why the uptake values obtained by Gustafsson et al., 2006, represent an upper limit to "gamma"0 based on the fact that the aerosol surface area was evaluated from the primary (spherical) particle size (pg. 27871, lines 18 and following). Do the authors imply that the geometric surface area is the correct effective area to be used for the initial value "gamma"0 (see remark made above)? What else could underestimate the sample surface area?

We mean that any deviation from the assumed ideal spherical shape of the particles would increase the particle surface area.

- What would be the value of "gamma"ss extrapolated to the radiation intensity of Monge et al., 2010 (pg. 27872, lines 1-9). If possible the authors should attempt an extrapolation.

Unfortunately, the extrapolation of our data to lower irradiation levels used in the study of Monge et al. would be speculative and inaccurate. The problem is that in our experiments the uptake coefficient was not sensitive to irradiation intensity (Figure 7).

- The mentioned N_2O product on pg. 27873, line 25, presumably comes from heterogeneous disproportionation of NO unless it results from reduction of HONO on the irradiated TiO_2 surface. Reference experiments should prove to be revealing, and the authors may consult the work of D.M. Smith (D.M. Smith et al., Appl. Spectr. 42, 674, 1988) for experimental results. In this case the N_2O yield should scale with the gas residence time of NO_2.

The extended discussion on the reaction mechanism and, in particular, on the possible reaction pathways leading to the formation of N_2O will be presented in our upcoming paper on the reaction products. Thank you for the provided information.

Some of the minor questions are:

- Does the TiO_2 suspension in ethanol affect the surface reactivity in any case considering that ethanol may be oxidized and/or reduced (pg. 27864, line7)?

No, the TiO_2 suspension in ethanol does not affect the surface reactivity. This was verified in the experiments with TiO_2 films prepared from TiO_2 suspension in water. TiO_2 suspension in ethanol was preferred because the preparation of the TiO_2 solid coating was much easier with rapidly evaporating ethanol than with water.

- The fact that the triple linear injector is cooled/heated using the same coolant does not mean that the temperature of the wall of the flow tube and the injector are identical (pg. 27865, lines 1-5).

In fact, this system is important specifically when measuring the initial uptake: solid film temperature should be equated to that of the main reactor prior introduction of the sample into the reaction zone (main reactor). In the studies of steady state uptake it is not necessary, as the solid sample introduced into the main reactor reaches its temperature in a few minutes. In all cases the temperature was controlled with a thermocouple positioned inside the tube with solid film.

- Reference Beaumont et al. (pg. 27874): R.M. Lambert.

Corrected.

- Pg. 27864, line 9: fan heater; pg. 27863, line 19: doped; pg. 27871, lines 12 and 17: Gustafsson;

Corrected.

Legend of Figure 6: Is T = 280K? Is the "initial" correct as it deals with the steady-state uptake coefficient?

T = 280 K, included in the legend; 'initial" is correct.