**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Interaction of NO$_2$ with TiO$_2$ surface under UV irradiation: measurements of the uptake coefficient" *by* A. El Zein and Y. Bedjanian

Anonymous Referee #1

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The present paper deals with redox chemistry of NO2 in the presence of irradiated TiO2 which has aroused the interest of the community and given rise to several papers in the recent past because of the potential importance of the resulting photoproducts. The authors report the uptake kinetics of NO2 on one type of TiO2 nanometric powder (P25) as a function of several important parameters such as relative humidity, irradiation intensity of the black lamps reported as the first-order photolysis rate of NO2, NO2 partial pressure and temperature, to name the most important ones. 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!). This investigation is certainly welcome in view of the sometimes contradicting results on TiO2 which may act either as a reducing or oxidizing substrate depending on conditions that are sometimes not obvious to the experimenter. However, there is room for improvement of the manuscript, and I would like to see the authors respond to my questions that are posed in the interest of a crisp and clear presentation of the author's results to the benefit of the readers of acp.

- The analysis of the rate law for NO2 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. 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?

- 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.

- 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 TiO2/NO2 interaction

corresponds to the BET surface area. Adsorbed nanometric TiO2 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 TiO2 agglomerates on "gamma". It is especially unrealistic to claim that "gamma"0 corresponds to instantaneous interaction of NO2 with the total internal and external sample surface because it takes some time for NO2 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.

- 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 NO2 on three different types of TiO2, among which on TiO2 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 NO2 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 TiO2-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.

- The NO2 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

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saturation behavior, notwithstanding claims to the contrary.

- 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".

- 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?

- 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.

- The mentioned N2O product on pg. 27873, line 25, presumably comes from heterogeneous disproportionation of NO unless it results from reduction of HONO on the irradiated TiO2 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 N2O yield should scale with the gas residence time of NO2.

Some of the minor questions are:

- Does the TiO2 suspension in ethanol affect the surface reactivity in any case considering that ethanol may be oxidized and/or reduced (pg. 27864, line7)?

- The fact that the triple linear injector is cooled/heated using the same coolant does

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not mean that the temperature of the wall of the flow tube and the injector are identical (pg. 27865, lines 1-5).

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

- Pg. 27864, line 9: fan heater; pg. 27863, line 19: doped; pg. 27871, lines 12 and 17: Gustafsson; legend of Figure 6: Is T = 280K? Is the "initial" correct as it deals with the steady-state uptake coefficient?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 27861, 2011.

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