

Interactive comment on “Is the photochemistry activity weak during haze events? – A novel exploration on the photoinduced heterogeneous reaction of NO₂ on mineral dust” by Tao Wang et al.

Anonymous Referee #3

Received and published: 21 June 2019

This is a new contribution aiming at understanding the effect of mild illumination on mineral dust proxies and linking those observations with a limited set of environmental data. The claim having motivated this investigation can be found in the fact that previous studies have not seriously discussed the photochemistry under weak sunlight during haze conditions, and have thus ignored some underlying processes. I would certainly agree on such a statement, that I found quite interesting.

However, I'm not fully convinced by the current version of the manuscript that would need significant revision to convey a better and stronger elaborated message.

C1

First of all, I do need to admit that I found it difficult to read this manuscript which contains a series of awkward sentences, such: “The growth of nitrate formation rate tends to be slow after the initial fast with increasing light intensity. For example, the geometric uptake coefficient (γ_{geo}) under 30.5 mW/cm² (5.72×10^{-6}) has exceeded the 50 % of that under 160 mW/cm² (1.13×10^{-5}). This case can be explained by the excess NO₂ adsorption under weak illumination while the excess photoinduced active species under strong irradiation. Being negatively associated with nitrate ($R^2=0.748$, $P<0.01$), nitrite acts as the intermediate and decreases with...”. This clearly weakens the content of this manuscript.

Then the link being made with the ambient measurements and the test on TiO₂ particles is far from being obvious, and would certainly need to more elaborated to make a stronger case.

Most of the data presented have been made at quite high NO₂ concentrations (tens of ppm), corresponding to a concentration regime where N₂O₄ is known to be a significant intermediate for NO_x conversion on surfaces. While such concentrations are inherent to the DRIFT technique, one can still wonder how this could affect the findings reported here. It is stated that “Since no saturation effects were observed in the DRIFTS experiments, the NO₂ adsorption rate can be regarded as constant.”, but this is strong contrast with previous studies dedicated to NO₂ heterogeneous chemistry. Could that be to the involvement of N₂O₄?

In TiO₂ driven photocatalysis, it is known that the conversion rate is linear function of light intensity at low intensity, and then levels off at high power to reach steady state conditions. While this seems to be also observed here (inset of figure 2a) but not really discussed nor mentioned, why? In addition, one could argue that the light intensities used here are far from being small and I would not consider this as being photochemistry under mild conditions.

One of the key finding here is associated with the nitrite levels between sustained (or

C2

more important) under mild illumination, but the section “mechanism” does not provide a real explanation for that.

You should try to define what you mean with cumulative uptake coefficients.

A few chemical reactions are described in a simplified i.e., wrong way with unbalanced stoichiometry. This should be avoided.

I did find Figure 3 quite difficult to understand and I am finally unsure about the message the authors wants to convey with this illustration. This maybe needs to be better discussed.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-315>, 2019.