

Interactive comment on “Interaction of NO₂ with TiO₂ surface under UV irradiation: measurements of the uptake coefficient” by A. El Zein and Y. Bedjanian

Anonymous Referee #2

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The manuscript by El Zein and Bedjanian presents the analysis of experimental study of NO₂ interaction with TiO₂ surface under UV radiation. The subject of the study seems to be within the scope of *ACP* journal as many aspects of heterogeneous chemistry of atmospheric constituents, photo-chemically induced in particular, are yet not well established. The authors used titanium oxide as a surrogate for photo-chemically active surface and nitrogen dioxide as a proxy for gaseous atmospheric pollutant. The choice seems to be reasonable although the authors admit the necessity of further studies on more atmospheric relevant substrates like mineral dust. By choosing one of the most active substrates the authors perhaps intended to make a proof-of-concept case but without extending this type of work to more atmospheric relevant substrates,

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like mineral dusts, one may have difficulties with using this data in atmospheric models. This is the weak side of the paper, in my opinion. The strong side is the variety of the conditions that were tested out. The main outcome of the work is the empirical dependence of NO₂ uptake coefficient on such important atmospheric variables as relative humidity, temperature and reagent initial mixing ratio. To my mind this is a useful piece of information for *ACP* audience and I could recommend the publication after the comments below have been addressed.

Specific comments:

The authors are encouraged to extend the Experimental section. Since the centerpiece of the work is experimental data, it is very important to give a full description of the instrumental setup, procedures and detection methods.

1. Detection. Give a short description of mass spectrometry system used. If electron impact was used give EI energy. Which signals (raw) were monitored, how the signals were calibrated, what were the sensitivities and detection limits? It is prerequisite to provide a separate figure, which depicts a typical uptake experiment (preferably showing raw massspec signal).
2. Add additional text to describe the way relative humidity was adjusted and detected. How water did prepared mixing ratio inside flow tube compared to real-world tropospheric values? Did humidity affect NO₂ signal?
3. Provide information on helium flow tube flowrate used (in volume units) for 1-10 torr range.
4. BET surface area is usually measured for particular powder samples. If BET surface area was measured in this work then the description of the method should be provided. Otherwise add the text describing which BET value was used.
5. From Experimental 2.1 section it is unclear how the thickness of the coatings was controlled during preparation. This needs to be described in details.

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Due to a significant number of parameters it would be very useful to expand figure captions so that each caption contains information on TiO₂ sample mass, NO₂ initial mixing ratio, number of lamps switched on (or mentioned dark experiment), flow tube pressure and temperature.

P27867 L13-16 The linear dependence shown on Fig.5 suggests that NO₂ reacts not only at the surface but diffuses inside the coating. This is quite critical for data interpretation and deciding how the uptake coefficient should be calculated and presented. The authors are encouraged to look at Underwood et al. (2000 *J.Phys.Chem.*) paper where such an analysis is given and consider geometric versus BET surface area arguments.

Minor suggestions:

P27862 L17-20 This text should be moved into Discussion section. Abstract should contain the major findings and the products described belong more to the planned future publication.

P27865 L12-14 The conditions of this experiment are very different from the others. Why such a high NO₂ mixing ratio was used and such a slow residence time? Provide explanation for using this settings.

P27866 L5 Nitrogen dioxide molecule velocity should be given for the temperature range used in this work.

P27866 L20 Fig.4 not Fig.3

P27866 L24-P27867 L3 Consider revising this paragraph. These three sentences are perhaps redundant as they echo previous statement.

P27867 L12 Add text, indicating assumption made about homogeneous, evenly dense coating.

P27867 L17 Define clearly "initial uptake coefficient". Which exactly time period is used

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to calculate gamma initial?

P27868 L22-24 The argument of "NO₂ photolysis frequency similar to above" is questionable. Firstly, with cooling liquid running to maintain T=280K, the intensity of light reaching inside is expected to be decreased. Secondly, the above photolysis experiments were performed at slower residence time.

P27873 L15 Check the value of "90 ppb of NO₂" because it looks like this NO₂ mixing ratio is outside of range P27868 L12-13.

Figure 5. Missing y-scale units.

Reference: Underwood, G. M., Li, P., Usher, C. R., and Grassian, V. H.: Determining Accurate Kinetic Parameters of Potentially Important Heterogeneous Atmospheric Reactions on Solid Particle Surfaces with a Knudsen Cell Reactor, *The Journal of Physical Chemistry A*, 104, 819-829, 2000.

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

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