

Interactive comment on “Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR” by F. Rohrer et al.

F. Rohrer et al.

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Reply to Anonymous Referee #1

The revised version of our manuscript was already submitted some time ago. However, we would like to thank the referee for his/her interest in our paper. The concerns raised are addressed below. However, we will not submit a newly revised version since some issues were brought up by the editor also and are already considered in the revised version.

“4. Results”, points (i) and (ii):

J(NO₂) and humidity are no independent parameters in our outdoor chamber, i.e. in each experiment J(NO₂) and relative humidity are changing by the interaction of so-

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lar zenith angle and ambient temperature. It is not possible to adjust solar irradiation, temperature, or relative humidity to a constant value and to derive a certain partial dependency, which is in contrast to an indoor chamber. Instead, the different data sets in Fig. 4 were normalised to a constant $J(\text{NO}_2)$ and temperature using the stated parameterisation to emphasise the humidity dependence. Plotting against $J(\text{NO}_2)$ would be possible, but only by normalising to constant relative humidity and temperature using the same parameterisation. The resulting plot does not give any relevant new information.

“4. Results”, point (iii):

We agree with the referee, that the results from the filter foil experiments are new and very important findings. By these experiments it could be unequivocally demonstrated for the first time that the photolysis of HNO_3 /nitrate cannot explain the photolytic HONO formation in our simulation chamber which was proposed in recent studies for other chambers. However, in these studies the wave length dependence of the photolytic source was not studied. To highlight the important findings of the present study we have already included a complete figure (Fig. 2) for this type of experiments, in contrast to the comment of the referee. Fig. 2 clearly demonstrates that our parameterisation is still valid, even when the short wavelength range, responsible for HNO_3 photolysis, has been absorbed. This conclusion is also visible from figure 4, which includes also experiments with the filter foil. In addition, a detailed interpretation of these experiments is already included in the discussion section (pages 7894-7896).

“4. Results”, point (iv):

As already stated on pages 7892-7893 of our manuscript and in the reply to the editors comments, the reason for the sudden change of the photolytic HONO source is not clear. In the time period of this change no significantly different experiments have been performed. Accordingly, we cannot give any definite answer to this question. We conclude that the chamber related source must be quantified in regular intervals to

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confirm its stability. We have added this conclusion in the revised manuscript which is already submitted. But this is really not a severe drawback. We have found a simple parameterisation which enables us to predict the radical production in our chamber for long periods of time and we have unequivocally identified HONO as the precursor. We think that this process is also important for other chambers and should certainly be taken into consideration.

“4. Results”, point (v):

We prefer giving this equation in the description of the model. The empirical formula is needed to explain the model and the fitting procedure. Therefore, it is necessary to introduce it before Fig 3 and 4 presented in order to understand the normalisation.

“5. Discussion”, point 1):

As already discussed in detail in the manuscript, there are only two mechanisms described in the literature about the photolytic HONO formation in simulation chambers, i.e. the photo-enhancement of the reaction $\text{NO}_2 + \text{H}_2\text{O}$ and the photolysis of nitrate/ HNO_3 . Both mechanisms could be clearly excluded from the present study. Accordingly, we do not think that an additional discussion is necessary.

“5. Discussion”, point 2):

In contrast to the referees comment, the photo-enhanced HONO formation in the SAPHIR chamber is even smaller compared to other chambers, when using similar conditions. Some examples:

Carter et al., 1981: $S(\text{OH}) = J(\text{NO}_2) * (0.3 + 2.9 * [\text{NO}_2])$ in ppb/min for 50% r.h. With the given value of $J(\text{NO}_2) = 0.49 \text{ min}^{-1}$ an OH production of 0.15 ppb/min can be calculated for $[\text{NO}_2] = 0$, which is higher than value of 0.06 ppb/min in the SAPHIR chamber for these conditions.

Carter et al. 1982: For low NO_2 concentrations and a $J(\text{NO}_2)$ of 0.32 min^{-1} a radical production of 0.03 ppb/min was observed at 30 % r.h. in a large outdoor chamber

which is two times higher than the value of 0.015 ppb/min estimated for the SAPHIR chamber under similar conditions.

Glasson and Dunker, 1989: For $[H_2O] < 150$ ppm and $J(NO_2) = 0.4 \text{ min}^{-1}$ a radical formation of 0.016 ppb/min was calculated, significantly higher than the SAPHIR value of 0.0025 ppb/min for these conditions.

EUPHORE chamber (Kleffmann, 2004, not published results): In the dry EUPHORE chamber 200 ppt HONO are observed after 2 h irradiation at $J(NO_2) = 0.006 \text{ s}^{-1}$. For similar conditions only ca. 20 ppt are observed in the SAPHIR chamber.

In contrast to the examples given above, we cannot compare our results with studies of Akimoto et al., 1987 and Sakamaki & Akimoto, 1988, since they have only published reaction rates for the photo-enhanced NO_2 reaction, which we definitely excluded for the SAPHIR chamber. The lower HONO formation in SAPHIR compared to other chambers is most probably caused by the different types of experiments in these chambers. Whereas in the SAPHIR chamber the experimental conditions (humidity, concentrations, etc.) are similar to the atmosphere, ppm levels were used in most other studies, leading probably to an increase in the precursor concentration (see discussion) on the chamber walls. However, as mentioned in the reply to the editors comments and in the already submitted revised manuscript, the parameterisation is given only for the SAPHIR chamber and should only be used for comparison with measured formation rates in other chambers. Since we do not expect similar formation rates in different chambers, we would like to stimulate other groups to also characterise the background reactivity of their chambers.

“5. Discussion”, point 3) (referee again 2):

The dark reaction of $NO_2 + H_2O$ was clearly not the topic of this paper and is discussed in detail in several other publications (see Finlayson-Pitts et al., 2003 and references therein). Although the reaction takes place in the SAPHIR chamber also, it cannot explain the HONO levels observed under irradiation, since it is orders of magnitude

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smaller than the photo-enhanced formation under our low NO_x conditions. We have starting conditions of a few ppt of NO_x, thus, we can safely exclude a mechanism depending on NO₂ reactions. Furthermore, since no photo-enhancement was observed for this reaction in SAPHIR (see page 7894), any discussion about a detailed mechanism of the dark reaction should not be given here.

“5. Discussion”, point 4) (referee 3)):

In contrast to the comment of the referee, the quadratic humidity dependence is already discussed on page 7897, lines 1-6.

“5. Discussion”, point 5) (referee 4)):

We have already specified the absorption features of the filter foil (<1 % transmission below 370 nm, increasing to 85 % in the range 370-420 nm) and the wavelength of the well known absorption band maximum of nitrate (ca. 300 nm) for the processes discussed in the paper. Accordingly, we do not think that an additional figure is necessary. Some discussion about possible precursors is given in the paper. However, since we could not identify the exact mechanism, we think that any further speculations are not helpful. The empirical relation between the HONO source and J(NO₂) simply shows that the unknown precursor absorbs in a similar wavelength range than NO₂.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 7881, 2004.

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