

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

Anonymous Referee #1

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Although this paper presents some new evidence which can contribute to elucidating the mechanism of photo-enhanced heterogeneous formation of HONO on the chamber surface, the data presentation and discussion are not straightforward and not well qualified. The present reviewer do not recommend the publication of this paper without thorough revision. Itemized comments are as follows.

“4. Results”

Experimental data from the runs as summarized in Table 2 should be presented in more systematic way focusing on the original findings in this study.

- i) First order dependence of $S(\text{HONO})$ to $J(\text{NO}_2)$ should be presented by a plot.
- ii) Second order dependence to relative humidity should be demonstrated by a linear

plot between $S(\text{HONO})$ and squared (RH) or by a log-log plot rather than Fig. 4.

iii) "Filter foil experiment" is one of new important findings in this study. The experimental results should be presented in more distinct way by a plot or a table. Brief description in the text on page 7890 is not enough for the reader to evaluate the implication of the results.

iv) There is no explanation why the HONO formation rates changed before and after July/August 2002 nearly by a factor of two. Plausible factors affecting the change should be discussed either in "Result" or "Discussion".

v) Empirical equation (1) should be presented after the data presentation suggested above.

"5. Discussion"

1) Since there has already been substantial number of studies on this topic, implication of the each original findings in this study should be discussed more deeply relating to the "mechanism" of photo-enhanced heterogeneous HONO formation.

2) Unequivocal identification of HONO under illuminated conditions in the present study would imply that photo-enhanced formation rate is more than an order of magnitude higher than previous chambers studies. Quantitative comparison of formation rates between the previous studies and the present study under similar experimental conditions is worth to be presented for demonstrating peculiar characteristics of SAPHIR. Discussion should be made what can cause such strong enhancement in this chamber; difference in wall material, in illumination mode of chamber through transparent FTP film versus illumination on coated FTP on steel chamber, or in other factors, etc.

2) The present author negates the photo-enhancement of heterogeneous $2\text{NO}_2 \rightarrow \text{HONO} + \text{HNO}_3$ mechanism based on the fact that HONO formation rate was not increased by the increase of gas phase NO_2 concentration. The early study presented a result that HONO formation rate was proportional to the first order to NO_2 under their experimental conditions suggesting that the rate order would depend on the surface adsorption mechanism. Since the heterogeneous $2\text{NO}_2 \rightarrow \text{HONO} + \text{HNO}_3$ mechanism proposed earlier implied only stoichiometric mechanism rather than real detailed

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process mechanism, the discussion here should be more on the insight into surface phenomena rather than simply negate the overall stoichiometric mechanism.

3) There is no discussion on the second order dependence of S(HONO) on relative humidity in the present manuscript.

4) Regarding the discussion to negate the hypothesis of photolysis of adsorbed nitrates, spectral distributions of photolytic light, absorption spectrum of filter foil and adsorbed nitrates should be presented as a figure for clarification. Discussion on plausible photo-absorbing species for the filter foil experiment should be made in some more detail. Also, it should be discussed how the evidence that S(HONO) is proportional to $J(\text{NO}_2)$ can be justified for a photo-enhancement reaction. The hypothetical proposal of involvement of excited state NO_2 is interesting but too speculative at this stage.

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

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