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Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR

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Abstract. HONO formation has been proposed as an important OH radical source in simulation chambers for more than two decades. Besides the heterogeneous HONO formation by the dark reaction of  $\mathrm{NO}_2$  and adsorbed water, a photolytic source has been proposed to explain the elevated reactivity in simulation chamber experiments. However, the mechanism of the photolytic process is not well understood so far. As expected, production of HONO and  $\mathrm{NO}_{\mathrm{x}}$  was also observed inside the new atmospheric simulation chamber SAPHIR under solar irradiation. This photolytic HONO and  $NO_x$  formation was studied with a sensitive HONO instrument under reproducible controlled conditions at atmospheric concentrations of other trace gases. It is shown that the photolytic HONO source in the SAPHIR chamber is not caused by NO2 reactions and that it is the only direct  $NO_v$  source under illuminated conditions. In addition, the photolysis of nitrate which was recently postulated for the observed photolytic HONO formation on snow, ground, and glass surfaces, can be excluded in the chamber. A photolytic HONO source at the surface of the chamber is proposed which is strongly dependent on humidity, on light intensity, and on temperature. An empirical function describes these dependencies and reproduces the observed HONO formation rates to within 10%. It is shown that the photolysis of HONO represents the dominant radical source in the SAPHIR chamber for typical tropospheric O<sub>3</sub>/H<sub>2</sub>O concentrations. For these conditions, the HONO concentrations inside SAPHIR are similar to recent observations in ambient air.

■ <u>Final Revised Paper</u> (PDF, 983 KB) ■ <u>Discussion Paper</u> (ACPD)

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