

Reply to the Review by Dr. J. Kleffmann

We thank Dr. J. Kleffmann providing us valuable review comments that have improved the manuscript. We have included the review comments in italic followed by our responses in blue. In the revision of this manuscript, we will highlight these changes accordingly.

Comment (1): The acronym LOPAP should not be used here, since the used instrument is different to the LOPAP which we have developed in our group: a) sampling at pH = 0 by fast chemical reaction, whereas by solubility at pH=7 in the HPLC instrument, b) use of an external sampling unit in our LOPAP, whereas inlet lines are used here c) on-line correction of interferences in our LOPAP by the use of two channel in series, only one channel used here. In addition, there is a registered trade mark on the name LOPAP by the company which fabricates this instrument.

Response: We did not realize that the acronym LOPAP is a registered trade mark when we prepared the manuscript. We have removed this acronym from the manuscript and renamed our HONO instrument as “a wet chemistry HONO instrument” in general.

The HONO instrument deployed in this study was different from the original instrument described in Huang et al. (2002). An HPLC was not used in this version of the instrument. The samples were directly introduced into the liquid waveguide capillary detection cell after the derivatization reactions without the HPLC separation.

Comment (2): page 7387, line 3: The reference by Langridge is on NO₂ reactions on self cleaning window glass, which may be too special here (not too much of these surfaces in the atmosphere yet...). May be add a more general paper by Ndour et al. on this topic (dust). In addition, since NO₂ has much higher reactive uptake coefficients on organics (NO₂+org = HONO) compared to bare surfaces (NO₂+H₂O=HONO+HNO₃) a references to the first reaction could be also added (studies by Markus Ammann's group).

Response: We have replaced Langridge et al. (2009) with Ndour et al. (2008) and added Ammann et al. (1998) here, as suggested.

Comment (3): page 7387, line 8: In Bröske et al., we explicitly excluded HONO formation on secondary organic particles, at least in the dark.

Response: We have removed this reference here.

Comment (4): page 7388, section 2.1: How long was the inlet line for both HONO instruments? Sampled from 20 m altitude? HONO losses in a very long Teflon line, on which alkaline particles (see text) have been precipitated, may also explain the low HONO levels of both instruments. Any line tests done?

Response: We have included the description of the inlet for both the wet chemistry HONO instrument and the CIMS instrument in Section 2.2.1 as: “Ambient air was pulled through a light-shielded Teflon tubing (OD = 0.375”, and ID = 0.25”, length = 18 m) at flow rate of 12 L min⁻¹, of which 2 L min⁻¹ was fed the HONO instrument housed in a trailer laboratory. The total residence time in the sample line was about 2.8 seconds.” and in Section 2.2.2, as “Ambient air was sampled through the same glass inlet described in Crouse, et al. (2006) with the exception that parts A, B, D, and E (Figure 1, Crouse et al 2006) were not part of the BEARPEX CIMS instrument configuration. Air was drawn through the large inlet tube (C) at a linear flow rate of ~10 m/s using a wet/dry vacuum. Air was sub-sampled for analysis from the center of the large flow as described in Crouse et al (2006) with the difference that ambient air was diluted with UHP N₂ in a 1:3.5 ratio to reduce the water vapor mixing ratio in the flow tube (J).”

For the wet chemistry instrument, the possible HONO loss through the sampling line was examined before and after the field deployment using the gas phase HONO source. We found that the wall loss was little and (99.2±1.3)% of HONO went through the tubing. As described in Section 2.3.3, we have done extensive interference tests, including the background check with a dry denuder coated with Na₂CO₃, in which the signals obtained from the ambient air through the denuder were essentially the same as the signals from zero air. For the CIMS instrument, because of its very short sampling line, fast air flow, and only center air sampled, we do not expect significant wall loss in the CIMS instrument.

As described in the text already, the inlet height was 14 m for the wet chemistry HONO instrument and 17.7 m for the CIMS.

Comment (5): page 7389, line 10: The references to Heland et al. and Kleffmann et al. do not fit here (different instrument).

Response: Although the instruments used by Heland et al. (2001) and Kleffmann et al. (2002) were not the same as the one used in this study (e.g., different inlet coil sampler design and different solution and pH of the stripping fluid), all the instruments used the same reactions and very similar detection system (i.e., liquid waveguide capillary cell with long path absorption photometry). We have removed these two references because of the differences in the sampling units.

Comment (6): page 7391, R3: Is the HFNO₂⁻ stable? Normally, an elimination of the very stable HF should be favoured. This should be temperature dependent. May be the strong periodic noise in Fig. 7 is caused by regular temperature variation of the instrument?

Response: Laboratory calibrations show HF·NO₂⁻ is the dominant product ion for both the CF₃O⁻ + HONO and CF₃O⁻·H₂O + HONO ion-molecule reactions (<0.2% yield of NO₂⁻ product in laboratory calibrations at ~296K). Reaction to form HF·NO₂⁻ product proceeds essentially at the collision rate, as calculated by the method of Su and Chesnavich (1982). Thus there is little reason to suspect that this ion-molecule reaction rate would have significant temperature dependence.

The reaction channel $\text{CF}_3\text{O}^- + \text{HONO} \rightarrow \text{NO}_2^- + \text{CF}_2\text{O} + \text{HF}$ is calculated to be endothermic ($\Delta G_{298\text{K}} = +2.5 \text{ kcal mol}^{-1}$). This supports the conclusions from laboratory calibrations that NO_2^- is not a product channel for this ion molecule reaction. Even for reactions of CF_3O^- with stronger acids (e.g., $\text{CF}_3\text{O}^- + \text{HCl}$, and $\text{CF}_3\text{O}^- + \text{HNO}_3$) where the above reaction channel is exothermic, the primary product ion is observed to be the cluster of $\text{HF}\cdot\text{X}^-$, where X corresponds to the respective anion (Huey, et al, 1996; Amelynck, et al, 2000). This possibly points to a high barrier for the above reaction channel.

Perhaps more concerning is the possibility of ligand exchange reactions of $\text{HF}\cdot\text{NO}_2^-$ with H_2O (e.g., $\text{HF}\cdot\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}\cdot\text{NO}_2^- + \text{HF}$). However, laboratory calibrations over a wide range of water vapor mixing ratios show that this does not occur to any great extent. This implies that the binding energy for HF with NO_2^- is somewhat larger than H_2O with NO_2^- which has been measured to be $-16 \text{ kcal mol}^{-1}$. This constraint on the binding energy between HF and NO_2^- also demonstrates that collisional dissociation of $\text{HF}\cdot\text{NO}_2^-$ is also unlikely under the conditions of the CIMS ion-molecule reaction region.

Lastly, the “periodic noise” (assuming this is the diurnal cycle which is referred to by this term) is also mirrored in the independent measurement technique. This gives confidence to the idea that the diurnal cycle which is observed is not an artifact of the instrumentation, but rather a real phenomenon occurring in the atmosphere.

Comment (7): page 7396, interference tests: Was pure SO_2 tested (there should be no interference...) or SO_2+NO_2 (known interference)?

Response: Both tests (pure SO_2 and SO_2+NO_2) were performed. The text now reads: “Interference from pure SO_2 was tested with an SO_2 /air mixture containing an SO_2 mixing ratio of ~ 50 ppbv, which was sampled by the HONO instrument. Interference from the SO_2+NO_2 /Air mixture was also tested. The interference in both tests was found to be small and negligible.”

Comment (8): page 7399, line 14: In Beine et al. no HONO formation was observed in Antarctica also under low snow pH, from which they question pure nitrate/ HNO_3 photolysis but postulated reactions similar to George et al., or Stemmler et al. on snow, which were recently confirmed in the lab.

Response: We agree with the reviewer that organics play an important role in photochemical HONO formation from various precursors. Meanwhile, we believe that the salt content and surface/snow pH are also very important in HONO formation/deposition (e.g., Beine et al., 2005).

Comment (9): page 7400, line 3: The study of Rohrer et al. is on a different reaction: a) artificial HONO formation in a Teflon chamber b) the photochemical production of HONO (=daytime chemistry) is studied. However, in the present study differences appear during night.

Response: We have removed this sentence, as suggested.

Comment (10): page 7400, differences cold/hot days: Was the wind speed (turbulence) different between the cold and hot days? Then the differences could be explained simply by differences in the BLH and the night-time formation of HONO on ground surfaces.

Response: We looked at the differences in wind speed, relative humidity, and NO₂ concentration during nighttime between hot and cold period. Although the nighttime wind speed during the cold period was higher by a factor of ~1.2 (0.78 m s⁻¹ versus 0.65 m s⁻¹), the relative humidity during the cold period was high by a factor of 1.25 (86% versus 69%), while NO₂ concentrations during these two periods were about the same. Considering the calm wind during the two periods and the higher RH during the cold period, we think the differences in the boundary layer height (BLH) can unlikely explain the differences in HONO during these two periods. The different nighttime HONO formation rates in ground surfaces may be the main reason for the different HONO levels during the two periods.

11) Intercomparison: There is a very strong periodic noise on the CIMS instrument (see Fig. 7) and the amplitude of the noise is almost similar to the HONO level. Any explanation? Considering this noise the agreement is excellent.

Response: As we have pointed out in the text (i.e., in Page 7400), we attribute the large CIMS noise to the relatively poor precision ($\pm 25\%$, 1σ) of the CIMS measurements and a small fraction (3%) of the CIMS measurement time dedicated to HONO measurement for the need of measuring other 25 species. We believe that the noise can be decreased by increasing the time fraction of CIMS measurements dedicated to HONO measurement.

References:

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