Referee 2:

We appreciate the reviewer's helpful comments on the manuscript. Thank you very much for your time and effort!

Comment:
• The authors use relative humidity throughout the manuscript as a measure for water in the atmosphere. This makes sense when analyzing heterogeneous chemistry as the amount of water on a surface is related to RH. On the other hand I am puzzled by the use of RH to understand the vertical structure of the atmosphere, as RH depends both on water mixing ratios and temperature. It is thus impossible to separate water vapor mixing ratios profiles from temperature profiles when showing RH alone. Vertical transport of water vapor will primarily depend on the mixing ratio gradients. It thus seems to me that, for the comparisons with HONO gradients, showing water mixing ratios or their gradients in figures 5 and 7 would make more sense.

The temperature dependence of RH is truly a problem when discussing the vertical structure of the atmosphere. As we are really interested in showing the relation of HONO and RH (see also discussion in section 3.4 and point 9. Referee 1) we will keep the vertical structure of RH in Fig. 7. For comparison with the mixing ratio differences of HONO and the coupling regimes (Fig.5), the relation to specific humidity differences at the two heights are now included in Fig. 5 (upper panel) instead of RH differences.

• Section 3.2.2: It is difficult to directly compare S/V of aerosol and surface to interpret chemistry as the gas transport processes to the respective surfaces may be the limiting factor in the heterogeneous conversion of NO2 to HONO. Gas transport to and from aerosol is much faster than that to and from the ground. Therefore, one cannot draw a clear conclusion that the low aerosol S/V necessarily means that there is no significant conversion of NO2 to HONO on the aerosol. A more detailed analysis and discussion is needed to support the authors claim that HONO formation on the aerosol can be neglected.

We agree with the reviewer that a direct comparison of the conversion of NO_2 to HONO on aerosol surfaces and the ground surface is difficult. In fact, a detailed analysis and discussion of the contribution of aerosol surfaces to the conversion of NO_2 to HONO is out of the scope of this manuscript. Since our original statement may be somewhat misleading, we have changed the corresponding passage, now stating that in our study, the contribution of aerosol surfaces to HONO formation seems to be less important than the ground surface, which is in line with other cited literature (e.g. Kleffmann et al. 2003).

• Page 21123, Line 9-11: Why would one expect a correlation of HONO concentration with NO2? Based on HONO chemistry it should be the HONO formation rate, i.e. d[HONO]/dt, that correlates with NO2 concentrations (or any other HONO precursor).

This is right. As information about the HONO formation rate is limited to 6 nights, its correlation to NO_2 was not discussed. Based on this limited data set, if there is a correlation at all, d[HONO]/dt is slightly anti-correlated to NO_2 at both heights (r^2~0.05). Although a direct correlation is not expected (see discussion above), higher NO_2 mixing ratios should cause higher HONO mixing ratios assuming similar heterogeneous conversion rates. HONO vs. NO_2 should reflect this general trend. We do not state that the lack of this trend (or the

correlation) means NO_2 is not a precursor for HONO. We simply do not see a correlation which is similar to results from another rural forest site (Zhou et al 2002a). This indicates that other processes like deposition or reemission are also important. The manuscript has been clarified accordingly.

• Section 3.3: This section would benefit from a slightly more detailed explanation of the origin of the different coupling regimes. Many readers may be unfamiliar with this classification and they would have to first read other manuscripts to follow the author's arguments. Also please add a reference to the Serafimovich et al (2010) manuscript in this section, as it will otherwise get lost in the experimental part of the paper.

We agree with this suggestion and included more information in the manuscript (see also comment Referee 1). We also added a reference to Serafimovich et al. (2010) in this section.

• The authors repeatedly state that HONO under the canopy is formed at the ground. Can it not also be formed at the bottom of the canopy?

We cannot exclude formation of HONO at the bottom of the canopy but profile measurements of ozone (which has a clear sink towards the ground) indicate that downward transport during the periods where HONO formation is observed close to the forest floor was not efficient, as the steepest ozone gradients (bottom of canopy to HONO measurement level at the ground) occurred during the same period. From micrometeorological measurements, there are hints that the lowest 1 m above ground was partially (in space and time) decoupled from layers above. Additionally, it is hard to explain why the bottom of the canopy should act as a HONO source if at the same time the canopy does not act as a source.

• Page 21128, line 27-30 and Figures 5&7: Fig. 5 shows that the time around 21:00 is dominated by wave motion with a decoupling of the atmosphere above and below the canopy. Fig. 7, on the other hand, shows simultaneous increase of HONO at both altitudes at 21:00. The manuscript states that this event was due to an airmass exchange. How do the authors reconcile the conclusion that at this time mixing was not important (Fig. 5) with the fact that the HONO increase on Sept 23 occurs below and above the canopy simultaneously (Fig. 7)?

Coupling regimes represent an average situation for a 30 min interval and they only refer to coherent structures. We used these regimes to figure out which compartments of the forest are coupled to the air above the canopy and used their occurrence as a measure of "effectiveness" of vertical mixing (see updated manuscript). The domination of wave motions means that turbulence is not well developed. Hence, there is no effective vertical transport as indicated by the occurrence of HONO mixing ratio differences up to about 200 ppt during this event (above canopy mixing ratios are twice that at the forest floor). However, this does not mean that there is no exchange at all. Unfortunately, due to routine zero air measurements, HONO data points during the increase are missing. If we instead refer to NO_2 measurements, a time lag of about 20 min can be inferred between above canopy and ground level.

• Figures 1 and 2 would benefit from showing the actual HONO mixing ratios measured by the two instruments. In the case of Figure 1 it appears that during times of low visibility the HONO mixing ratios were also low, which would lead to large relative discrepancies between the two instruments at small absolute differences between the HONO measurements. In the case of Figure 2, showing the upper level HONO mixing ratios would allow to put the below canopy data into perspective and support the conclusions of heterogeneous formation on the

ground. It would also help to show NO2 and NO data in this plot as it is used and discussed in the manuscript, but never displayed.

We added both HONO mixing ratios in Fig. 1 (see also comments 3 and 4 of Referee 1) and NO_x measurements in Fig. 2. As Fig. 2 is already quite busy we do not follow the reviewer's suggestion to include upper level HONO mixing ratios in this figure as the diurnal mixing ratio differences are discussed extensively in section 3.3, Figs. 5, 6, and in more detail in Fig.7. But Fig. 3 now contains the upper level HONO measurements as well as NO, NO_2 and ozone measurements at this height.

• Figure 7: While I like the aesthetics of this figure it is extremely difficult to actually see the gradient between the two HONO measurements. Please make this figure clearer.

For clarity, an upper panel has been added to Fig. 7 which shows the HONO mixing ratio differences (“gradient”) and the coupling regimes for that day.