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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Daytime HONO Vertical Gradients during SHARP 2009 in Houston, TX" *by* K. W. Wong et al.

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Response to Referee #2

We would like to thank the reviewer for the helpful comments on our manuscript. Below are our responses (in italics) to the specific comments by the reviewer.

General comment on "photolysis": The usage of the term "photolysis" is sometimes confusing. The formation of NO2* is a photo excitation (beyond the dissociation threshold) as, photolysis by definition implies a breakup of the molecule (e.g. P24366 and P24384). Although the authors use consistently photolysis frequency for J(HONO) throughout the text, on page 24367 it is called photolysis rate. If you like to use

another term, this would be the photolysis rate constant as the photolysis rate would be J(HONO)x[HONO]. Furthermore, on P24369 the HONO yield depends on NO2 photolysis frequency not on NO2 photolysis (this may refer to more passages in the text). On the same page the humic acids are not photolyzed. They absorb light (photo excitation) and then transfer this gained energy to another molecule (so called "photosensitized reaction").

Corrections were made in the text for consistency of photolysis frequency and photolysis rate.

P24368, L 6-21: As this paragraph is a summary of the last 30 years of research on atmospheric HONO the cited references are only a selection. You may indicate that by "e.g." in front of the citations. L 24: Ziemba et al. (2010) find no light-dependence of their proposed reaction (see also below comment).

Correction was made.

P24370, L21: As the proposed heterogeneous source is not light dependent (Ziemba et al., 2010), I suggest deleting or moving this citation. What is the influence of such a non-light-dependent reaction at the aerosol surface on your vertical profiles?

Sentence was deleted. Dark reactions at the aerosol surface have no impact on the vertical profiles of HONO at night according to our previous modeling study (Wong et al., 2010). Therefore, non-light-dependent reactions at the aerosol surface are not expected to have an impact on the vertical profiles of HONO during the day.

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Wong, K.W., H.-J. Oh, B.L. Lefer, B. Rappengluck, J. Stutz, Vertical profiles of nitrous acid in the nocturnal urban atmosphere of Houston, TX, Atmos. Chem. Phys., 11, 3595-3609, 2011.

P24371, L21: Kleffmann et al. (2003) did not measure gradients during daytime. All discussed gradient measurements in this publication refer to nighttime. During daytime these authors measured at constant altitude (30m). But I am aware of two other publications (Häseler et al., 2009, Sörgel et al., 2011) about daytime HONO vertical distribution.

The reference "Kleffmann et al., (2003)" was corrected to "Kleffmann et al., 2007". The two studies on vertical gradients of HONO were added to the text. The sentences "However, vertical gradient measurements at 0.5 m and 25 m in a forest showed no vertical gradients of HONO (Sorgel et al., 2011a)." and "However, airborne measurements of HONO in the lowest 1000 m showed no vertical gradients (Häseler et al., 2011)." were added to the introduction.

P24372, L25: Please explain what "UCLA" means. Presumably: University of California Los Angeles.

Sentence in the text is revised as "Measurements of daytime HONO and NO_2 vertical concentration profiles were made from April 20 to May 30 during the 2009 Study of Houston Atmospheric Radical Precursors (SHARP 2009), in Houston, TX, using the long-path differential optical absorption spectroscopy instrument (LP-DOAS)."

P24374, L7: How were these concentrations scaled?

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The calculations of concentrations were shown in Figure 1 (as indicated in the text).

P24374/75: 2.2 radiation measurements: In their later analysis the authors discuss correlations of the HONO source to actinic flux and solar irradiance in the visible and the UV. As the instrument to measure solar (visible) irradiance is only sensitive to wavelength from 400-700nm I assume that UV-irradiance (290 – 385 nm) was retrieved from the spectroradiometer (SAFS). Although, possibly contained in the cited literature, it would be nice to add a sentence about how actinic flux and irradiance values were retrieved from the same instrument. As the differences in both are essential parts of the discussion. Furthermore, where was the optical collector of the SAFS mounted? This may be critical as the reflected radiation (large part of the difference between irradiance and actinic flux) might be very heterogeneous in the urban canopy. So my question is, are the actinic flux values only representative for moody tower or do they reflect an averaged scenario. In a more general way, what is the influence of the rough urban canopy (shading patterns, street canyons) on the difference of irradiance and actinic flux?

The sentence "The UV irradiance in the range of 286.5 – 363 nm was measured by the Brewer MkIV Spectrophotometer." has been included in the text. As already mentioned in the paper, the visible irradiance in the range of 400 nm to 700 nm was measured at the same location by the BF3 Sunshine Sensor. The actinic flux, which is used to calculate the photolysis frequencies, was taken by the actinic flux spectroradiometer (SAFS).

The actinic flux and solar irradiance measurements were taken on the roof of Moody Tower. They are expected to be representative along our LP-DOAS measurements, which were located above urban structures. The urban structures along our measurement path, are mostly one- to two-story buildings. A very small fraction of our

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measurements is located in Downtown Houston, where buildings are expected to impact solar irradiance and actinic flux significantly. However, the impact of urban ground surface structure is not expected to play a significant role on the difference between actinic flux and solar irradiance since our measurements were horizontally integrated over 4-5 km distances.

P24377, L 7: "Elevated daytime HONO mixing ratios". Elevated with respect to what?

This sentence has been revised as "Cloudy days also showed daytime HONO mixing ratios which were larger than the expected photostationary state mixing ratios. . . ." to avoid confusion.

P24378, L16: In contrast to the presented data, these observations were made in rural environments (Zhou et al., 2001 even in the arctic). Measurements in urban areas showed a diurnal cycle similar to your observations, as stated in your conclusions.

This sentence has been clarified and revised as "Measurements in urban areas showed similar diurnal variations in HONO mixing ratios. In contrast to our observations, some measurements in rural environments showed a peak in HONO mixing ratios at solar noon (Acker et al., 2006b; Zhou et al., 2001)."

P24379, L4-6: This implies that HONO formation at that time of the day could be well explained by gas phase chemistry only, as also suggested by Fig. 5. As from Fig. 3 I would suggest 7:00 CST being shortly after sunrise one would still expect "excess HONO" from the nighttime accumulation leading to higher observed HONO/NO2 ratios. Do the authors have any explanation for that? For example, is the HONO/NO2 ratio lower due to traffic emissions in the early morning (Fig. 3 and Fig. 5)?

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The observed [HONO]/[NO_2] ratios were only about 1% before sunrise on 21 April and 18 May. Therefore, the observed ratios in the early morning as shown in Figure 3 and Figure 4 were similar to those before sunrise. The reason why the [HONO]/[NO_2] ratios were only 1% before sunrise was not within in the scope of this study and was thus not investigated.

L15: Any explanation for the jump in boundary layer height in the late afternoon (Fig.4a). Does this have an observable influence on the vertical gradients?

We do not know the exact cause of the sudden increase in boundary layer height on this day. Change in meteorological conditions at this time is believed to be the cause. We do not see any observable impact on the vertical gradients. However, one may expected the jump of boundary layer height could lead to the decrease of mixing ratios of trace gas. This seems to be reflected more obviously in the NO_2 mixing ratios in the lower height intervals, than in the HONO mixing ratios.

P24380, L15: This should be 18th May instead of 19th.

Correction was made in the text.

P24382, L13-19: The NO2 scaling approach is similar to that of Sörgel et al (2011) for a semi-rural environment.

This comment has been included in the text. The sentence "The approach of normalizing the unknown HONO formation rate with NO_2 mixing ratio was also used by a

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recent study in a semi-rural environment (Sörgel et al., 2011b)." was added.

P24383: 4.2 Possible daytime HONO formation pathways: A new possible source was published after this manuscript (Su et al., 2011). Can the authors comment on the possible influence of soil produced HONO in the urban area of Houston.

We included this study in the revised paper. The following sentences were added in the text.

"A recent study by Su et al., (2011) suggested that soil nitrite can also be a strong source of daytime HONO. The emission of HONO from soil showed diurnal variations with a maximum at noon, with a similar magnitude than the observed missing HONO source." was added to the introduction. The sentences "Proposed photolytic HONO formation pathways that occurs on the ground include the photolysis of HNO_3, NO_2 conversion on humic acid and HONO formation from soil nitrite (Zhou et al., 2003; Stemmler et al., 2006; Su et al., 2011)." and "HONO formation from soil nitrite is not shown to depend on gas-phase NO_2 concentration, but on nitrite concentration in the soil, which depends on soil acidity and temperature (Su et al., 2011). We do not have sufficient data to evaluate if soil nitrite can be the missing daytime HONO source." were added to the discussion section of the paper. The sentence "Our results showed that it is also possible that photolysis of adsorbed nitric acid at the ground and soil nitrite could be important sources." are included in the conclusion section.

L 17: I'm curious to know, how the 5 min vertical transport timescale was estimated.

The 5 min vertical transport timescale is the average turbulence mixing timescale calculated by a 1-D chemistry and transport model which was adopted for our previous modeling study (Wong et al. 2011). The vertical transport timescale is an average

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timescale between 130 and 300 m at noon, as indicated by our model.

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P24384, L 20: This has also been shown by a very recent kinetic study (Amedro et al., 2011; published after this manuscript).

A reference to this study is now included in our paper. The sentence "Recent laboratory study by Amedro et al. (2011) also found that this reaction is not important for daytime HONO formation." was included in the text to support our findings on HONO formation by $NO_2^* + H_2O$.

P24387, L 3: Given that the differences in the correlation coefficients between Pnorm and ultraviolet respectively visible irradiance are significant, how does this compare to the mechanism of Stemmler et al. (2006) which also works for the visible region (400-700nm).

In the mechanism proposed by Stemmler et al., 2006, HONO formation due to UV irradiance occurs more efficiently than due to visible irradiance at the same intensity of irradiance. HONO formation in the visible irradiance is expected to contribute more to HONO formation since the intensity of visible irradiance is larger than that of the UV irradiance in the atmosphere. However our study does not show significant differences in the correlation coefficients between Pnorm and UV irradiance and Pnorm and visible irradiance.

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P24387, L16: It would be less confusing using consistently “solar irradiance” instead of alternating between “solar irradiance” and “solar radiation” especially as your measurements of solar irradiance only reflect a part of the solar radiation. This also applies to Figs. 8, 9 and 10 where the axis titles are “solar visible radiation”, “solar radiation” and “solar visible irradiance”. Do they all mean the same?

Corrections were made in the text to change “solar radiation” to “solar irradiance” for consistency. The axis title in Figure 8 was changed to “Solar Visible Irradiance” from “Solar Visible Radiation”.

P24390, L13: Kleffmann et al. (2003) did not measure daytime gradients (see above comment). Thus I suggest deleting this reference.

This reference “Kleffmann et al., 2003” is corrected to “Kleffmann, 2007”..

P24403/4, Figure 3 and Figure 4: If possible avoid overlapping of numbers. In the text and the axis title J(HONO) is used as proxy for actinic flux, whereas in the figure caption J(NO2) is given as measured quantity. Please clarify. If possible use different symbols (dots, triangles,: : :) for the different heights and explain them in the figure caption.

Corrections in the figure caption were made. J_{HONO} was shown in Figure 3 and 4. The two figures were also modified so that there is no overlapping of numbers.

Technical: P 24373, L28: (“. . . path-integrated mixing”) ratios. . . P 24383, L10: 300_m

Corrections were made.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24365, 2011.