Chapter 1
Field Observations of Daytime HONO Chemistry and Its Impact on the OH Radical Budget

Jochen Stutz, Kam Weng Wong, and Catalina Tsai

Abstract Measurements of daytime nitrous acid (HONO) are reviewed and possible daytime sources of HONO are discussed. The importance of the observed daytime HONO mixing ratios for the HOx budget in urban and rural environments is assessed and recommendation for future work are given.

Keywords Nitrous Acid • Daytime radical chemistry • Heterogeneous chemistry

1.1 Introduction

The formation of nitrous acid, HONO, during the day has received considerable attention in recent years due to its potential impact on the chemistry of hydroxyl radicals, OH, in the lower troposphere. It is well known that the photolysis of HONO accumulated throughout the night:

$$HONO + hv \xrightarrow{\lambda<400\,\mathrm{nm}} OH + NO \tag{1.R1}$$

is a significant, and often the dominant, source of OH-radicals in the early morning, when other primary HO_x ($OH + HO_2$) sources, such as ozone and HCHO photolysis, are still weak [3, 4]. HONO mixing ratios typically decrease after sunrise, and for many years it has been assumed that HONO reaches a photo-stationary state, $[HONO]_{ss}$, between its photolysis (1.R1), the gas-phase formation from NO and OH (1.R2), and its reaction with OH (1.R3):

$$NO + OH \rightarrow HONO \tag{1.R2}$$

$$HONO + OH \rightarrow NO_2 + H_2O \tag{1.R3}$$

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$$[HONO]_{ss} = \frac{k_2[NO][OH]}{J_{HONO} + k_3[OH]} \tag{1.1}$$

However, atmospheric observations in recent years have found daytime HONO mixing ratios of up to 100–300 ppt, that considerably exceeded the expected $[HONO]_{ss}$ (e.g. [1, 19, 30, 47]).

Urban daytime HONO mixing ratios are generally found to be highest in the morning and to decrease throughout the day, or to show a minimum at noon [2–4, 11, 39]. Remote and semi-rural HONO mixing ratios were found to peak at noontime [1, 44] or showed similar diurnal profiles as in urban areas [18, 30, 47]. Most of these observations were performed at one altitude, often within the lowest 10–20 m from the surface, and information on the vertical distribution of daytime HONO is still sparse. Significant vertical HONO gradients were not observed in a semi-rural area in Germany on a 190 m high tower [18] or in the lowest 25 m of a forest [29], while Villena et al. [39] found higher daytime HONO mixing ratios at 6 m compared to 53 m altitude in an urban area in Chile. Negative HONO vertical gradients were also observed by aircraft in the lowest 2,500 m of the atmosphere in northern Michigan [43], while airborne measurements of HONO in the lowest 1,000 m above the ground in Germany showed no vertical gradients [15].

The observed daytime HONO mixing ratios are expected to impact the HO_x budget in urban and rural areas [2, 19, 22, 27, 47]. Previous analyses have attributed up to 55% of the total primary OH formation to HONO photolysis [1, 3, 5, 11, 19, 23]. Nevertheless, the magnitude and impact of daytime HONO on the OH budget is still not well established. The observation of vertical HONO profiles implies that the OH formation from HONO photolysis could be altitude dependent, but little effort to investigate this effect and its impact on the tropospheric OH budget has been made.

To address the questions of the vertical distribution of HONO, its daytime formation, and the impact on OH, we have performed observations of HONO vertical concentration profiles with long-path Differential Optical Absorption Spectroscopy (LP-DOAS) in Houston, Texas, USA, in spring 2009. Here we will use these observations to identify possible sources of HONO during the day. In addition, the altitude dependence of primary OH formation by HONO photolysis, and its contribution relative to those from ozone, and HCHO photolysis, will be discussed.

1.2 Daytime Chemistry of HONO

The presence of HONO mixing ratios above the simple photo-stationary state during the day has now been firmly established. Nevertheless, the exact mixing ratios are still under discussion due to the difficulty of accurately measuring HONO, as well as a still sparse dataset on daytime HONO in different environments.

The source(s) of daytime HONO also remain elusive. It is, however, clear that the non-photolytic conversion of NO_2 on humid surfaces, which is believed to be responsible for the nocturnal accumulation of HONO [13, 35, 41], is too slow to explain the observed daytime HONO mixing ratios [17]. Consequently a number of new HONO formation pathways have been proposed. Following atmospheric and laboratory observations most of these mechanisms have in common that they require solar radiation [14, 21, 31, 47].

Two gas-phase mechanisms have been proposed: The photolysis of *ortho*-nitrophenols [7] leads to the formation of HONO with a rate that is linearly dependent on the *ortho*-nitrophenol concentration and the actinic flux. HONO formation through the formation of photo-excited NO_2, NO_2^*, followed by its reaction with water vapor is expected to be proportional to the actinic flux, NO_2 concentrations, and water vapor concentrations. The rate and branching ratio of the $NO_2^* + H_2O$ reaction is currently uncertain [8, 9, 21]. Only at the higher rate reported by Li et al. [21] is this mechanism important [12].

Two different heterogeneous mechanisms are currently under discussion. The first is based on the photo-enhanced conversion of NO_2 on organic surface films. Laboratory studies found that the conversion of NO_2 to HONO on aromatic hydrocarbon films, such as phenols and aromatic ketones, was accelerated by 1–2 orders of magnitude upon irradiation with UV light (300–420 nm) compared to the dark reaction [14]. A similar enhancement was found on humic acid (HA) surfaces [31]. To explain these observations a mechanism forming HONO through the reaction of NO_2 with photolytically activated reductive centers (A^{red}) has been proposed [31]. The formation of HONO on these surfaces was found to be first order in NO_2 for low to semi-polluted conditions and linearly dependent on irradiance in the spectral range from 300 to 700 nm (see Eq. 1.2).

$$\frac{d[HONO]}{dt} \propto surface\ area\ concentration \times [NO_2] \times Irradiance \tag{1.2}$$

The second heterogeneous HONO formation mechanism is the photolysis of surface adsorbed nitric acid (HNO_3), which has been suggested based on a number of field measurements in remote areas [6, 10, 16, 47] and a glass sample manifold experiment [45, 46]. Further evidence for this mechanism was recently presented by Zhou et al. [48]. The formation of HONO is expected to be proportional to UV solar irradiance and the amount of the surface adsorbed HNO_3.

These mechanisms can occur either on surfaces at the ground or on aerosols. Stemmler et al. [32] suggests that the humic acid pathway is unimportant on aerosols. However, other similar HONO formation processes on aerosols, or the photolysis of aerosol nitric acid cannot be excluded. The main difference between the ground surface and aerosol pathways is their dependence on solar radiation. While surface processes should be proportional to solar irradiance (Eq. 1.2), aerosol processes should be proportional to the actinic flux.

Su et al. [37] recently proposed that soil nitrite was also a strong source of daytime HONO. HONO soil emissions did not depend on gas-phase NO_2, but rather on soil nitrite, which, by itself, was dependent on soil acidity and temperature. Finally, it should be noted that direct emission is also a possible source of daytime HONO in urban areas [20, 25]. This source would solely depend on temporal traffic patterns and correlate, through co-emission, with NO_x ($NO + NO_2$).

1.3 Spectroscopic Observation of Daytime HONO

Observations of daytime HONO, NO_2, O_3 and HCHO were performed using LP-DOAS [26] in April and May 2009, in Houston, Texas, USA. The LP-DOAS telescope was set up on the roof of a 70 m high building on the campus of the University of Houston. The telescope sequentially sent light from a Xe-arc lamp onto three arrays of retroreflectors, which were mounted at different altitudes (20 m, 130 m and 300 m agl) on buildings in downtown Houston (Fig. 1.1). The light returning from the retroreflectors was detected by a spectrometer-detector combination in the wavelength interval from 300 to 380 nm, as described in detail in Wong et al. [42]. Spectral retrieval of NO_2, HONO, O_3 and HCHO concentrations was achieved using the DOAS method (see [3, 36] for details), using literature absorption cross section of the different trace gases [24, 34, 38, 40]. The mixing ratio errors reported here were derived by the retrieval routine and are 1σ statistical uncertainties [33, 42]. The detection limit of path averaged HONO mixing ratios was in the range of 10–30 ppt. Figure 1.2 shows that daytime HONO was clearly identified spectroscopically in Houston. Path-averaged mixing ratios of the lower and middle light paths are

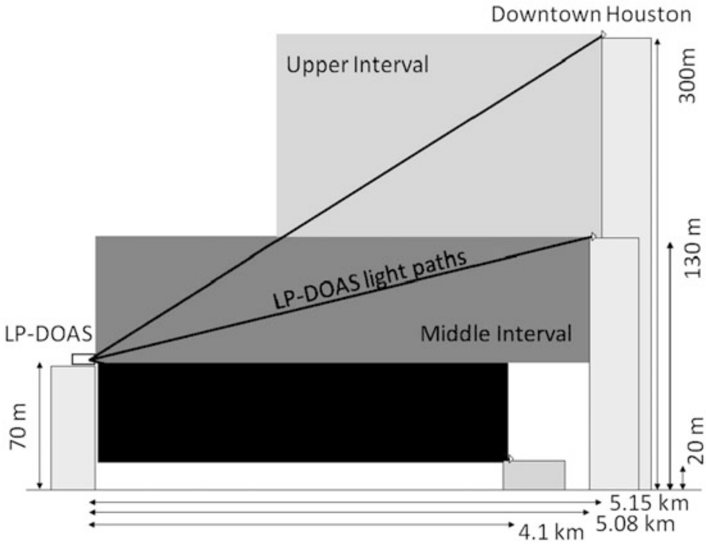
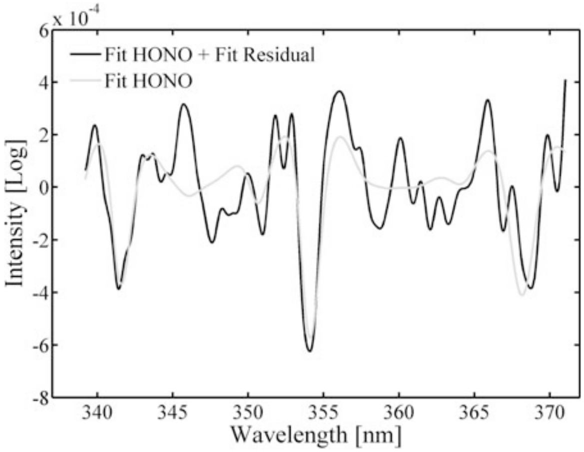


Fig. 1.1 Setup of LP-DOAS instrument in Houston, TX

Fig. 1.2 Comparison of a HONO reference spectrum (*gray line*) with the retrieved HONO signal (*black line*), i.e. the HONO absorption together with unexplained spectral structures [42]. A HONO mixing ratio of 0.139 ± 0.013 ppb was clearly identified in the spectrum



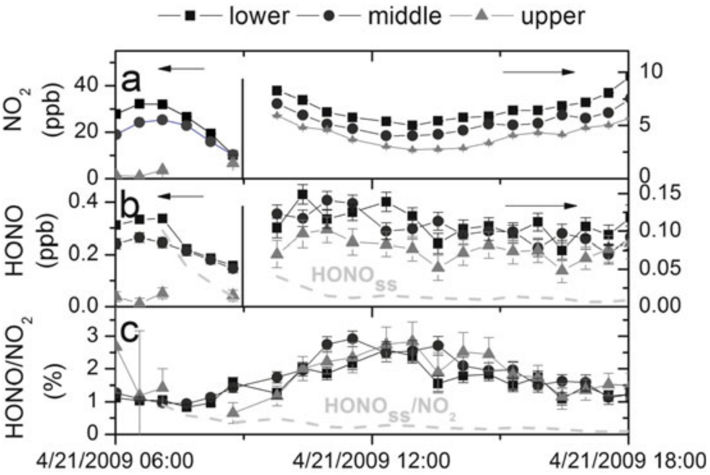


Fig. 1.3 [NO_2], [HONO], and [HONO]/[NO_2] for a sunny day (21 April 2009) in Houston, TX (Adapted from Wong et al. [42])

representative for the respective height intervals: (20–70 m and 70–130 m). The mixing ratio in the upper height interval (130–300 m) was calculated by subtracting the scaled mixing ratios of the middle light path from the upper light path.

Figure 1.3 shows NO_2 and HONO mixing ratios in the three height intervals during a sunny April day in Houston. Clear vertical gradients with higher mixing ratios in the lower height interval were found for both species. The diurnal cycle of NO_2 showed a minimum at noon, while HONO mixing ratios displayed a slow decrease throughout the day. The HONO behavior is similar to that observed in other urban studies [2, 11, 39]. The [HONO]/[NO_2] ratio, which can be used as a parameter to analyze HONO formation, shows a clear maximum around noon. This is in agreement with previous observations, which found this behavior to correlate with NO_2 photolysis and thus is indicative of a photolytic HONO source [2, 11, 39]. Our observations show no statistically significant vertical profile in [HONO]/[NO_2], in contrast to previous reports that sometimes found larger [HONO]/[NO_2] ratios aloft [39].

1.4 Daytime HONO Sources

Using observations of [OH], [NO] and HONO photolysis frequencies, J_{HONO}, we calculated $[HONO]_{ss}$ following Eq. 1.1 [42]. A comparison with the observations shows that the observed HONO mixing ratios exceeded this value considerably during the day (Fig. 1.3), confirming previous reports of an unknown source of HONO during the day (e.g. [17, 30]).

Using a pseudo steady state approach between the various HONO formation and loss pathways we can calculated the strength of the unknown HONO source, $P_{unknown:}$

$$P_{unknown} = J_{HONO}[HONO] + k_3[HONO][OH] - k_2[NO][OH] - emission \quad (1.3)$$

Emission rates previously determined in Houston [41] were used in this calculation. A comparison between the HONO loss rate and $P_{unknown}$ shows that $P_{unknown}$ is the dominant source term for daytime HONO (Fig. 1.4a). The difference between loss and $P_{unknown}$ in the morning can be explained by traffic emissions and the OH + NO pathway, which is higher in the morning, due to elevated NO levels in Houston.

$P_{unknown}$ shows a clear asymmetry throughout the day, with higher levels in the morning than the afternoon. Considering that many daytime HONO formation mechanisms assume a dependence on [NO_2], one of the likely HONO precursors, we normalized $P_{unknown}$ to [NO_2]: $P_{unknown}{}^{*} = P_{unknown}/[NO_2]$. $P_{unknown}{}^{*}$ shows a symmetric diurnal profile that varies with actinic flux and/or solar irradiance (courtesy of B. Lefer, N. Grossman, U. Houston). This result, which was observed on other sunny days in Houston, supports the conclusion that the formation of daytime HONO involves NO_2 (Eq. 1.2), or a species that shows the same diurnal profile as NO_2.

Figure 1.4b also shows the observed NO_2 photolysis frequencies and the visible solar irradiance. It is clear from these observations that, while these two quantities are related, they have a different diurnal profile. Through a correlation analysis of the dependence of $P_{unknown}{}^{*}$ on these two parameters one can gain insight on daytime HONO formation, i.e. ground vs. gas-phase/aerosol. We performed this analysis for $P_{unknown}{}^{*}$ in the lower and middle height interval on the four cloud free days during the Houston experiment. The range of correlations of $P_{unknown}{}^{*}$ with NO_2 was $R^2 = 0.58$–0.89 with an average $R_{avg}{}^{2} = 0.76$, while the correlation coefficient with visible solar irradiance (400–700 nm) was in the range of $R^2 = 0.65$–0.96 with an average of $R_{avg}{}^{2} = 0.85$ and that of UV solar irradiation (286.5–363 nm) was in

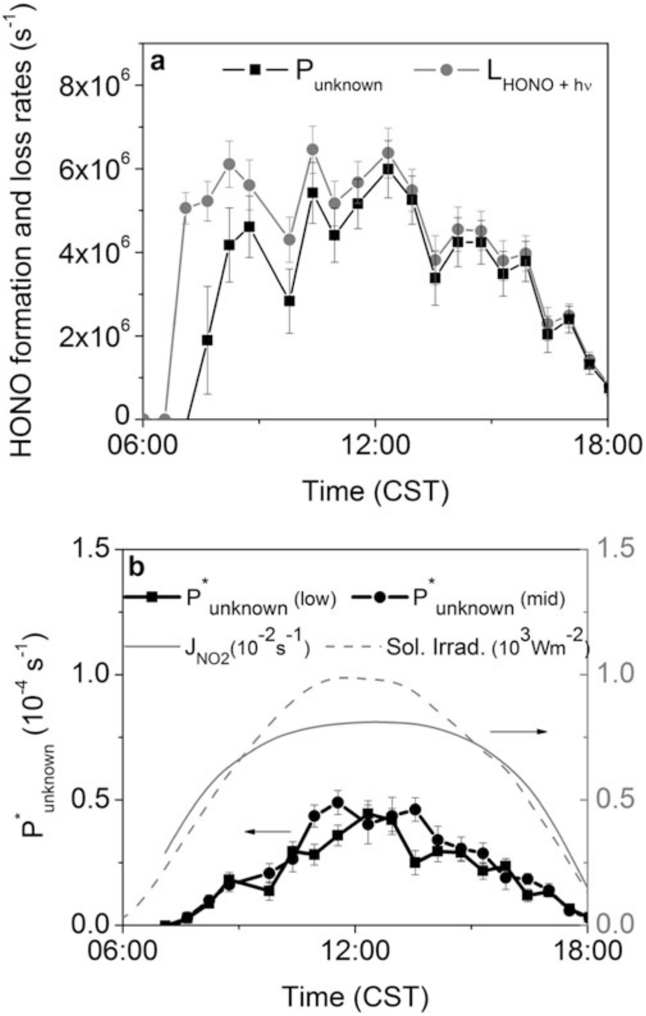


Fig. 1.4 Analysis of HONO observations on 21 April 2009. (**a**) Comparison of photolytic HONO loss with the rate of the unknown HONO source, $P_{unknown}$. (**b**) Normalized unknown HONO source rate, $P_{unknown}{}^{*}$, in the lower and middle height intervals (*left* y-axis), and NO_2 photolysis frequency and solar irradiance (*right* y-axis) (Adapted from Wong et al. [42])

the range of $R^2 = 0.70–0.97$ with an average of $R_{avg}{}^2 = 0.87$ (see [42] for details). These values indicate that $P_{unknown}{}^{*}$ correlates better with solar irradiance than the actinic flux, implying that HONO is predominately formed at the ground [42]. The difference between UV and solar irradiance is not statistically significant and no conclusion can be drawn on the wavelength dependence of the formation process.

A second line of argument against a conversion of NO_2 to HONO in the gas-phase or on the aerosol can be made using the $[HONO]/[NO_2]$ ratio. We will use the well justified assumption that the HONO loss during the day is dominated by its

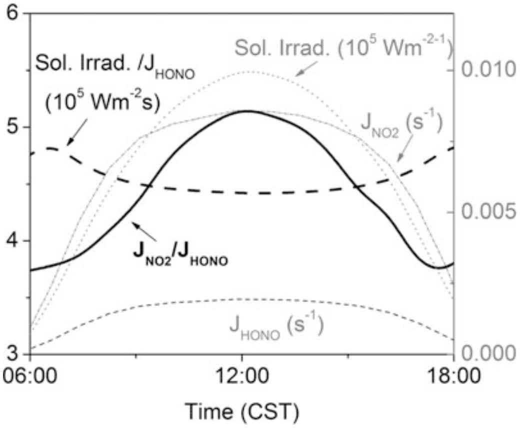


Fig. 1.5 Visible solar irradiance, J_{NO2}, J_{HONO} (*right* y-axis) and the ratios of solar irradiance/J_{NO2} and J_{NO2}/J_{HONO} (*left* y-axis) on a sunny day in Houston (Adapted from Wong et al. [42])

photolysis. As we have shown above the source of HONO in Houston depends on the NO_2 concentration and on either solar irradiance or the actinic flux, which we will for simplicity call J_{source}. As shown above all other potential factors influencing the photolytic HONO source are minor compared to NO_2 and J_{source} in Houston, and are here summarized in a constant. We can now perform a pseudo steady state calculation to determine the function dependence of [HONO]/[NO_2].

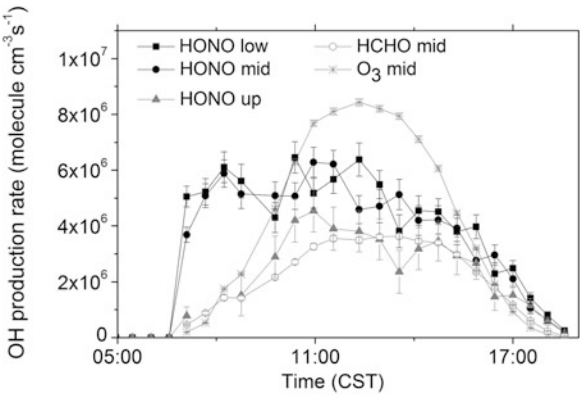
$$\frac{d[HONO]}{dt} = J_{source} \times [NO_2] \times \text{const.} - J_{HONO} \times [HONO] = 0 \qquad (1.4)$$

$$\frac{[HONO]}{NO_2} \propto \frac{J_{source}}{J_{HONO}} \qquad (1.5)$$

From this simple argument one can see that [HONO]/[NO_2] should depend on the ratio between the radiation term in the HONO formation and HONO photolysis. Using observed HONO and NO_2 photolysis frequencies and solar irradiance (Fig. 1.5) one can now apply Eq. 1.5 and compare the calculated diurnal profile of [HONO]/[NO_2] to the observations (Fig. 1.3).

In the case that the HONO source depends on the actinic flux, here J_{NO2} is used as a proxy, the calculated [HONO]/[NO_2] diurnal profile is fairly constant with a slight minimum at noon. This is in contrast to the observations, which showed a clear maximum of [HONO]/[NO_2] at noon (Fig. 1.3). The calculated diurnal profile can be explained by the fact that both, the HONO source and loss rate depend on the actinic flux and thus this dependence mostly cancels out. Consequently [HONO]/[NO_2] is fairly constant throughout the day, or, depending on the wavelength dependence of the photolytic source, has a slight minimum at noon. On the other hand, if the HONO source is linked to solar irradiance Eq. 1.5 results in a maximum of solar irradiance/J_{HONO} and thus a maximum of [HONO]/[NO_2] at noon (Fig. 1.5), in agreement with the observations (Fig. 1.3). This argument thus also leads to the conclusion that HONO formation is most likely occurring at the ground rather than in the gas-phase or on aerosols.

Fig. 1.6 OH formation rates from HONO, O_3, and HCHO photolysis on 21 April 2009, in Houston, TX. Rates from HONO photolysis are shown in all the altitude intervals



1.5 OH-Radical Formation Profiles from HONO Photolysis

HONO mixing ratios showed clear vertical profiles in Houston (Fig. 1.3). As a consequence one would expect that the OH formation rate from HONO photolysis should also be altitude dependent. To illustrate this point we performed calculations of the OH formation rate from HONO photolysis based on our LP-DOAS observations in the three height intervals and direct measurements of the HONO photolysis frequency (Fig. 1.6). The back reaction of OH + NO → HONO was not considered in this calculation, as it has only a minor impact on the HONO budget. For comparison we also calculated the OH formation rate from ozone photolysis to $O(^1D)$ followed by its reaction with water vapor, based on LP-DOAS ozone observations (not shown) and direct measurements of $J_{O3 \rightarrow O1D}$ and water (courtesy of N. Grossberg and B. Lefer, University of Houston). Ozone showed only a small vertical gradient during the day and thus only the results of this calculation for the middle height interval is shown in Fig. 1.6. We also considered the photolysis of HCHO to HO_2 followed by the reaction of $HO_2 + NO \rightarrow OH + NO_2$ as a primary OH source, assuming that the conversion of HO_2 to OH is fast in the polluted atmosphere of Houston, where NO is always present at high concentrations. HCHO mixing ratios by the LP-DOAS instrument (not shown) and observations of J_{HCHO} were used in this calculation. As in the case of ozone, no strong vertical profiles of HCHO were observed during the day. Thus only the OH production rate from HCHO photolysis for the middle light path is in Fig. 1.6.

HONO photolysis dominates in the lowest and middle light path in the morning over O_3 and HCHO photolysis (Fig. 1.6). This result is in agreement with previous observations of the contribution of early morning HONO photolysis to the OH budget, which were all performed close to the surface (for example [3, 4]). In contrast, HONO photolysis is less important as an OH source above 130 m altitude, where it is approximately of the same magnitude as the photolysis of ozone and HCHO. After 10:00 CST ozone photolysis becomes the dominant primary OH source in all height intervals. However, both HCHO and HONO photolysis continue to contribute significantly to primary OH formation. Below 130 m altitude

HONO photolysis is more important than HCHO as an OH precursor, while both processes are about equal in importance aloft. It is interesting to note that HONO photolysis again becomes the dominant OH source in the late afternoon.

These results confirm that OH formation from HONO photolysis is altitude dependent, in particular in the morning. The morning behavior can be explained by considering the meteorology during the morning transition from a stable to a well-mixed boundary layer. It is well known that HONO accumulates in the nocturnal boundary layer, showing very strong vertical HONO concentration gradients [41]. The break-up of the nocturnal boundary layer by solar heating typically occurs a few hours after sunrise, i.e. around 10:00 CST in our case. In the period between sunrise and the nocturnal boundary layer break-up, photolysis of HONO is occurring while vertical mixing remains inhibited. Consequently HONO levels near the surface remain high, mostly due to HONO left over from the previous night and due to the enhanced HONO formation caused by high NO_2 near the surface. HONO levels aloft are low as nocturnal HONO, $[NO_2]$, and the available surface area for heterogeneous chemistry are small. Since photolysis frequencies do not show a vertical profile in the lowest atmosphere, the strong HONO vertical profiles in the morning thus lead to altitude dependent OH formation. As soon as the boundary layer is more efficiently mixed, the HONO profile and the OH formation profile becomes weaker. It should be noted that the mechanism that maintains the observed HONO profile throughout the day is currently under investigation.

1.6 Conclusions and Recommendations for Future Work

Despite the now well established presence of HONO mixing ratios significantly above the simple photo-stationary state between OH, NO and HONO, many aspects of daytime HONO chemistry remain poorly understood. Here we presented open-air LP-DOAS observations of daytime HONO in Houston, Texas, USA. Our HONO observations are similar to those from previous studies [1, 2, 11, 19, 28–30, 39, 43, 45], but fall on the lower end of reported mixing ratios. A comparison of our observations with pseudo steady state HONO mixing ratios confirms that a strong daytime source of HONO is present in the urban atmosphere (see for example Kleffmann [17, 42]). A detailed analysis of our observations leads to the following conclusions:

- The strong daytime HONO source identified in our observations is correlated to NO_2 concentrations. It thus appears that the HONO formation mechanism involves NO_2 or other species that shows a diurnal behavior very similar to NO_2.
- Our results strongly suggest that daytime HONO formation in urban areas occurs at the surface. This conclusion is supported by two different lines of argument. First, the NO_2-normalized daytime HONO formation rate correlates better with solar irradiance than with J_{NO2}, which served as a proxy for the actinic flux. Second, observed $[HONO]/[NO_2]$ ratios show a diurnal profile with a maximum at noon, which can be explained if the formation depends on solar irradiance,

rather than on the actinic flux. Our arguments seem to contradict the proposed gas-phase HONO formation through the reaction of photo-excited NO_2^* with water vapor [21] or photolysis of *ortho*-nitrophenols [7] as an important HONO source in urban areas.

- HONO photolysis contributes significantly to primary OH formation in Houston in the lowest 300 m of the atmosphere. The morning peak in primary OH formation due to the photolysis of HONO accumulated throughout the night [41], is restricted to the lowest 130 m of the atmosphere, which has an impact on the significance of the morning photolysis of nocturnal HONO. The morning behavior can be explained by considering that the break-up of the nocturnal boundary layer occurs a few hours after sunrise, while photolysis starts at sunrise when the boundary layer is still stratified.

A number of open questions on the sources and consequences of daytime HONO remain to be answered. While it has now been established that a significant photolytic daytime source of HONO is present in many environments [17], the exact mechanism of HONO formation is still under discussion. More targeted investigations of the dependence of the photolytic daytime source on environmental parameters are needed. This includes a better understanding of dependence on NO_2 or the identification of other precursors in the atmosphere. The impact of the characteristics and composition of the reactive surfaces and/or films on surfaces needs to be better understood. In particular, the question whether the surfaces investigated in the laboratory are truly representative for surfaces found in the atmosphere needs to be addressed. The dependence of HONO formation on solar irradiance and its wavelength dependence also deserve further attention. The question of a daytime HONO volume source, gas-phase or on aerosols, requires further investigation, as it could be significant in the upper daytime boundary layer and in the free troposphere, where ground surface chemistry has little or no influence. Ultimately, a detailed mechanistic understanding of daytime HONO formation on a molecular level is highly desirable. In light of more and better observations of daytime HONO, as well as the emerging understanding of the altitude dependence of OH formation, more detailed studies on the impact of this OH source on tropospheric chemistry in polluted and remote areas are needed.

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