Atmospheric
Chemistry
and Physics
Open Access
Discussions
EGU

Interactive comment on "Light-induced protein nitration and degradation with HONO emission" by Hannah Meusel et al.

Anonymous Referee #2

Received and published: 1 May 2017

Overview

In this paper, titled "Light-induced protein nitration and degradation with HONO emission" by Meusel et al., the authors present an interesting dataset focused on the uptake of NO2 and subsequent emission of HONO by protein surfaces. HONO is an important reservoir for OH radicals and NOx, but very little is known about its formation and subsequent photochemistry on the surface of aerosol particles, which represent a significant amount of reactive surface area in the atmosphere. Therefore, the topic is very much atmospherically relevant. Based on a series of flow tube experiments, the authors find a dependence of NO2 uptake and subsequent emission of HONO on light intensity, relative humidity, NO2 concentration, and flow tube coating thickness. The authors argue that surface-enhanced NO2 conversion to HONO follows a Langmuir-Hinshelwood reaction mechanism. While I find the topic to be of general interest to

the community, I have several concerns regarding the experimental approach and interpretation, and therefore request that the authors make significant revisions to their manuscript before publication in ACP after considering my comments listed below.

General Comments

1. Section 3.1 (lines 22-23): The authors indicate that additional continuous exposure of the protein surface by light fully decomposed the protein so that no intact protein could be detected. However, the authors should clarify if only the nitrated protein residues decompose or all (nitrated and non-nitrated), and how that might affect ND.

2. Could the authors discuss the atmospheric implications of the irradiance intensity applied in this study compared to the solar irradiance intensity? They mention that their irradiance was 40% of clear sky conditions, similar to cloudy days, so does that imply that this chemistry could be more relevant in the atmosphere than the results suggest? Please elaborate.

3. In the VIS light wavelength range of the lamps used in this study (between 400 nm and 700 nm), NO2 photolysis could be significant and play an important role in the degree of protein nitration and HONO production. Was NO2 photolysis a concern and how might it affect the results?

4. In the last paragraph of the results section 3.1, the authors compare their results, which were conducted in the presence of NO2, with other nitration studies conducted in the presence of both NO2 and O3. How are these comparable, since NO2 and O3 combine to make N2O5 and NO3, which is a much more effective nitrating agent? The authors argue that their low ND may be due to light exposure, whereas the studies with larger ND that they compare to were conducted in the dark in the presence of NO3, so wouldn't the authors expect more ND in the other studies anyway because of the higher reactivity of NO3?

5. Section 3.2.4: The authors conclude that HONO production is greater for larger pro-

tein coating thicknesses. However, the coatings also covered different surface area of the flow tube. Do you expect surface area to be important in the context of this study? My concern is that by shortening the coated length of the flow tube for the thicker coating experiments, the authors potentially introduce bias in their measurement since both NO2 and HONO are exposed to different coated surface areas of the flow tube. Following NO2 uptake by the shorter coated length flow tube, the HONO that is emitted is subsequently exposed to less coated surface area for the remaining length of the flow tube. If a fraction of the HONO is taken up by the protein surface, less protein surface area implies more of the HONO is present in the gas phase. A better approach would have been to either maintain the same length of coated flow tube between experiments or to maintain the same surface concentration of protein between experiments for different coated lengths. The authors should at least discuss potential caveats for changing the coated surface area of the flow tube between experiments.

6. The rate of HONO emission decay as a function of exposure time as presented in Fig. 6 is also a bit confusing; the authors report emission decay rates in the range of 10-20 ppt hr-1, but it is difficult to tell from the y-axis since [HONO] is reported in ppb. It would help if the y-axis and reported rates had the same concentration units. The authors might also consider changing their y-axis to a log scale or plotting the red data points on a separate y axis, so the reader can better observe the decay for different time periods. However, it appears the rate is more on the order of 160 ppt hr-1 (linearly interpolated between 0 and 3 hrs). Why were the HONO emission decay rates only reported near the end of the exposure period (assuming the reported rates cover the exposure periods indicated by the arrows in Fig. 6)?

7. Given the apparent strong dependence on coating thickness, how relevant are the thicknesses of the coatings applied to the flow tube (>200 nm) compared to typical atmospheric aerosol? The authors should at least discuss the implications of coating thickness and HONO formation in the context of atmospheric aerosol particles.

8. Section 3.2.6: Have the authors considered to what extent photolysis of HONO

(in the case of the UV/VIS experiment) plays in the temporal evolution of the HONO concentration? The authors argue that the plateau in the HONO concentration in Fig. 8, followed by continuous and relatively stable emission of HONO from the protein surface is consistent with a Langmuir-Hinshelwood reaction mechanism. However, HONO photolyzes under UV conditions (300 nm $< \lambda <$ 400 nm), so might there be a point when the temporal HONO emission profile becomes limited by photolysis? The authors might consider including a photolysis term in their kinetics calculation (for both NO2 and HONO), e.g. d[NO2]s/dt = k1×[NO2]g − j(NO2)×[NO2]g and d[HONO]g/dt = k3×[HONO]s − j(HONO)×[HONO]g.

9. Section 3.3 and Fig. 8: Here, it appears the authors apply a series of kinetic equations to describe the temporal HONO emission profile shown in Fig. 8 based on Langmuir-Hinshelwood reaction kinetics. First, it is unclear if the lines plotted on top of the "UV/VIS" blue line in Fig. 8 are actually based on the kinetic equations described in section 3.3 or if they are simply linear fits with no theoretical basis, because in the figure description it states, "Straight lines...show the regressions..." If they are simply linear fits and then the kinetic terms were derived from the linear regression, my concern is this introduces significant ambiguity in the derived kinetics terms, because then the choice for each modeled section is entirely dependent on the user and not based on a sound theoretical description. Please clarify in both the Fig. 8 description and in sec. 3.3 whether these are simply linear fits or modeled based on the kinetic equations described in sec. 3.3. Furthermore, the authors must clarify what values were used (or derived from the linear fit) for k1, k2, k3, k4, k5, and k'. As a sensitivity test and validation of their model, I encourage the authors to apply their derived kinetic terms to model [HONO] as a function of [NO2], as shown in Fig. 5. Can [HONO] as a function of [NO2] be reproduced from the Langmuir–Hinshelwood terms described in sec. 3.3? Regarding Fig. 5, what do the dashed lines represent, are they fits to the data or just there to guide the eye? Please clarify in the figure description. Alternatively, the authors could plot their derived uptake coefficients (instead of [HONO]) as a function of time, and apply the Langmuir–Hinshelwood framework, e.g., as described in Ammann et al.

[2003]. This would also enable derivation of key kinetic terms describing NO2 uptake by proteinaceous aerosol surfaces, including the Langmuir equilibrium constant, surface accommodation coefficient and second-order surface reaction rate constant, which the community might find useful.

10. Have the authors considered the impact of photolysis of adsorbed HNO3 on the production of HONO in this study?

$HNO_3(ads) + h\nu \rightarrow HONO + O$
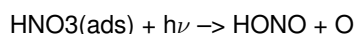
Given the high relative humidity and [NO2], HNO3 adsorption or formation on the surface of the flow tube could be substantial. While there was some mention in the introduction that HONO production from the photolysis of HNO3 may be important on organic substrates and soot, it was not discussed in the context of this study. The authors might consider estimating the contribution of adsorbed HNO3 photolysis to HONO produced in their flow tube experiments. Adsorbed HNO3 could be estimated based on the applied relative humidity and [NO2] (and assuming some reasonable surface coverage of HNO3), and the photolysis rate of HNO3, e.g., as determined in a very recent study by Laufs and Kleffmann [2016].

Minor Comments

1. Page 6, lines 8-9: It's not clear what the authors mean by "condensing condition" at a relative humidity (RH) of 98%, but not at 92%? Does this mean that the protein undergoes deliquescence at RH=98% and not 92%?

2. Figure 6: Along with the surface concentration of the coating (in units of μg cm-2), please include the calculated thickness of the coating in units of nm.

3. Summary and conclusions section, page 11 line 34: What is the significance of 1m2 of BSA surface or how was that surface area chosen?

References

C5

Ammann, M., U. Poschl, and Y. Rudich (2003), Effects of reversible adsorption and Langmuir-Hinshelwood surface reactions on gas uptake by atmospheric particles, Phys Chem Chem Phys, 5(2), 351-356.

Laufs, S., and J. Kleffmann (2016), Investigations on HONO formation from photolysis of adsorbed HNO3 on quartz glass surfaces, Phys. Chem. Chem. Phys., 18, 9616-9625.