

Interactive comment on

“Light-induced protein nitration and degradation with HONO emission”

by Hannah Meusel et al.

Anonymous Referee #2

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 NO_x, 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.

Comment:

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.

Response:

The nitration degree in this study was detected with HPLC-DAD which only can detect the intact protein and the nitrated protein, but no possible degradation products like peptides, single amino acids and their nitrated forms, as those compounds are “filtered out” by the chromatography. According to our HPLC-DAD results also the non-nitrated proteins decomposed, i.e., the peak was below detection limit. If only nitrated-proteins decompose, the results would indicate that all proteins were firstly nitrated prior of being decomposed. Amino acids and peptides might still be present, either nitrated or not.

Now better specified in the main text of the manuscript (page 5, line 27): “Note that no intact protein (nitrated and non-nitrated) could be detected by HPLC-DAD after another 20 hours of irradiation without NO₂, indicating light induced decomposition of proteins”

Comment:

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.

Response:

There are two different processes to discuss: 1) the degradation of nitrated proteins with HONO formation and 2) the heterogeneous NO₂ conversion. As shown in Fig.3 the light dependency of HONO formation from previously nitrated proteins is almost linear in the range of applied light intensity. So here, yes during sunny days, when irradiance is higher than our applied light intensity, an even higher HONO formation can be anticipated, accompanied by a faster degradation of the nitrated proteins. However, as the dependency for higher light intensities was not investigated, we cannot make a firm statement here. The observed light dependency of the heterogeneous conversion of NO₂ on BSA was not linear as shown in Fig. 4b. Here our results rather indicate an upper limit for the HONO formation, as was reported similarly by Stemmler et al. (2006, 2007).

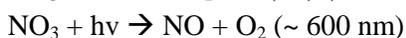
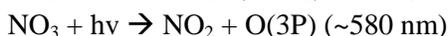
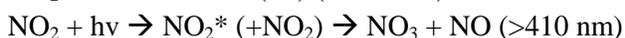
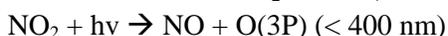
Now added in the conclusion (page 13, line 4-7): “While heterogeneous HONO formation of BSA exposed to NO₂ revealed light saturation at intensities higher than 161 W m⁻², the HONO formation from previously nitrated OVA was linearly increasing over the whole light intensity range investigated. The latter let assume even higher HONO formation under sunny (clear sky) ambient atmospheric conditions.”

Comment:

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?

Response:

Direct NO₂ photolysis (<400 nm) won't occur under conditions applied in this study (Gardner et al., 1987; Roehl et al., 1994). There might be some electronic excitation of NO₂, which disproportionate to NO and NO₃. Stemmler et al., 2007, determined a photolysis frequency of NO₂ of up to 5 x 10⁻⁴ s⁻¹ for very similar light conditions as we used, which is much lower than in the atmosphere (e.g. up to 1 x 10⁻² during the CYPHEX campaign 2014, Meusel et al., 2016). But NO₃ will probably directly deplete under this irradiation back to NO₂ or NO (Johnston et al., 1996).



Overall we assume the effect to be negligible. Furthermore, Shiraiwa et al. (2012) could exclude the importance of NO₃ (in their case formed by reaction of NO₂ + O₃) uptake on BSA.

Now added in section 3.1 (page 6, lines 16-23): “Shiraiwa et al. (2012) performed kinetic modelling and found that maximum 30% (conservative upper limit) of N-uptake on BSA could be explained by NO₃ or N₂O₅, which are generated by the reaction of NO₂ and O₃, while overall nitration was governed by an indirect mechanism in which a radical intermediate was formed by the reaction of BSA with ozone, which then reacted with NO₂. On NaCl surface N-uptake was dominated by NO₃ and N₂O₅. Furthermore, NO₃ radicals, which in this study could be formed by photolysis of NO₂ (>410 nm, disproportionation of excited NO₂), are not stable under the light condition applied (400-700 nm) (Johnston et al., 1996).

Therefore, in the present study reactions with NO_3 were neglected. Photolysis of NO_2 forming NO (< 400 nm) can also be neglected (Gardner et al., 1987; Roehl et al., 1994). A photolysis frequency for NO_2 of up to $5 \times 10^{-4} \text{ s}^{-1}$ under similar experimental light conditions was determined by Stemmler et al., 2007.”

Comment:

In the last paragraph of the results section 3.1, the authors compare their results, which were conducted in the presence of NO_2 , with other nitration studies conducted in the presence of both NO_2 and O_3 . How are these comparable, since NO_2 and O_3 combine to make N_2O_5 and NO_3 , 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 NO_3 , so wouldn't the authors expect more ND in the other studies anyway because of the higher reactivity of NO_3 ?

Response:

Shiraiwa et al. (2012) estimated that maximum 30% of the N-uptake is due to NO_3 and N_2O_5 uptake on BSA, while overall nitration was governed by an indirect mechanism in which a radical intermediate was formed by the reaction of BSA with ozone, which then reacted with NO_2 . On NaCl surfaces, on the other hand, NO_3 and N_2O_5 uptake dominate. Therefore, the higher ND of BSA exposed to O_3 and NO_2 is mainly due to higher activation by O_3 and due to BSA decomposition by light. Please also see the comment above.

Comment:

Section 3.2.4: The authors conclude that HONO production is greater for larger protein 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 NO_2 and HONO are exposed to different coated surface areas of the flow tube. Following NO_2 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.

Response:

As we manually coated the reaction tube, it was difficult to obtain equally/consistent surfaces. Therefore, each coating was different and also the covered surface area could only be roughly estimated. So, we agree with the referee that the coating thickness/surface is the biggest uncertainty in the experiment. And yes, there might be a bias based on NO_2 /HONO uptake/emission on/from different coating surface areas. But we expect that HONO uptake coefficients on both proteins (as slightly acidic) as well as on glass surfaces were small (Syomin and Finlayson-Pitts, 2003), so that the difference of HONO uptake due to different surface areas and covered tube length is low. Also NO_2 uptake on glass is supposed to be significantly lower than on proteins. We don't expect a difference in tube coverage of 20% would increase HONO concentrations about three times.

According to the referee's suggestion, we now added in the main text (page 8, lines 19-24): "Exposing (20%) different coated surface areas in the flow tube, potentially introduced bias comparing different data sets. Emitted HONO might be re-adsorbed differently by proteins and glass surface. However, as the protein is slightly acidic, a low uptake efficiency of HONO by BSA can be anticipated, which should not differ too much from the un-covered glass tube surface (Syomin and Finlayson-Pitts, 2003). Accordingly, NO₂ uptake on glass is assumed to be significantly lower than on proteins."

Comment:

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)?

Response:

Fig. 6 does not show emission rates as a function of time, but normalized (to reaction tube coverage) HONO concentrations vs time! The numbers in the diagram represent the slope (decay rates) at the end (time period indicated by arrows), and indicate a stable HONO formation (as also seen in Fig.8). In figure 8 also several decay rates are shown for earlier exposure times, so that in the respective figure 6 the decay rates are only shown in the end when the concentrations are stable.

The unit of the y axis was changed from ppb to ppt.

Comment:

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.

Response:

Typical aerosol concentrations of bacteria, fungal spores and pollen are 0.1, 0.1-1 and 1 μg m⁻³, respectively (Despres et al., 2012). Aerosol particles may contain up to 5% proteins. But it is not known how much proteins cover the aerosol surface nor how thick this coating would be. This was already mentioned in the conclusion part of the manuscript; and which is why it is hard to make a firm statement here. However, to address this important issue we now added in the text (page 13, lines10-17): "Typical aerosol surface concentrations in rural regions are about 100 μm² cm⁻³. Stemmler et al. (2007) estimated a HONO formation of 1.2 ppt h⁻¹ on pure humic acid aerosols in environmental conditions. As NO₂ uptake coefficients and HONO formation rates on proteins are similar to humic acid but only about 5% of the aerosol mass can be assumed to consist of proteins, it can be anticipated that HONO formation on aerosol is not a significant HONO source in ambient environmental settings. However, proteins on ground surfaces (soil, plants etc.) might play a more important role. Accordingly, Stemmler et al. (2006 and 2007) suggested that NO₂ conversion on soil covered with humic acid would be sufficient to explain missing HONO sources up to 700 ppt h⁻¹."

Comment:

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 ($300 \text{ nm} < \lambda < 400 \text{ nm}$), 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 NO_2 and HONO), e.g. $d[\text{NO}_2]/dt = k_1[\text{NO}_2]g - j(\text{NO}_2)[\text{NO}_2]g$ and $d[\text{HONO}]/dt = k_3[\text{HONO}]s - j(\text{HONO})[\text{HONO}]g$.

Response:

HONO photolysis was not considered. The overlap of UV light spectrum and HONO absorption/photolysis spectrum is quite low about 340-400 nm. The quartz glass tube has a transmission of 90% at these wavelengths. The applied light intensity (with 7 lights on) is about 40% of a clear sky irradiance for a solar zenith of 48° . In clear sky HONO photolysis frequencies are in the range of $1.2\text{-}1.5 \times 10^{-3} \text{ s}^{-1}$ (e.g., on Cyprus in summer 2014; Meusel et al. 2016). In the reaction tube the photolysis frequency would therefore decrease down to $0.4\text{-}0.5 \times 10^{-3} \text{ s}^{-1}$. When only irradiated with VIS lights (exclusion of HONO photolysis, emission profile not limited) the pattern is the same as with UV (only a smaller absolute concentration) indicating a stable formation.

Now revised in the manuscript in the kinetic section (page 11, line 34 – page 12 line 3): “In this study, neither HONO nor NO_2 photolysis is considered, as the overlap of the applied UV/VIS or VIS range (340-700 nm or 400-700 nm) and the HONO and NO_2 photolysis spectrum ($<400 \text{ nm}$) is low. Furthermore, the applied light intensity is lower compared to clear sky irradiance and the respective UV light is partly absorbed by the reaction tube although quartz glass was used (transmission $\sim 90\%$) and the photolysis frequency would decrease down to 10^{-4} s^{-1} . Hence, the photolysis is assumed to be not significant.”

Comment:

Section 3.3 and Fig. 8: a) 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 k_1 , k_2 , k_3 , k_4 , k_5 , and k' .

b) As a sensitivity test and validation of their model, I encourage the authors to apply their derived kinetic terms to model $[\text{HONO}]$ as a function of $[\text{NO}_2]$, as shown in Fig. 5. Can $[\text{HONO}]$ as a function of $[\text{NO}_2]$ 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.

c) Alternatively, the authors could plot their derived uptake coefficients (instead of $[\text{HONO}]$) 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.

Response:

a) The lines in fig 8 are linear fits (no theoretical basis). The slopes of those were taken to calculate k_{eff} . Other rate constants ($k_1, k_2, k_3, k_4, k_5, k'$) were not calculated. Single equations were moved to a new supplement.

b) In fig 5. the dotted lines are regressions of the measured data points (exponential fittings, e.g., $y = y_0 + A * e^{-x/t}$) only to guide the eye (now better described in the figure captions).

In our kinetic study we calculated an effective rate constant for the NO₂ conversion on BSA. In a range of 0-100 ppb NO₂ the HONO formation is almost linear (fig 5), which would be also indicated by the Langmuir-Hinshelwood mechanism (here first rate: $d[\text{HONO}]/dt = k * [\text{NO}_2]$).

c) It is not possible to extract a full set of parameters for a LH model based on the present data. As pointed out in Bartels-Rausch et al. (2010) and to some degree also in the Stemmler et al. studies, the saturating behavior of photochemical HONO production may be due to either the adsorbed precursor on the surface or due to a photochemical competition process, which also leads to a Lindemann-Hinshelwood type kinetic expression (Minero, 1999). Therefore, mathematically, the rate expressions get a comparable NO₂ pressure dependence. Therefore, measurements of the NO₂ dependence at different light intensities would be required to disentangle the two. The nearly single exponential (linear in the log-log plot) decay of γ vs time in the figure below (fig. R1) indicates that the system is governed by degradation and not by reaction steady state, so that modelling the system explicitly in terms of all the kinetic parameters would be ambiguous.

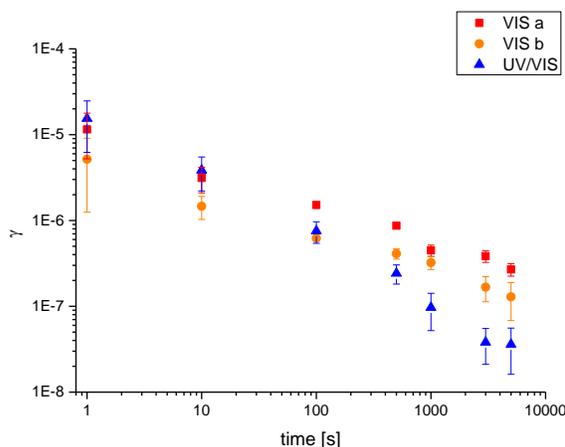


Fig. R1: log-log plot of the uptake-coefficients vs time for the three different experiments, indicated with the different colors (from the long term and kinetic study)

Added to the manuscript (page 12, lines 24-28): “It was not possible to extract a set of parameters for a Langmuir Hinshelwood mechanism (like Langmuir equilibrium constant, surface accommodation coefficient or second order rate constant) from the presented data. The saturating behavior of photochemical HONO production may be due to either the adsorbed precursor on the surface or due to a photochemical competition process, which also leads to a Lindemann-Hinshelwood type kinetic expression (Minero, 1999).”

Comment:

Have the authors considered the impact of photolysis of adsorbed HNO₃ on the production of HONO in this study? $\text{HNO}_3(\text{ads}) + h_{\nu} \rightarrow \text{HONO} + \text{O}$

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].

Response:

Gas phase reaction doesn't produce HNO₃, because N₂, but not synthetic air was used as the carrier gas. Usually HNO₃ photolysis happens at < 350 nm. Photolysis of adsorbed HNO₃ might be shifted to slightly higher wavelength. In the publication of Laufs and Kleffmann (2016), J values (HNO₃→HONO) as low as 10⁻⁷ s⁻¹ were obtained. Our UV lamps had a spectral range of 340-400 nm. As a conclusion, HNO₃ photolysis was negligible in this study.

Added to the section 3.2.6 (page 10, lines 18-23), as only here UV light was applied: “HONO formation by photolysis of (adsorbed) HNO₃ is assumed to be insignificant in this study. With N₂ as carrier gas, gas phase reactions of NO₂ do not produce HNO₃. Even when small amounts of HNO₃ would be formed by unknown heterogeneous reactions, photolysis of HNO₃ is only significant at wavelengths < 350 nm, which is close to the lowest limit of the UV wavelength applied in this study. Likewise, the respective photolysis frequency recently proposed by Laufs and Kleffmann (2016) of about 2.4 x 10⁻⁷ s⁻¹ is very low.”

Minor Comment:

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%?

Response:

At 98% RH water vapor condensed (visible water layer), but not at lower RH of 92% (Reinmuth-Selzle et al., 2014). Deliquescence of BSA already occurs at 35% (see section 3.2.4).

Minor Comment:

Figure 6: Along with the surface concentration of the coating (in units of $\mu\text{g cm}^{-2}$), please include the calculated thickness of the coating in units of nm.

Response:

According to the referee's advice, we now added the layer thickness in the plot:

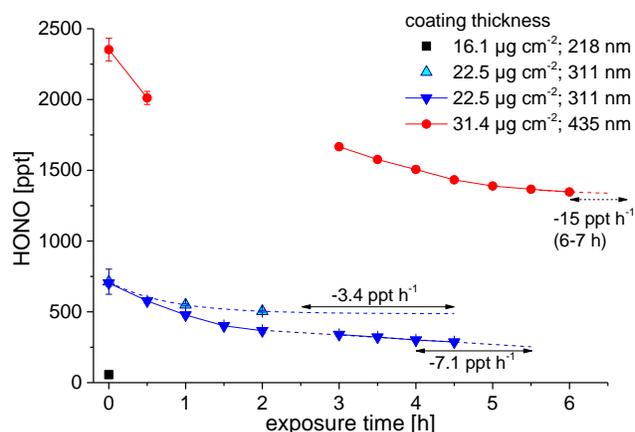


Fig. R2 = new Fig. 6: HONO concentration vs exposure time for different coating thicknesses.

Minor Comment:

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

Response:

HONO formation per m² [ppt h⁻¹ m⁻²]

Now the main text of the manuscript (page 13, lines 2-4) is rephrased to: “At 20 ppb NO₂ HONO formation of 19.8 ppb h⁻¹ m⁻² could be estimated”

References

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