

## ***Interactive comment on “Light-induced protein nitration and degradation with HONO emission” by Hannah Meusel et al.***

**Anonymous Referee #1**

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General Comments. This manuscript reports results of a study aimed at investigating photochemical formation of HONO from proteins exposed to NO<sub>2</sub>. The study employs coated wall flow tube techniques with LOPAP detection of HONO and chemiluminescence detection of NO<sub>2</sub>. The methods are appropriate for such a study and the results appear to meet the standards required by ACP. The topic is important as it addresses the byproducts associated with light-induced nitration of protein aerosols (e.g., pollen and other biological aerosols); it is novel in that it attempts to address the photochemical fate of the nitrated proteins. The relevance of protein nitration to the potency of allergens has been discussed in several publications, so that is clear. However, it is not so clear that nitrated proteins will be an important component of the daytime HONO budget since proteinaceous aerosols would constitute only a minor fraction of the total aerosol surface area in the atmosphere. Furthermore, strong evidence has

C1

recently surfaced showing that the daytime HONO source is not linked to NO<sub>2</sub> (see Pusede et al. Environ. Sci. Technol. 2016). In addition, there are limited situations where the aerosol phase has proved to have an impact on atmospheric HONO concentrations. Perhaps the authors could add a more extensive discussion of settings where they predict this chemistry to be important? Regardless, it is my opinion that the chemistry presented is interesting enough to warrant publication after these issues are addressed.

Specific Comments.

Page 1, line 20: The authors write that “nitration degrees of about 1% were derived applying NO<sub>2</sub> concentrations. . .” How was the nitration degree determined?

1, 21: The term “Gas exchange measurements of TNM-nitrated proteins” is ambiguous.

1, 23: The term “fumigation” is not appropriate here. Please replace.

3, 22-24: I note that nitrated ovalbumin (OVA) was used in only one experiment in this study (section 3.2.1) while bovine serum albumin (BSA) was used for everything else. Ideally, one would use one protein for all the studies to facilitate comparison of results. Please explain why one protein was not used for everything.

3, 32: The methods section indicates that tetranitromethane is used to nitrate the OVA samples. This is a highly toxic and explosive reagent. Appropriate warnings should be included in this section to bring awareness of the dangers of using this reagent to anyone wishing to repeat these experiments.

9, 33 (and other places in the text, e.g. 10, 4): The term “catalytic converter” is an engineering term and is not appropriate in this context. I would replace with “catalytic surface”.

10, 6: It is not clear what ND refers to in this line. Please clarify.

10, 27: It seems to me the term [HONO]<sub>1</sub> + [HONO]<sub>2</sub> is incorrect. Instead of indicating

C2

concentrations, should one not be using rates (i.e.,  $d[\text{HONO}]_1/dt + d[\text{HONO}]_2/dt$ )?

10, Kinetics studies section: The derivation of some of the indicated terms is not so clear. I question the need to go into the level of detail displayed in eq. 1-5. Please check over the derivation of  $k_{\text{eff}}$ . Also, perhaps I missed this explanation, but why are the reversible reactions in Figure 9 not included?

Figure 1: Ozone is included above the arrow in the first step. However, there is no indication that ozone was used in this study. Please clarify or correct.

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