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Reply to the 'Comment on "Investigations on HONO formation from photolysis of adsorbed HNO₃ on quartz glass surfaces"' by M. N. Sullivan, L. T. Chu and L. Zhu, *Phys. Chem. Chem. Phys.*, 2018, 20, DOI: 10.1039/C8CP04497J

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In their comment to our recent paper about low HONO and NO₂ formation by photolysis of adsorbed HNO₃ Sullivan *et al.* confirmed their former results of HNO₃ adsorption on silica under dry conditions using a quartz crystal microbalance. The authors concluded that the differences between their results and our conclusions are caused by the different experimental conditions, *i.e.* adsorption under very dry conditions compared to our experiments at 50% r.h. While we agree that adsorption of the highly water soluble HNO₃ will strongly depend on humidity, there is still the conflict in the photolysis frequency of adsorbed HNO₃ under atmospheric conditions to which the authors referred in their previous publications (see their atmospheric implication sections) and to which also our paper refers. If their results on both the adsorption cross sections of HNO₃ (two to three orders of magnitude larger compared to the gas phase) and the quantum yield for NO₂ formation (close to unity) are applicable under conditions prevailing in the atmosphere, then the photolytic lifetime of HNO₃ on surfaces would be only ~5 min for atmospheric solar flux (0° SZA), which is highly unlikely.

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In our previous paper¹ we studied the photolysis of HNO₃ adsorbed on quartz and Pyrex surfaces under conditions close to the atmosphere (actinic flux, HNO₃ concentration, and humidity) and observed very low values of $J(\text{HNO}_3 \rightarrow \text{NO}_2)$ and low secondary heterogeneous formation of HONO, which were based on well quantified levels of adsorbed HNO₃ (ion chromatography analysis) and gas phase HONO and NO₂ concentrations (LOPAP techniques). Since the spectral actinic flux was also quantified in our study by a calibrated spectroradiometer, we used the absorption cross sections of adsorbed HNO₃ published by the group of L. Zhu^{2,3} to calculate an average quantum yield of adsorbed HNO₃ for NO₂ formation of $\phi(\text{HNO}_3 \rightarrow \text{NO}_2) = (3.4 \pm 2.6) \times 10^{-4}$, see eqn (4).¹ This value is orders of magnitude lower compared to the studies of Zhu *et al.*⁴ and Abida *et al.*⁵ and the present comment by Sullivan *et al.*⁶ In these studies, quantum yields near unity were observed in excimer laser photolysis experiments at 308 and 351 nm, which cover the same spectral range as we used in our study. If both quantities are applied, the photolytic lifetime of HNO₃ adsorbed on silica surfaces would be only ~5 min for

atmospheric spectral actinic fluxes (0° SZA), which is highly unlikely. Accordingly, we tried to explain this conflicting data either by overestimated absorption cross sections (by underestimated levels of adsorbed HNO₃^{2,3}) and/or overestimated quantum yields (by using excimer laser photolysis experiments^{4,5}). In our previous paper¹ we left both explanations open, but finally used the high cross sections to calculate our low quantum yield, which rely on the measured adsorption isotherms.^{2,3}

In their comment, Sullivan *et al.*⁶ now conclusively showed by quartz crystal microbalance measurements that these adsorption isotherms are valid, resulting in monolayer coverage ($\sim 10^{14} \text{ cm}^{-2}$) of adsorbed HNO₃ under completely dry conditions at *ca.* 16 mTorr HNO₃ gas phase partial pressure (~ 20 ppm mixing ratio at 1 atm), while we obtained the same amount in the lower ppb range at 50% r.h. Although some of the differences may still be caused by the very different saturation times applied (2 min in Sullivan *et al.*;⁶ overnight in our study¹), the explanation by Sullivan *et al.*⁶ is indeed reasonable, since HNO₃ adsorption strongly increases with increasing humidity. It is worth mentioning that we observed in former experiments⁷ that low ppb levels of HNO₃ easily pass through PFA (perfluoroalkoxy alkane) and Teflon tubes in very dry conditions, while it takes ~2 h until HNO₃ levels reach 90% of final values when passing through a 2 m long PFA tube (4 mm i.d.) at 1 l min⁻¹ and 50% r.h. This is

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explained by the extremely high solubility of HNO_3 in the adsorbed water layer at higher humidity. In addition, with respect to the comment by Sullivan *et al.*,⁶ it is not surprising that HNO_3 does not form a physical monolayer on the surface at $10^{14} \text{HNO}_3 \text{ cm}^{-2}$ in the presence of several layers of adsorbed water at 50% r.h., where it will be present as a mixed $\text{HNO}_3/\text{H}_2\text{O}$ phase. Since we quantified the amount of adsorbed HNO_3 in our previous study (see *e.g.* Fig. 5),¹ the used term “monolayer” clearly refers to a formal monolayer ignoring the unknown amount of co-adsorbed water. The same holds for the four (formal) monolayers of adsorbed H_2O at 50% r.h. mentioned in Sullivan *et al.*,⁶ which is also strictly not correct (see island adsorption of H_2O ⁸).

However, besides this somewhat academic discussion, for the main question, *i.e.* the photolysis frequency of HNO_3 and the resulting NO_2/HONO formation, it is completely unimportant whether the $10^{14} \text{HNO}_3 \text{ cm}^{-2}$ are adsorbed as a pure (hypothetical) monolayer or in a mixed $\text{HNO}_3/\text{H}_2\text{O}$ phase (reality). For both situations the UV light irradiates all HNO_3 molecules. The photolysis frequency is by definition independent of the amount of HNO_3 (first order kinetics) and can be simply calculated from the ratio of formed products divided by the amount of adsorbed HNO_3 (see *e.g.* eqn (2)¹), which were both directly measured in our study.

Since we performed our experiments under typical atmospheric conditions with respect to HNO_3 concentration, humidity and actinic flux, we are still convinced that our atmospheric implications are correct, *i.e.* at typical atmospheric humidity either the published high absorption cross sections of adsorbed HNO_3 or the near unity quantum yields for its photolysis are not valid. In contrast, we cannot draw this conclusion for completely dry conditions under which the former studies^{2–6} were performed. However, these studies should then not be extrapolated to the atmosphere (*e.g.* for the discussion on potential “renoxification” *etc.*), as the authors have done in their former publications.^{2–4,9} Accordingly, photolysis of HNO_3 adsorbed on non-reactive substrates – which is the topic of all papers cited above^{1–6,9} – will be of minor importance in the atmosphere. However, as we already discussed in our previous paper,¹ the situation may change for HNO_3 adsorbed on complex substrates, *e.g.* on photosensitizer surfaces like humic acids – but that is a different story.

Conflicts of interest

There are no conflicts to declare.

References

- 1 S. Laufs and J. Kleffmann, Investigations on HONO formation from photolysis of adsorbed HNO_3 on quartz glass surfaces, *Phys. Chem. Chem. Phys.*, 2016, **18**, 9616–9625.
- 2 C. Zhu, B. Xiang, L. Zhu and R. Cole, Determination of Absorption Cross Sections of Surface-adsorbed HNO_3 in the 290–330 nm Region by Brewster Angle Cavity Ring-down Spectroscopy, *Chem. Phys. Lett.*, 2008, **458**, 373–377.
- 3 J. Du and L. Zhu, Quantification of the Absorption Cross Sections of Surface-adsorbed Nitric Acid in the 335–365 nm Region by Brewster Angle Cavity Ring-down Spectroscopy, *Chem. Phys. Lett.*, 2011, **511**, 213–218.
- 4 C. Zhu, B. Xiang, L. T. Chu and L. Zhu, 308 nm Photolysis of Nitric Acid in the Gas Phase, on Aluminum Surfaces, and on Ice Films, *J. Phys. Chem. A*, 2010, **114**, 2561–2568.
- 5 O. Abida, J. Du and L. Zhu, Investigation of the Photolysis of the Surface-adsorbed HNO_3 by Combining Laser Photolysis with Brewster Angle Cavity Ring-down Spectroscopy, *Chem. Phys. Lett.*, 2012, **534**, 77–82.
- 6 M. N. Sullivan, L. T. Chu and L. Zhu, *Phys. Chem. Chem. Phys.*, 2018, **20**, DOI: 10.1039/C8CP04497J.
- 7 J. Kleffmann, T. Benter and P. Wiesen, Heterogeneous Reaction of Nitric Acid with Nitric Oxide on Glass Surfaces under Simulated Atmospheric Conditions, *J. Phys. Chem. A*, 2004, **108**, 5793–5799.
- 8 A. L. Sumner, E. J. Menke, Y. Dubowski, J. T. Newberg, R. M. Penner, J. C. Hemminger, L. M. Wingen, T. Brauers and B. J. Finlayson-Pitts, The nature of water on surfaces of laboratory systems and implications for heterogeneous chemistry in the troposphere, *Phys. Chem. Chem. Phys.*, 2004, **6**, 604–613.
- 9 L. Zhu, M. Sangwan, L. Huang, J. Du and L. T. Chu, Photolysis of Nitric Acid at 308 nm in the Absence and in the Presence of Water Vapor, *J. Phys. Chem. A*, 2015, **119**, 4907–4914.

