

This manuscript reports a careful lab study on the reactive quenching of electronically excited atmospheric NO_2^* and NO_3^* radicals by water vapour as potential primary sources of atmospheric HOx radicals.

The topic is relevant for ACP.

The manuscript is divided into two parts.

Firstly, the reactive quenching rate of NO_2^* by water vapour is re-investigated in order to elucidate the controversially discussed role of this photoreaction as a relevant primary source of atmospheric OH. From their results the authors inferred a new upper limit of 6×10^{-6} (at an excitation wavelength of 562 nm) about an order of magnitude lower than previously measured. Extended measurements across the whole non-dissociative part of the absorption spectrum of NO_2 lead to the conclusion that atmospheric OH formation by $\text{NO}_2^* + \text{H}_2\text{O}$ is insignificant.

Secondly, the reactive quenching of NO_3^* was studied. Although daytime concentration of NO_3 are usually very low the authors estimated that under certain conditions the formation rate of OH by the title reaction could compete with the primary formation of OH from ozone photolysis. The measured quenching rate constant for the bath gas N_2 compares well with the literature value of Nelson et al. The measured total quenching rate constant for H_2O for which only one measurement is available in the literature was found to be a factor of four lower. In an elegant series of well-thought-out experiments it is shown that the majority of excited NO_3^* is deactivated by water vapour via radiationless processes and only an upper limit of <3% was found to react with water to form OH.

The experiments were conducted in a well-proven and tested apparatus. Concentrations of reactants are directly measured by UV/VIS absorption spectroscopy reducing the uncertainties to <10%. All relevant experimental details are reported, measurement uncertainties and experimental limitations are always well defined. Figures are meaningful and support the thorough and critical analysis and the discussion of the results.

I recommend the well written manuscript for publication once the following minor comments are addressed.

Specific comments

Is there a deeper reason for the application of two different OH formation pathways (R13, R14) to convert the LIF raw signal to OH concentrations? In the experimental section both methods are described but it is pointed out later in the text (page 7, line 9) that in the presence of NO_2 193 nm photolysis (R14) would produce small amounts of O^1D atoms from NO_2 in a two-photon process which finally rules out this reaction for the NO_2^* study.

On the other hand Figure 3 shows OH formation from the photolysis of water vapour. Why not from HNO_3 photolysis as applied in the NO_2^* experiment? Is there a corresponding figure?

This point certainly needs some clarification and I would suggest to re-write the first paragraph of page 6 accordingly.

In order to enhance the concentration of excited NO_3^* radicals to a maximum of 50% the absorption transition at 662 nm was "saturated" using very high laser power intensities. How can saturation be experimentally verified and which laser fluence was applied?

The discussion of the potential OH formation rate from $\text{NO}_3^* + \text{H}_2\text{O}$ closes with the words "... it may still represent an important contribution to OH formation in some environments."

I am not happy with this general and more or less meaningless statement. It should be either substantiated or omitted.

Technical corrections

Page 3, line 30 – I calculate an excitation energy of 180.85 kJ/mol from the absorption of 662 nm photons. Hence, the given values of the reaction enthalpies require correction as well.

Page 5, line 25 – add type of light source, presumably *low pressure Hg lamp*

Page 7, line 5 – add absorption cross section of H₂O at 193 nm
line 28 – typo: OH

Page 9, line 1 – typo: excited state
line 15 – typo: 1.6×10^{-10} / factor of four...

Page 12 – reference Dillon et al.: two names in the list of co-authors are missing
(Vereecken, Peeters)

Page 17, Fig 3 – add concentration of H₂O: 1.5×10^{17} molec cm⁻³
– correct 'the the'