

## ***Interactive comment on “Evidence of the water-cage effect on the photolysis of $\text{NO}_3^-$ and $\text{FeOH}^{2+}$ , and its implications for the photochemistry at the air-water interface of atmospheric droplets” by P. Nissenon et al.***

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The authors present interesting findings concerning the influence of the air-water interface of atmospheric droplets on photochemical processes induced by various photoactive species. This is a well written paper with very interesting findings for the atmospheric chemistry.

Below, please find some of my comments on the manuscript:

1) Water-cage effect is the concept used to interpret possible enhancement/inhibition

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of various photochemical processes occurring at the interface between the air and atmospheric water droplets.

Increasing the concentration of an organic molecule, that can be used as an OH radical scavenger, close to the water-cage avoids a readily sink of photoactive OH radicals generated through the photolysis of  $\text{NO}_3^-$ ,  $\text{FeOH}^{2+}$  or  $\text{H}_2\text{O}_2$ . Data in Figures 2, 3 and 4 come and prove the above mentioned statement made by the authors. However, regarding nitrite and acetone formation upon an increase in the 2-propanol concentration, there are similarities and dissimilarities in their behaviour which would allow inferring few comments. Figure 2 shows that at high concentration of 2-propanol, acetone is almost constant while nitrite seems to decrease. For sure there are additional reactions involving both products, of whose a secondary nitration would be the most probable. On the other hand, slow increase or negative rate in nitrite formation can also suggest that some reactions will not take place at high concentration in the organic molecule (reactions 2, 3 and 5).

2) The investigations were performed by the authors at  $\text{pH}=2.5$ . Based on the data from the literature they claim that at  $\text{pH}=2.5$  the most important photoactive species of Fe(III) is  $\text{FeOH}^{2+}$ .

Air, aqueous and solid phase of a species may coexist in the atmosphere. We know that for  $\text{Fe}(\text{OH})_3$  the following constants are governing the equilibriums in the system:  $K_s(\text{Fe}(\text{OH})_3) = 3.2 \times 10^{-38}$  for  $[\text{Fe}^{3+}, 3\text{OH}^-]$  (I)  $= 2.0 \times 10^{-26}$  for  $[\text{FeOH}^{2+}, 2\text{OH}^-]$  (II)  $= 4.0 \times 10^{-17}$  for  $[\text{Fe}(\text{OH})_2^+, \text{OH}^-]$  (III) For  $\text{Fe}(\text{ClO}_4)_3$ ,  $10^{-4}$  M solution, one can calculate at which pH these species are in equilibrium: stage I with  $\text{pH} = 2.83$ , stage II with  $\text{pH} = 3.15$  and stage III with  $\text{pH} = 1.68$ . Thus at  $\text{pH} = 2.5$ , where the authors performed their study, it seems that in the working solution may exist especially  $\text{Fe}(\text{OH})_2^+$ . Under these circumstances the authors should provide more details to make sure that the water cage effect on the photolysis of  $\text{FeOH}^{2+}$  but not of  $\text{Fe}(\text{OH})_2^+$  was investigated.

If indeed  $\text{pH}=2.5$  is meant for the investigation than the authors should justify either or

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not this value is significant for atmospheric droplets.

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