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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evidence of the water-cage effect on the photolysis of NO_3^- and $FeOH^{2+}$, and its implications for the photochemistry at the air-water interface of atmospheric droplets" *by* P. Nissenson et al.

Anonymous Referee #1

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This is a highly speculative manuscript which would benefit greatly from either some additional experimental effort, or a considerable shortening and toning down of the conclusions.

The authors claim (even in the abstract) to have measured photolysis quantum yields of various OH-producing species in the bulk and at the surface of aqueous solutions. In fact, the measurements were all made in the bulk solution. Quantum yields in the absence of a solvent cage effect (which promotes recombination of nascent photoproducts) were estimated by the addition of an OH trapping species, the assumption being

that the newly-formed OH would react preferentially with the trap, rather than undergo recombination. Water surface quantum yields were then assumed to show no solvent cage effect.

There are several major and untested assumptions made in this work. First is the assumption that the "solvent cage-free" quantum yields may be estimated using the chosen trapping method. This may not be appropriate, since propanol was not present in excess over much of its concentration range in these experiments. Therefore, loss of OH via recombination of could occur even outside of solvent cages. Second is the assumption that there is no such effect at the water surface. This certainly sounds somewhat reasonable, but to my knowledge has never been tested in any experimental study. It is certainly not tested here. Third is the assumption that the OH-producing reagents are present at the interface. The case of nitrate is somewhat in doubt (as acknowledged by the authors); small positively-charged ions, such as the iron compound reported here, are almost all *repelled* from the surface (with the possible exception of hydronium). The case of hydrogen peroxide is moot, as no cage effect was measured for this compound.

The calculations on the atmospheric relevance of an enhanced surface quantum yield, while interesting, are rendered entirely speculative by these assumptions. If the authors wish to write a speculative paper, pointing out the effect and guessing at its importance, I think it should be much shorter than this.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13123, 2009.