

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.

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The authors thank the reviewer for taking time to comment on our work. The manuscript will benefit greatly from such feedback. The referee correctly states that the experiments do not measure quantum yields at the air liquid interface. Rather, the experiments determine quantum yields with and without a solvent cage effect in the bulk-liquid. The authors will make this distinction clearer in the paper.

The referee also has raised concerns about three assumptions made by the authors:

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(1) The reviewer is concerned that loss of OH via recombination may occur outside the solvent cage since 2-propanol is not present in excess over much of its concentration range in the experiments. This would mean that the “solvent-cage free” quantum yields are not accurately estimated using the trapping method.

The authors believe that the recombination of OH + NO₂, OH + Fe²⁺, and OH + OH outside the solvent cage at elevated [2-propanol] is unlikely. Detailed calculations for OH + NO₂ by Minero et al. (2007) showed that photogenerated nitrite traps practically all the OH, even in the absence of other scavengers, preventing recombination between OH and NO₂. This fact is valid a fortiori in the presence of 2-propanol as an OH scavenger.

2-propanol is the main OH scavenger for Fe(II) above 10 μM. At the highest adopted 2-propanol concentration (0.1 M), Fe(II) scavenges less than 0.01% of the photogenerated OH. In the case of H₂O₂, the recombination of OH + OH is inhibited by the presence of hydrogen peroxide and a fortiori by 2-propanol in excess.

The manuscript will be modified to make these points clearer.

(2) The reviewer asks if there is a reduced solvent-cage effect at the surface of water, which is assumed in the simulations.

Nissenson et al. (2006) found experimental evidence for a reduction in the solvent-cage effect at the air-liquid interface when Mo(CO)₆ in a 1-decene solvent was irradiated in aerosol form and as a bulk-liquid. The quantification of the solvent-cage effect in aqueous solution presents a number of experimental difficulties, which could explain why limited data are available on the topic. Winter and Benjamin (2004) conducted molecular dynamics simulations of ICN in water and found photolysis quantum yields are significantly higher near the surface compared to the bulk. Therefore, the authors believe it is reasonable to assume that the solvent-cage effect is reduced in the surface layer of water. The authors will include this discussion in the manuscript.

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(3) In the simulations, the authors assume that the concentration of nitrate and FeOH_2^+ is uniform within the droplet, while the concentration of H_2O_2 is enhanced by a factor of two at the surface compared to the bulk. The reviewer is concerned that the authors are overestimating the surface concentration of nitrate and FeOH_2^+ .

While initial calculations on the nitrate ion at infinite dilution (Salvador et al., 2003) suggested it has a propensity for the air-liquid interface, more recent studies at finite concentration (Dang et al., 2006) indicate that the ion tends to remain below the surface. Molecular dynamics simulations (Thomas et al., 2007) of nitrate ions in a 1 M solution suggest that nitrate is less solvated close to the interface compared to the bulk. For example, on average there are about 8 water oxygen atoms within 4 Å of the nitrate N in the bulk, but only 6 water oxygens in the case of nitrate near the interface (defined in that study as being within 8 Å of the surface). However, this still may be sufficiently close to the interface that a full solvent shell is not active and enhancement of surface photochemistry could occur.

Due to the uncertainty in the degree of surface segregation of nitrate in water droplets, the authors assume the concentration of nitrate is uniform throughout the droplets in the simulations. If this study overestimates the concentration of nitrate at the surface, the fraction of total benzene-OH reaction within the droplet that occurs at the surface would be reduced.

For FeOH_2^+ the authors note that even in the absence of any data, its surface concentration might be reduced compared to the bulk. However, doubly charged species likely are not completely repelled from the surface, especially in the presence of organic compounds or anions with some affinity for the surface (Sadiki et al., 2003). It is possible that the surface and bulk concentrations of FeOH_2^+ are equal in the presence of benzene and formate.

The concentration of H_2O_2 is enhanced by a factor of two at the air-liquid interface compared to the bulk (Vácha et al., 2004).

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The authors will emphasize these caveats in the manuscript.

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