

Comment on acp-2021-875

Anonymous Referee #1

Referee comment on "Enhanced photodegradation of dimethoxybenzene isomers in/on ice compared to in aqueous solution" by Ted Hullar et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-875-RC1>, 2021

The manuscript by Hullar et al presents new experimental result on the photochemistry in snow. This is a controversial topic and more data to assess the role of snow as medium hosting chemistry that impacts atmospheric chemistry is needed. Therefore the manuscript's topic is fully within the scope of ACP. The manuscript is well written, conclusions are clearly supported by data and the argumentation is clear to follow. All relevant work is cited and addressed. I support publication in ACP after addressing some minor points:

The major point of the minor comments is a question: Do you have an explanation why the quantum yield are larger, and the photo decay more efficient, at the interface? If I'm not mistaken, dimethoxybenzene are well known to form triplet states upon irradiation in aqueous solution. Could this enhancement be a consequence of higher local concentrations and thus an increase in the secondary chemistry such as reduction induced by intermolecular electron transfer from such triplets? If so, I think it would be worth to mention, or even speculate on, this as it opens the door to a wider relevance. Triplets play a wide role in chemistry at the air ice interface for example in HONO formation (Bartels-Rausch, Atmospheric Environment, 2010)

Lines 16: «or in quasi-liquid layers (QLLs) at the air-ice interface, where they can readily exchange with the firn air.»

Photochemistry could also occur at the air-ice interface at too cold temperature for QLL formation. Interestingly, some chemicals have been shown to form solvation shells at the interface (Bartels-Rausch, Earth and Space Chemistry, 2017), maybe this is even more relevant for photochemistry? Additionally, I might add that internal LLR could also be in exchange with air if located in grain boundaries as diffusion of any products from there is fast.

Abstract: Could you detail a little more on the impact for atmospheric chemistry? The abstract remains a little bit too much on the technical result level for my taste. Please

open up and explicitly mention the significance of this work.

Lines 52-62: Leaves the reader wondering. Are reasons known? Do you have a suggestion? Are concentrations comparable? You mention high concentrations as a problem when determining absorption spectra, later in the manuscript. Could you exclude and/or discuss how the studies differ in this respect.

line 91: Does this paragraph only apply to solar, or also lab light sources?

Line 107: photochemical reaction instead of loss?

Line 114: Any environmental relevance or these compounds that is worth highlighting? Please sketch structure and photo-chemical pathways, or refer to Figure 1 already here.

Line 163, I think the vapor pressures are also of high interest in this context.

Line 271. Personally, I think it's odd to start the result section with data in the S1. That privilege should be reserved to data that makes it to a figure in the manuscript. Either make it a figure or start with current Figure 1.

Line 277: illuminated samples often show considerably greater loss, presumably due to photodegradation,
«presumably»...what else could it be? Why so careful?

Line 309: What is AB?

- This is indeed a repetition from lines 271 -289. I suggest to delete 271 -289.

324: Why is that. Is it because you had a larger surface to volume ratio in snow and thus higher concentration for analysis? What was the surface to ice volume ratio, anyway? Or, did you have more ideal flow conditions to deposit the chemical? How much did you deposit?

Discussion & Results in general: could you discuss concentration dependence – and rule out secondary photochemical reactions.