

Interactive comment on “Electron-induced chemistry in microhydrated sulfuric acid clusters” by Jozef Lengyel et al.

Anonymous Referee #2

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Overall:

The manuscript describes mass spectrometric measurements and quantum chemical calculations on the sulphuric acid water system. The authors propose a caging mechanism in which an intermediate $[(\text{H}_2\text{O})_n\text{H}.\text{HSO}_4^-]$ species forms, before the neutral hydrogen atom is released. This mechanism applies probably only in cases where H_2SO_4 is charged directly by an e^- . However, to my knowledge thermal electrons will most likely attach first to more abundant species. H_2SO_4 would then react with those ions and form HSO_4^- . If the authors have any references to more recent work that indicate direct charging of H_2SO_4 by free electrons in the Earth atmosphere they should cite them. H_2SO_4 is an important compound for the formation of aerosol particles, even if more recent research draws a more complex picture. This aspect of the manuscript

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fits therefore well into the scope of ACP. In general I agree with Ref 1 remarks about the quantum chemical calculations and this part should be extended.

Scientific:

- To what temperature does the He/ H_2SO_4 / H_2O gas mixture drop after nozzle?
- What relative humidity would be reached in the cluster formation zone after the nozzle?
- How long is the reaction time to form these clusters (before ionisation)?
- How long is the reaction time the charged clusters (after ionisation)?
- Is it possible that some water is condensing on the cluster after the ionisation?
- Could you determine the lifetime of the intermediate by adjusting the reaction time?
- I assume the charged clusters are accelerated by an electric field in a low pressure environment, is evaporation and fragmentation a potential problem in your setup?
- How do your dissociation constants compare to bulk phase sulphuric acid?

Technical:

Data statement is missing. https://www.atmospheric-chemistry-and-physics.net/about/data_policy.html

A brief overview of current developments in the quantum chemical treatment of H_2SO_4 - H_2O clusters is missing.

P 1 L 19: I think aerosols should be replaced with clusters as the paper shows only results for clusters containing a few sulphuric acid molecules

P 1 L 27: I suggest to replace neutral structure by undissociated structure and (optionally) ion pair structure by dissociated structure (ps: probably solved by following referee 1 request)

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P2 L 3-9: Is the Sulphuric acid charging by e- capture actually important for the production of charged sulphuric acid cluster (especially in the context of boundary layer nucleation events)? Some older and more recent literature is missing in the context of ion induced nucleation Raes and Jansen 1985 DOI:10.1016/0021-8502(85)90028-X (or even earlier), a more recent one would be Kirkby et al 2011 (DOI: 10.1038/nature10343) or the most recent for H₂SO₄ water Kürten et al 2016 (10.1002/2015JD023908). There are also field observations that try to estimate the fraction of ion induced nucleation in the total nucleation rate (Hirsiko et al 2011, doi:10.5194/acp-11-767-2011).

P2 L14-15: Charged sulphuric acid clusters in the atmosphere where already measured before, example literature Eisele, 1989 DOI: 10.1029/JD094iD02p02183 I have the impression this sentence is out of context and should be moved to the previous paragraph.

Methods: P4 L 2: What was the criterion for choosing the clusters for re-optimisation? How many isomers were used?

Results: P4 L 17: The results of the quantum chemical calculations should be compared to previous work.

P8 L 21: could this be quantified more? Is the cross section and e- concentration high enough so that electron attachment in the troposphere is a major source of HSO₄-? What is the free e- concentration in the troposphere?

P9 L 3: How was that calculated? You probably used all structures for a given isomer, please be a bit more precise here.

Conclusion: P10 L 16-17: The dipole in the dissociated cluster could also enhance the uptake of ions such as NO₃-. With the quantum chemical calculations you could calculate this enhancement (see Su & Chesnavich DOI:10.1063/1.442828).

Figures: - figure 2: The figure and data will be much easier to comprehend if the dotted

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lines are replaced by symbols (e.g. square, disk, triangle up/down) at the top of the corresponding peaks. currently the colours are too similar.

- figure 3: You should provide the geometry of the clusters as text files (pdb or xyz). Allows readers to visualise the results in a molecule viewer.

- figure 4: If possible combine the curves in figure 4 for each row, using different colours and symbols.

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