

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

Anonymous Referee #1

Received and published: 18 August 2017

Lengyel, Pusanenko and Fárnik have studied the attachment of electrons to small sulfuric acid - water clusters, and complement their experimental results by density functional theory calculations. I can not comment in depth on the experimental details of the study (as far as I can tell they seem sound, but hopefully another reviewer will have more expertise on this), and will thus focus my review mainly on the atmospheric chemical and computational aspects.

Sulfuric acid, as stated by the authors, is one of the most important molecules for atmospheric aerosol processes, in particular new-particle formation. While neutral pathways are likely to dominate new-particle formation in the contemporary boundary layer, (as shown e.g. by results from the CLOUD consortium), ion-mediated processes can be an important minor channel, and also increase in importance with altitude (as well as

C1

being more important in cleaner atmospheres, including the preindustrial and hopefully also the future). The present study is thus likely to be of interest to the atmospheric science community.

The computational methods employed here are fairly modest - state-of-the-art studies on similar systems nowadays tend to employ coupled-cluster energy corrections to account for the limitations of DFT, or at the very least use triple-zeta basis sets in the DFT calculations of final energies (rather than double-zeta as done here). However, the methods used are of sufficient quality for the required purposes (i.e. capturing reaction energy differences on the order of 0.1 eV or more). The computations are also, for understandable technical & computational reasons, also restricted only to closed-shell species (plus an isolated H radical), but then quite extensive conclusions are drawn about the structures and behaviour of radical (transient or final) structures, e.g. concerning "H caging" and so on.

I have one major question for the authors, along with one suggestion for (a fairly limited set of) additional computations, and a number of minor suggestions or corrections.

My main question is, why does the concentration of clusters with 3 or more H₂SO₄ molecules drop when more water is added (e.g. figure 1)? According to both classical thermodynamics and quantum chemical calculations (as well as chemical common sense), water should promote clustering of sulfuric acid significantly. Thus one would assume that the concentration of larger clusters would increase when the water content goes up. Or to put it another way, typically the nucleation rate increases with increasing RH for constant [H₂SO₄] and T. Does perhaps the absolute H₂SO₄ concentration (which the authors don't actually report) decrease from the low-water runs to the high-water runs?

My main suggestion is that the authors add some calculations on the (H₂O)_nH₂SO₄-radical anionic clusters to support their extensive speculation on "H caging" and similar effects. While I understand their reluctance to work with larger open-shell clusters

C2

(with more than one H₂SO₄/HSO₄⁻ moiety), the (H₂O)_nH₂SO₄⁻ system with small (e.g. 1-4) *n* is certainly treatable at the UM06-2X/aug-cc-pVDZ level, and while the resulting energies may not be as accurate as for the closed-shell systems, the structures would certainly be good enough to investigate the “caging” phenomenon the authors repeatedly speculate about.

Minor comments:

-In the abstract, the authors state that “the (H₂SO₄)_m(H₂O)_nHSO₄⁻ clusters are formed after the dissociative electron attachment to the clusters containing the (HSO₄⁻·H₃O⁺) ion-pair structure”. This is a reasonable conclusion to draw from their data, but their reasoning is based on somewhat indirect evidence - I would modify the sentence to account for this, e.g. by adding a word “likely”, or starting the sentence with “Our results indicate that” or something similar.

-In the introduction, the authors call the sulfuric acid - water clusters where the sulfuric acid remains undissociated “neutral”. While this is not wrong, it can lead to confusion, as also the ion-pair clusters (HSO₄⁻·H₃O⁺) are “neutral” in the sense of having a overall electrical charge of zero. I would thus recommend the authors use some other term to denote the undissociated clusters. (Later on they themselves use the term “covalently-bonded”, which is one option; “hydrogen-bonded molecular cluster” would be even more accurate but somewhat lengthy.)

-On page 7, the authors talk about the “presumably larger dipole moment” of the ion-pair structures. They do not need to presume anything about dipole moments, as their quantum chemical calculations contain the dipole moments of all their structures - they should instead report (in the supplement) the dipole moments of all their global minima, and for the “borderline” cases where the molecular cluster and ion pair structures are close in energy, perhaps report dipole moments for the best structures of both cases. These data could then be used to see whether the reasoning is indeed correct or not.

-On page 9, the authors mention the “polarization of the second H₂SO₄ molecule when

C3

the HSO₄⁻ ion is generated” as the reason for the very exothermal formation of HSO₄⁻·H₂SO₄ (and neutral free H) from (H₂SO₄)₂. This is not in itself wrong, but a more informative/illustrative way to phrase it would be that the HSO₄⁻·(H₂SO₄) cluster has a much higher binding energy (by tens of kcal/mol) than the (H₂SO₄)₂ cluster.

-Line 2 of section 2: “home-build” should be “home-built”.

-Figure caption of figure 1: “decreasing H₂O mole fraction” should presumably be increasing (as we go from a to b to c, *x*(H₂O) goes up)

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-573>, 2017.