

Author's response to the discussion paper:

Electron-induced chemistry in microhydrated sulfuric acid clusters

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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 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.

We would like to thank the referee for reading our manuscript, his valuable comments and overall positive evaluation of our manuscript. Before going to his particular questions, we would like to provide some general comments. First, some of the reviewer's questions and comments concern the theory. Indeed, we try to answer them and incorporate his suggestions in revised manuscript, nevertheless, we would like to stress the point which we have made in our reply to reviewer #1: the major contribution of our present paper is the experiment and the calculations were performed only to provide a support for the unambiguous experimental observations and conclusions. Please, see our reply to reviewer #1, page 1 and 2.

Second, as outlined below, many of the reviewer's questions (points 1-8) originate probably from a slight confusion of our molecular beam method with the condensation-

chamber type experiments generally used in the aerosol community. Therefore, we provide an extensive explanation of the questioned experimental points for the reviewer below. However, we have not substantially extended the experimental part of our manuscript in this respect, since most of our arguments can be found in basic textbooks on molecular beams and clusters, e.g., [Scoles, G.: Atomic and molecular beam methods, Oxford University Press, 1988; Haberland, H.: Clusters of atoms and molecules. Springer series in chemical physics, vol. 52, Springer-Verlag, 1994; Pauly, H.: Atom, molecule, and cluster beams I & II. Springer-Verlag, 2000]. The conditions specific to our apparatus are then either outlined in the method section or in the cited publications.

Concerning the reviewer's question: "...to my knowledge thermal electrons will most likely attach first to more abundant species. H₂SO₄ would then react with those ions and form HSO₄-...". The reviewer is correct and this has been pointed out in our manuscript on page 2: *"The cosmic rays are the principal source of ionization and free electrons in the upper troposphere and lower stratosphere, where the electron collisions can influence the gas-phase chemistry. Typically, the electrons are effectively thermalized to low energies ($\gtrsim 1$ eV) via multiple inelastic collisions (Campbell and Brunger, 2016) . At these low energies, they are rapidly captured by abundant molecules, in particular O₂."* However, we focus on the mixed H₂SO₄/H₂O clusters and use the electron attachment to ionize these species for the mass spectrometry which delivers some information also about the neutral clusters, their properties and elementary processes in them such as the acidic ionization. In addition, our experiments provide some information about the free electron attachment to these clusters. The main purpose of our study is the molecular level insight into these species and processes, which can be further relevant for atmospheric chemistry.

1) To what temperature does the He/H₂SO₄/H₂O gas mixture drop after nozzle?

It ought to be noted that a supersonic expansion is generally a non-equilibrium process for which the concept of temperature is not well defined. Due to the gas rarefaction in the expansion, the collisions cease at some point (freezing/quitting surface) and the molecules and clusters then fly in the vacuum without further interactions. Typically the molecules undergo $\sim 10^4$ collisions in the expansion and they all happen within ~ 20 nozzle radii [Pauly, H.: Atom, molecule, and cluster beams I & II. Springer-Verlag, 2000]. In our case this represents ~ 2 mm from the nozzle throat, and the molecules pass through this region in a few microseconds. Please, see also our answer to referee #1, point I). A temperature can still be used in supersonic expansion to describe the species in the beam, however, one has to be aware that

different degrees of freedom require different number of collisions to cool and equilibrate. Therefore we can speak about rotational, vibrational and translational temperatures which can all be quite different (sometimes even the concept of parallel and perpendicular translational temperature is introduced despite the temperature not being a vector).

Determination of the cluster temperature experimentally is very challenging and has been accomplished only for a few special cases, e.g., for rare gas clusters (~ 35 K for Ar_N) and a few other species by electron diffraction [Farges, J., et al.: Structure and temperature of rare gas clusters in a supersonic expansion. *Surf. Sci.*, 106, 95–100, 1981; Farges, J., et al.: Noncrystalline structure of argon clusters. II. Multilayer icosahedral structure of Ar_N clusters $50 < N < 750$. *J. Chem. Phys.*, 84, 3491–3501, 1986]. For the special case of superfluid helium nanodroplets the vibrational-rotational temperature of a molecule deposited in the cluster was measured spectroscopically giving the temperature of 0.37 K [Hartman, M., et al.: Rotationally resolved spectroscopy of SF_6 in liquid helium clusters: A molecular probe of cluster temperature. *Phys. Rev. Lett.*, 75, 1566–1569, 1995]. For small clusters spectroscopic methods can be used in some cases. Nevertheless, for most of the larger molecular clusters, we have to rely on model approaches combined with an indirect experimental evidence to estimate their temperatures, e.g., the evaporative ensemble theory [Klots, C. E.: Evaporative cooling. *J. Chem. Phys.*, 83, 5854–5860, 1985; Klots, C. E.: Temperatures of evaporating cluster. *Nature*, 327, 222–223, 1987; Klots, C. E.: Kinetic methods for quantifying magic. *Z. Phys. D*, 21, 335–342, 1991]. A relaxation model was introduced more recently to estimate the temperatures of water clusters [Brudermann, J., et al.: Isomerization and melting-like transition of size-selected water nonamers. *J. Phys. Chem. A*, 106, 453–457, 2002] and methanol clusters [Steinbach, C., et al.: Isomeric transitions in size-selected methanol hexamers probed by OH-stretch spectroscopy. *Phys. Chem. Chem. Phys.*, 8, 2752–2758, 2006]. Further non-equilibrium numerical models were employed to analyze the cluster temperatures in seeded supersonic expansions of water vapor with Ar and Ne [Jansen, R., et al.: Nonequilibrium numerical model of homogeneous condensation in argon and water vapor expansions. *J. Chem. Phys.*, 132, 244105, 2010; Gimelshein, N., et al.: The temperature and size distribution of large water clusters from a non-equilibrium model. *J. Chem. Phys.*, 142, 244305, 2015], which were also studied spectroscopically by sodium doping method [Buck, U., et al.: A size resolved investigation of large water clusters. *Phys. Chem. Chem. Phys.*, 16, 6859–6871, 2014; Zeuch, T., Buck, U.: Sodium doped hydrogen bonded clusters: Solvated electrons and size selection. *Chem. Phys. Lett.*, 579, 1–10, 2013]. Different models revealed

temperatures between 70 K and 200 K for the water clusters, depending on cluster size and expansion conditions.

It ought to be mentioned that there are special Laval-type nozzle expansions where the equilibrium conditions can be reached, and experiments were designed to study nucleation in the nozzle and post-nozzle flows [Wyslouzil, B. E., et al.: Binary condensation in a supersonic nozzle. *J. Chem. Phys.*, 113, 7317–7329, 2000; Manka, A., et al.: Freezing water in no-man's land. *Phys. Chem. Chem. Phys.*, 14, 4505–4516, 2012; Wyslouzil B. E, Wölk, J.: Overview: Homogeneous nucleation from the vapor phase—The experimental science. *J. Chem. Phys.* 145, 211702, 2016; Schläppi, B., et al: A pulsed uniform Laval expansion coupled with single photon ionization and mass spectrometric detection for the study of large molecular aggregates. *Phys. Chem. Chem. Phys.*, 17, 25761–25771, 2015; Ferreiro, J. J., et al.: Observation of propane cluster size distributions during nucleation and growth in a Laval expansion. *J. Chem. Phys.*, 145, 211907, 2016; Chakrabarty, S., et al.: Toluene cluster formation in Laval expansions: Nucleation and growth. *J. Phys. Chem. A*, 121, 3991–4001, 2017]. However, the molecular beam experiments are not well suited to investigate the nucleation of aerosols in general. In molecular beam experiments, the expansion conditions are tuned to produce the desired species and then other experiments are performed with them. We did not attempt to study the nucleation of sulfuric acid but our aim was rather to produce the hydrated sulfuric acid clusters and investigate them by electron attachment and mass spectrometry.

It should be mentioned that the molecular beam experiments can also yield some information useful for molecular level understanding of the nucleation –e.g., in our previous experiments the cross sections of water clusters for pickup of various atmospheric molecules from gas phase could be measured which is essential for the cluster growth [Lengyel, J., et al.: Uptake of atmospheric molecules by ice nanoparticles: Pickup cross sections. *J. Chem. Phys.*, 137, 034304, 2012]. However, this is not the subject of our present publication.

We provide this extensive answer and literature review, to illustrate that the question about the temperature in the expansion is not a trivial one and cannot be easily answered –in fact, this question has been answered so far only for a few specific systems. For the present system, the cluster temperature has not been measured experimentally and the above mentioned theoretical approaches are far beyond the scope of our present research. For pure water clusters the temperature would probably be around 100 K for our present expansion conditions. However, it is well known that already a small admixture of other gas in the expansion can change the conditions significantly, and consequently the resulting

temperature. Therefore we would like to refrain from any speculations about the cluster temperature at this point.

2) What relative humidity would be reached in the cluster formation zone after the nozzle?

Under our most humid conditions (figure 1c in the main paper) the partial water vapor pressure was approximately 42 mbar while the partial vapor pressure of H₂SO₄ was 2.04 mbar and we used 2 bar of He buffer gas. Please, see also our reply to Reviewer #1, page 3, last paragraph. RH corresponds to the ratio of the partial pressure of water vapor to the equilibrium vapor pressure of water at the temperature in the expansion. The clusters are formed still in the nozzle within few millimeters from the nozzle throat. The reservoir and nozzle temperatures were 453 K and 458 K, however, these temperatures are irrelevant for the actual temperatures in the gas flow which cools down by the supersonic expansion and the temperature can be as low as 100 K or even lower, leading to supersaturation in the expansion which in turn leads to the cluster formation [Pauly, H.: Atom, molecule, and cluster beams I & II. Springer-Verlag, 2000]. The temperature is not known for the present system, as discussed above, therefore we cannot give any RH value. The partial pressures of component molecules and buffer gas are sufficient to determine the cluster sizes and compositions in supersonic expansions (together with other expansion conditions such as the nozzle temperature, size and shape).

3) How long is the reaction time to form these clusters (before ionisation)?

There are several time-windows in our experiment. First, there is the time during which the collisions occur and the clusters are generated. This has been explained above that the collisions occur within ~2 mm from the nozzle throat, and the molecules pass through this region in about 2 μ s (based on the cluster velocity $\sim 1.0\text{--}1.5 \times 10^3 \text{ ms}^{-1}$ which can be actually measured on our apparatus using a pseudo-random chopper and cross-correlation method [Fedor, J., et al.: Cluster cross sections from pickup measurements: Are the established methods consistent? J. Chem. Phys., 135, 104305, 2011; Lengyel, J., et al.: Uptake of atmospheric molecules by ice nanoparticles: Pickup cross sections. J. Chem. Phys., 137, 034304, 2012]). Thus the first “reaction time” in which the clusters are generated is ~2 μ s.

Then the collisions cease completely. After the skimmer (~1.5 cm from the nozzle) the beam enters high and ultra-high vacuum regions (10^{-6} – 10^{-10} mbar) where the mean free path for molecules exceeds several meters, i.e., the clusters fly undisturbed, isolated, not interacting with anything (except for the black-body-radiation photons from the apparatus walls which are at room temperature). The distance to the ionization volume of the TOF

spectrometer is ~ 1.5 m which the clusters fly in about 1.5 ms. During this time only evaporation of molecules from the cluster can occur (if the clusters were generated in excited states) or spontaneous intra-cluster reactions can happen, e.g., the acidic dissociation. However, we believe that this process occurs already during the cluster generation, as soon as the sulfuric acid molecule is surrounded by enough water molecules in the cluster. So the second “reaction time” of 1.5 ms is rather an idle time. Then the ionization by electron beam occurs.

4) How long is the reaction time the charged clusters (after ionisation)?

The electron beam is pulsed for 2 μ s during which the clusters can interact with the electrons. After the electron pulse there is a delay of 0.5 μ s before the extraction pulse for ions is switched on. During this delay all remaining free electrons leave the ionization volume so that the spectra cannot be disturbed by any effects caused by these electrons accelerated by the extraction voltage. Then the ions are accelerated by an 8 kV pulse into the TOF where the total flight path to the detector is 95 cm. The flight time between the cluster ionization and detection represents several tens of microseconds –the exact value depends on applied voltages, and the cluster mass to charge ratio. The pressure in the TOF is below 10^{-8} mbar, i.e., the ions do not collide with any residual gas molecules. Also the cluster density in the beam is so low that any collisions of the nascent cluster ions with other clusters or molecules in the beam are highly unlikely.

In summary, the “reaction time” after the cluster ionization is several tens of microseconds (depending on the mass to charge ratio). However, during this time the cluster ions do not collide with any other species and thus only intracuster reactions can occur. If the cluster ion fragmentation would occur during the time after the cluster extraction and before it enters the reflectron mirror, it would be reflected in the position and shape of the corresponding mass peaks [Wei, S., Castleman, A. W.: Using reflectron time-of-flight mass spectrometer techniques to investigate cluster dynamics and bonding. *Int. J. Mass. Spectrom. Ion Processes*, 131, 233–264, 1994]. We did not observe any of these effects in the mass spectra, therefore we excluded metastable fragmentation of the clusters after the ionization. Indeed, we observed the cluster ion fragments in the mass spectra, but the fragmentation had to be fast, completed between the ionization and extraction pulse, i.e. within 0.5 μ s (taking into account also the ionization pulse duration, the maximum time available for this fragmentation could be 2.5 μ s).

5) Is it possible that some water is condensing on the cluster after the ionisation?

The cluster formation, which includes also the addition of water molecule, is strictly connected only to the supersonic expansion. As described above, the TOF chamber is ~1.5 m downstream from the nozzle chamber divided by several differentially pumped vacuum chambers and there are no further collisions possible in the ultrahigh vacuum in our TOF chamber (the corresponding pressure of $\sim 10^{-8}$ mbar corresponds to the mean free path in the order of 10 km for molecules).

6) Could you determine the lifetime of the intermediate by adjusting the reaction time?

We are not sure what the Reviewer means by the “intermediate” and “reaction time” but we have probably answered this question above, point 4). If some intermediate is generated after the electron attachment which then fragments to the final cluster ion, the fragmentation has to occur within the 0.5 μ s delay between the electron pulse and the ion extraction (at most 2.5 μ s if we take into account also the ionization pulse duration). Any metastable decay which would occur after the ion extraction during the flight time to the reflectron mirror would be recognized in the spectral peak position and shape. Since no such effects were observed in the spectra the intermediate lifetime must be shorter than 0.5 μ s. We could make this delay time even shorter, however, some unwanted effects from residual free electrons could disturb the spectrum. Therefore this is the shortest time window we could provide at the moment.

7) 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?

We believe that we have answered this question already above. If the cluster mass changes after its extraction during its flight time to the reflectron mirror, the fingerprint of the mass change can be unambiguously recognized in the spectrum [Wei, S., Castleman, A. W.: Using reflectron time-of-flight mass spectrometer techniques to investigate cluster dynamics and bonding. *Int. J. Mass. Spectrom. Ion Processes*, 131, 233–264, 1994]. There was no evidence for such metastable fragmentation in our spectra.

8) How do your dissociation constants compare to bulk phase sulphuric acid?

The dissociation constant is a characteristics of a macroscopic bulk systems in equilibrium. For individual isolated clusters in vacuum we cannot measure the dissociation constants in our experiment. From our mass spectra we can make some conclusions about the acidic dissociation of sulfuric acid in water clusters. In principle we can answer the question: how many water molecules are needed to acidically dissociate a sulfuric acid molecule? Actually,

this question has been treated by similar methods in the past for nitric acid [Kay, B. D., et al.: Studies of gas-phase clusters: The solvation of HNO₃ in microscopic aqueous clusters, Chem. Phys. Lett., 80, 469, 1981] (see also our answer to point 3) of reviewer #1. Such question cannot be solved in the bulk where the dissociation constant characterizes the macroscopic system. However, it is a fundamental question and the answer to this question provides molecular level understanding to the processes occurring in the bulk.

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

The data statement has been added at the end of the manuscript.

10) A brief overview of current developments in the quantum chemical treatment of H₂SO₄-H₂O clusters is missing.

As mentioned above, the major contribution of our present paper is the unique experiment. The calculations were performed to provide a support for the experimental conclusions. The major conclusions, e.g., about the acidic dissociation or fragment caging in the clusters could be derived essentially just based on the experimental evidence. Please, see our reply to the reviewer #1, page 1-2 for more details. Besides, we would like to point out that our benchmark calculations proved that the used computational approach is in reasonable agreement with the higher-level *ab initio* methods. These benchmark calculations are now presented in supporting information and also discussed in our reply to the reviewer #1 on p. 2.

Since the present manuscript is not a theoretical paper, and as experimentalists we rather focus on the previous experimental evidence directly relevant to the investigated phenomena, we believe that an extensive overview of the previous quantum chemical calculations of the H₂SO₄-H₂O system would unnecessarily extend the theory-related part of our manuscript and distract the reader from the main message. We believed that we have covered most of the recent theoretical papers directly relevant to our investigations in our references. However, we could miss some important contributions and we would be happy to add some more references, if the reviewer provides some explicit suggestions what we missed in our survey.

11) 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

We followed the reviewer's suggestion and replace "aerosols" with "clusters".

12) 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)

We followed the suggestion of both referees and the respective terminology has been changed to avoid any confusion.

13) 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).

As already mentioned above, we do not focus on the nucleation of atmospheric sulfuric acid aerosols. We investigate the properties of the individual mixed H₂SO₄-H₂O clusters which have not been observed by mass spectrometric experiments before. Therefore we have avoided an extensive discussion of the atmospheric nucleation of sulfuric acid aerosols in the introduction, since we found it unnecessarily lengthening our paper and distracting the reader from the main topic. Nevertheless, we have now added a brief overview of the nucleation in the introduction on page 2 citing the above publications:

14) 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.

The introduction has been changed as outlined above.

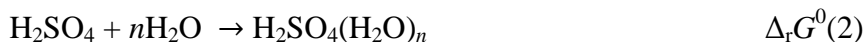
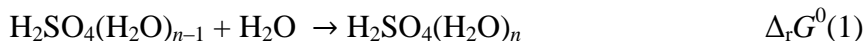
15) Methods: P4 L 2: What was the criterion for choosing the clusters for reoptimisation? How many isomers were used?

We used previously observed energetic minima from literature as the initial structures and equilibrated them in molecular dynamics runs. From the MD simulation, several structures were randomly taken and re-optimized at the M06-2X/aug-cc-pVDZ level. Altogether 8 different isomers on average were optimized from various starting structures for each cluster type ((H₂SO₄)₁₋₂(H₂O)₀₋₅, (H₂SO₄)₀₋₁(H₂O)₀₋₅HSO₄⁻) including the hydrogen-bonded, H₂SO₄⋯H₂O, and ion-pair, HSO₄⁻⋯H₃O⁺, structures in neutral clusters. Only the most stable

isomers were considered for further calculations. The section ‘2 *Experimental and theoretical methods*’ has been extended with the aforementioned discussion.

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

The comparison with the previous theoretical work has been added to the discussion concerning the binary nucleation of H₂SO₄/H₂O clusters. As an example, the calculated free energies of the addition of water molecule were in reasonable agreement with the literature values [Kurtén, T., et al.: Quantum chemical studies of hydrate formation of H₂SO₄ and HSO₄[−]. Boreal Environ. Res., 12, 431, 2007; Loukonen, V., et al.: Enhancing effect of dimethylamine in sulfuric acid nucleation. Atmos. Chem. Phys., 10, 4961, 2010; Henschel, H., et al.: Hydration of atmospherically relevant molecular clusters: Computational chemistry and classical thermodynamics. J. Phys. Chem. A, 118, 2599, 2014]. The seemingly different values in free energies were caused by different definitions of the nucleation event in the calculated chemical reactions:



In the present paper, we calculate the free energy $\Delta_r G^0(1)$ for an addition of single water molecule to a preexisting cluster. The free energy can be calculated also from the accumulation of all molecular component to the cluster $\Delta_r G^0(2)$. The former way of calculation, $\Delta_r G^0(1)$, is more illustrative for our discussion. When we calculated $\Delta_r G^0(2)$, it was in a good agreement with the previously published data as shown in Table 1.

Table 1: Free energies (in kcal mol^{−1}, at $T=298\text{K}$ and $p^0=1\text{atm}$) of binary nucleation of H₂O/H₂SO₄ clusters

$n =$	$\Delta_r G^0(1)$	$\Delta_r G^0(1)$	$\Delta_r G^0(2)$	$\Delta_r G^0(2)$	$\Delta_r G^0(2)$
	our results	Kurtén, et al.	our results	Henschel, et al.	Loukonen, et al.
1	−2.7	−2.81	−2.7	−2.60	−2.93
2	−1.7	−1.87	−4.4	−4.40	−6.26
3	−0.8	−2.37	−5.2	−5.83	−7.11
4	−2.3	−0.90	−7.5	−7.05	−8.11
5	−1.2	–	−8.7	−6.81	−10.01

The corresponding discussion has been added to the manuscript, and the respective chemical equations included in a new Table 1 in the manuscript.

17) 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?

The cosmic ray ionization rate varies between about 2 ion pairs cm⁻³ s⁻¹ close to Earth's surface and 40 ion pairs cm⁻³ s⁻¹ at the top of the troposphere [Carslaw, K. S., et al.: Cosmic rays, clouds, and climate, *Science*, 298, 1732–1737, 2002]. The observed density of free electrons is very low in stratosphere around 5×10³ cm⁻³ [Smith, D., Adams, N. G.: Elementary plasma reactions of environmental interests. *Top. Curr. Chem.* 89, 1–43, 1980] because they rapidly interact with abundant molecules, in particular O₂. For the lower altitudes, the number of the free electrons is significantly reduced. Therefore we expect a minor importance of free electrons for tropospheric ion chemistry. The tropospheric HSO₄⁻ ions are most likely formed in reaction of gas-phase sulfuric acid and various molecular anions, such as O₂⁻. At higher altitudes the contribution of free electrons is larger, therefore we have suggested that the free electron attachment may actually contribute. However, our major focus is the molecular level understanding to the mixed H₂SO₄/H₂O clusters and the electron attachment process to them. We are not qualified to make speculations about the actual contribution of such processes, however, the corresponding sentence can stimulate the interest of scientists modelling the atmospheric processes.

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

The computational procedure was described in detail in the section ‘2 *Experimental and theoretical methods*’, page 4, line 3 (in the original manuscript): “Only the most stable isomers were considered for further calculations.”

19) 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).

The reviewer is correct and the dipole or positive charge in the dissociated cluster could also enhance the uptake of ions such as NO₃⁻. This could be calculated theoretically. However, we would like to stress again, that the main value of our contribution is the solid experimental evidence from an advanced experiment with particles in the molecular beam. To perform such

experiment for the proposed NO_3^- ion attachment would require substantial changes in our experimental arrangement and would be difficult –for example, already the initial question of a good source for an intense NO_3^- ion beam would be difficult to solve. This goes far beyond not even our present publication but also our near future experimental plans. But we thank the reviewer for an interesting input for some future plans.

Our present study is focused on the binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ clusters. Apparently the detection of these hydrated clusters seems to be not trivial for laboratory experiments since they have not been detected in the aerosol chamber experiments so far [Kirkby, J., et al.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, *Nature*, 476, 429, 2011, Kürten, A., et al.: Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real time under atmospheric conditions. *Proc. Natl. Acad. Sci. USA*, 111, 15019, 2014]. Here we have demonstrated an efficient way of generating these hydrated sulfuric acid clusters using the molecular beam technique, and characterized them by the electron attachment mass spectrometry. Adding additional calculations of ternary complexes with NO_3^- ion to our present manuscript would be confusing without any experiment connected to this topic.

20) figure 2: The figure and data will be much easier to comprehend if the dotted 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.

The symbols have been added to Figure 2.

21) 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.

The respective geometries have been added to the Supplement.

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

We agree with the reviewer that there seems not to be much information in figure 4, except that the energy dependent ion yields look essentially all the same. However, that is exactly our message. As outlined also in the text, the ion yield curves were identical for all the mass peaks (within the experimental errors). Figure 4 should illustrate this point for a few examples (there are plenty of electron energy dependencies measured for other mass peaks, and we have added some more examples in the supporting information for illustration). If we plotted all the energy dependencies in one single plot (normalized) they would be just overlapping. We

believe that showing the individual plots separately provides a clearer picture, and the reader can also see the different signal intensities and the level of the noise in the data. This presentation of figure 4 provides a clear picture of what is meant in the text by “the same energy dependencies”. We believe that this message would not be so clear in the representation suggested by the reviewer, therefore we would like to keep the present form of figure 4.