Author's response to the discussion paper:

Electron-induced chemistry in microhydrated sulfuric acid clusters

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Reply to the interactive comment of Referee #1:

We would like to thank the referee for his valuable comments and overall positive evaluation of our manuscript. Before addressing his particular points in more detail, we would like to make a general comment.

We would like to stress that the major contribution of our present paper is the 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. Actually, such conclusions were derived previously for similar systems (nitric acid–water clusters) just from the experimental mass spectra in the early work of Castleman's group [Kay, B. D., Hermann, V., and Castleman Jr., A. W.: Studies of gas-phase clusters: The solvation of HNO_3 in microscopic aqueous clusters, Chem. Phys. Lett., 80, 469, 1981]: the number of water molecules needed to acidically dissociate an HNO_3 molecule in $HNO_3(H_2O)_N$ clusters was derived from the shape of the $HNO_3(H_2O)_nH^+$ mass spectra (see also our work: [Lengyel, J., Pysanenko, A., Kočišek, J., Poterya, V., Pradzynski, C. C., Zeuch, T., Slavíček, P., and Fárník, M.: Nucleation of mixed nitric acid-water ice nanoparticles in molecular beams that starts with a HNO_3 molecule, J. Phys. Chem. Lett., 3, 3096, 2012]). Recently, we have shown that for the $(HNO_3)_M(H_2O)_N$ clusters the conclusions drawn from the mass spectra are actually in excellent agreement with the theoretical calculations [Lengyel, J., Ončák, M., Fedor, J., Kočišek, J., Pysanenko, A., Beyer, M. K., and Fárník, M.: Electron-triggered chemistry in HNO_3/H_2O complexes, Phys. Chem. Chem. Phys., 19, 11753, 2017]. Therefore, in the present

case we implement the theoretical calculations to support our conclusions drawn from the experimental evidence –and once again the experiment and theory are in excellent agreement.

We understand that our present level of theory might not exceed the theory level required for a stand-alone theoretical paper. However, that was not our ambition –we performed the calculations at the level accessible to our experimental group and they were in agreement with the experiment. Therefore we published them alongside with the experiment as they can provide more (pictorial) insight into what is actually happening in the clusters. It ought to be mentioned that even the calculations performed at the highest possible level of theory are not guaranteed to deliver a reliable picture of what is going on in the real system, unless they are backed up by some experimental evidence.

Besides, we would like to stress that our benchmark calculations proved that the used computational approach using double zeta basis set are in reasonable agreement with the higher-level *ab initio* methods. **Table 1** summarizes the benchmark calculations of electron affinity of HSO_4, ionization potential of H_2SO_4, and reaction enthalpies for deprotonation of gas-phase H_2SO_4 calculated at different levels of theory. The M06-2X/aug-cc-pVDZ energies are comparable with the CCSD/aug-cc-pVDZ values with the exception of the IP(H_2SO_4). The comparison of double-zeta with triple-zeta basis sets of the M06-2X functional shows that there is essentially constant shift from the experimental values and therefore we do not expect any significant shift in reaction energies even upon hydration. The calculated reaction enthalpies for deprotonation of gas-phase H_2SO_4 are in good agreement with the experimental value. The error of the DFT method is 0.1-0.2 eV. Please note that, in the present work, chemical trends with respect to hydration are of the main concern, and a possible systematic shift of few tenths of eV does not influence our conclusions.

Table 1: Electron affinity of HSO_4, ionization potential of H_2SO_4, and enthalpy of deprotonation at various levels of theory (all in eV). DZ and TZ represent aug-cc-pVDZ and aug-cc-pVTZ, respectively. Enthalpies were calculated at 298.15 K within the harmonic approximation.

	B3LYP/DZ	M06-2X/DZ	M06-2X/TZ	MP2/DZ	CCSD/DZ	Experiment
EA(HSO_4)	4.69	4.92	5.01	5.21	4.92	4.75±0.10[a]
IP(H_2SO_4)	11.4	11.6	11.8	12.4	12.5	12.4±0.05[b]
ΔH($H_2SO_4 \rightarrow H^+ + HSO_4^-$)	13.7	13.5	13.5	13.4	13.6	13.4±0.24[a]

[a] Wang, X.B., Nicholas, J.B., Wang, L.S.: Photoelectron spectroscopy and theoretical calculations of SO_4^- and HSO_4^-: Confirmation of high electron affinities of SO_4 and HSO_4, J. Phys. Chem. A, 104, 504, 2000.

[b] Snow, K.B., Thomas, T.F.: Mass spectrum, ionization potential, and appearance potentials for fragment ions of sulfuric acid vapor, Int. J. Mass Spectrom. Ion Processes, 96, 49, 1990.

Now we would like to address the actual referee's points:

I) 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?

The referee is, indeed, correct that increasing water concentrations promotes the sulfuric acid clustering in condensation chamber type experiments where equilibrium conditions can be reached. However, such conditions are far from our experimental method of the cluster generation. In supersonic expansions the clusters are generated in a very limited space and time span. Typically the molecules undergo ~10^4 collisions in the expansion and they all happen within ~20 nozzle radii. In our case this represents ~2 mm from the nozzle throat, and the molecules pass through this region in a few microseconds. After that (freezing/quitting surface) the molecules undergo no more collisions and the clusters which have been formed essentially do not change until the interaction with the electron beam in the mass spectrometer 2.5 m downstream from the nozzle. An important aspect is also the strong cluster cooling in the expansion due to the inelastic collisions with the buffer gas –the buffer gas atoms carry away the energy in their kinetic energies transforming the internal cluster energy into the kinetic energy of the gas flow in the direction of the beam. The clusters can be cooled by this mechanism to very low temperatures (e.g. for pure water clusters temperatures below 100 K can be routinely achieved). Due to the gas rarefaction the supersonic expansion is a non-equilibrium process and the cluster composition is determined by the collisions between the constituent molecules in the expansion and by the cooling in the collisions with the buffer gas.

In the spectra in figure 1 in the main paper, the He buffer gas pressure is kept constant at ~2 bar and we control the H_2O: H_2SO_4 ratio in the vapor by controlling the temperature of the reservoir T_R containing the sulfuric acid. Our aim was to obtain the mixed clusters. Panel (a) in figure 1 corresponds to concentrated sulfuric acid (98.5%) in the reservoir at T_R = 453 K. The partial vapor pressure of water and sulfuric acid under these conditions was 3.09 mbar and 2.12 mbar, respectively [Perry, R. H., Green D. W., Maloney, J. O.: Perry's chemical engineers' handbook, 7th, MacGraw-Hill, New York, 1997], corresponding to the mole

fractions indicated in the figure. These conditions yielded almost exclusively the pure H_2SO_4 clusters. The spectrum in panel (b) corresponded to the sulfuric acid concentration of 98.0% at the same T_R, i.e., the partial vapor pressures of H_2O and H_2SO_4 were 4.92 mbar and 2.04 mbar, respectively [Perry, R. H., Green D. W., Maloney, J. O.: Perry's chemical engineers' handbook, 7th, MacGraw-Hill, New York, 1997]. In panel (c) we added more water directly into the carrier gas using the humidifier –this is a new very successful method introduced by our group just recently for microhydration of biomolecules [Kočišek, J., Pysanenko, A., Fárník, M., and Fedor, J.: Microhydration prevents fragmentation of uracil and thymine by low-energy electrons, J. Phys. Chem. Lett., 7, 3401, 2016]. This way we increased the partial water vapor pressure to approximately 42 mbar while the partial vapor pressures of H_2SO_4 remained 2.04 mbar. This finally yielded the substantial hydration and the mixed clusters.

Thus the water concentration increases from (a) to (c). First, there is very little water and there are mostly collisions between H_2SO_4 molecules and He generating the pure $(H_2SO_4)_N$ clusters. Increasing the water concentration, the collisions with water molecules become more frequent and some H_2O molecules stick to the sulfuric acid and the mixed clusters appear. At the same time the collisions between H_2SO_4 molecules become less frequent resulting in smaller $(H_2SO_4)_N$ clusters.

Under equilibrium conditions in nucleation chambers, the most likely mechanism how the water promotes clustering is by generating mixed clusters in the first place, and subsequently the water is replaced with H_2SO_4 molecules in these clusters. Therefore, essentially only sulfuric acid clusters without water can be observed in the nucleation chamber type experiments. However, this is not the case in our supersonic expansions where the collisions cease after a short time before all water can be replaced in collisions with H_2SO_4 molecules. Our aim was to generate and investigate the elusive mixed clusters as the early stage in the sulfuric acid nucleation upon humid conditions. The molecular beams are an ideal tool for such type of experiment. The hypothesis of H_2SO_4 replacing water molecules could be also tested in our molecular beam experiment by pickup of H_2SO_4 on pure $(H_2O)_N$ clusters, however, it is technically very demanding far beyond our present experiment.

II) 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 (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.

We followed the suggestion of the referee and calculated the negatively charged $(H_2O)_nH_2SO_4^-$ clusters system with n = 1-5. **Fig. 1** represents the most stable energy isomers of $(H_2O)_nH_2SO_4$ (n= 0-5) clusters (figure 3 of the main paper) re-optimized as the negative ions at the M06-2X/aug-cc-pVDZ level of theory. Comparing the neutral and corresponding anionic structures, the main difference was reducing a dihedral angle between two OH groups from ~158° to ~75° of the sulfuric acid molecule, which resulted in changing of the water molecule orientation in the mixed clusters. The re-optimization of the s1w5-c structure was always followed by spontaneous H_3O formation.

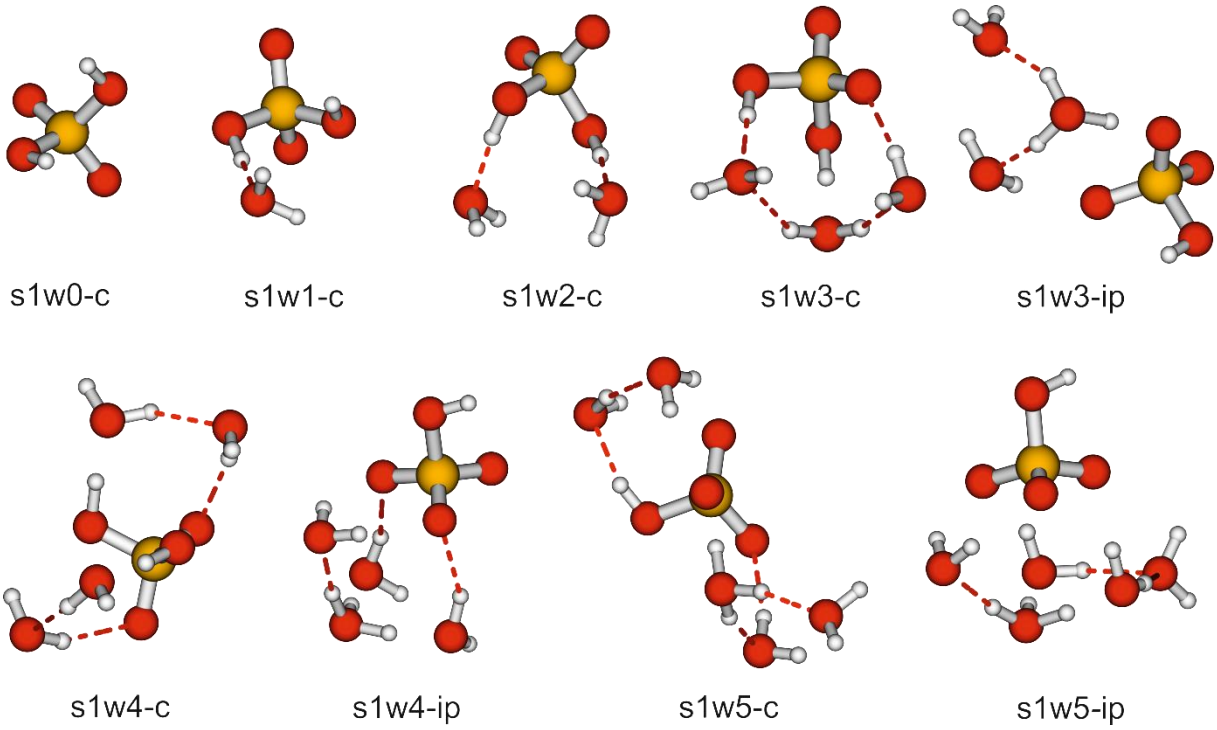

Figure 1. Re-optimized neutral most stable energy isomers of $H_2SO_4(H_2O)_n$ (n= 0-5) clusters with both covalent-bonded (c) and ion-pair (ip) structures as anions. The clusters were optimized at the M06-2X/aug-cc-pVDZ level of theory. The corresponding neutral structures are shown in figure 3 of the main paper.

Although, we have performed the calculations as suggested by the referee, we are not convinced that any further conclusions about the hydrogen caging can be made from these calculations. It ought to be mentioned that the caging, in the present case, is rather a solid experimental observation than a speculation. The electron attachment to a molecule is in principle a dissociative process (DEA) even if a stable anion exists for the molecule (even for zero kinetic energy electrons) [Fabrikant, I. I., Eden, S., Mason, N. J., and Fedor, J.: Recent progress in dissociative electron attachment, Adv. At. Mol. Opt. Phys., 66, 545, 2017]. For sulfuric acid the $H_2SO_4^-$ ion does not exist –neither experimentally nor theoretically and the hydration does not seem to stabilize the small $(H_2O)_n$ $H_2SO_4^-$ species sufficiently. Yet, the observation of these ions in the mass spectra is an unambiguous experimental fact, therefore the $H_2SO_4 + e^- \rightarrow HSO_4^- + H$ dissociation after the DEA process has to be hindered and the hydrogen must be caged by the solvent in order to observe the $(H_2O)_nH_2SO_4^-$ series in the spectrum. We do not wish to speculate what kind of structural arrangement the $(H_2O)_nH_2SO_4^-$ clusters assume, since there are probably numerous possibilities (there will be also a distribution of the neutral starting $(H_2O)_nH_2SO_4$ cluster configurations of which figure 3 in the main paper represents only some examples to illustrate that there are neutral structures where the water molecules can hinder the free hydrogen dissociation).

Minor comments:

1) 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□Â° uÂ°uÂ°uH3O+) 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.

We have changed the corresponding sentence according to referee's suggestion. It now starts with "Our results indicate that…"

2) 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.)

We have changed the term "neutral" to "covalently bonded H_2SO_4" wherever possible in the main article according to the referee's suggestion.

3) 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.

The argument that the dipole moment of the cluster increases upon the ion pair generation in the cluster was used for the explanation of the mixed $HNO_3(H_2O)_N$ cluster mass spectra [Kay, B. D., Hermann, V., and Castleman Jr., A. W.: Studies of gas-phase clusters: The solvation of HNO_3 in microscopic aqueous clusters, Chem. Phys. Lett., 80, 469, 1981]. Essentially the same argument was used in the interpretation of recent experiments where the mixed $HCl(H_2O)_N$ clusters were deflected in electric fields [Guggemos, N., Slavíček, P., and Kresin, V. V.: Electric dipole moments of nanosolvated acid molecules in water clusters, Phys. Rev. Lett., 114, 43401, 2015] (and also earlier for $HNO_3(H_2O)_N$ cluster [Moro, R., Heinrich, J., and Kresin, V. V.: Electric dipole moments of nitric acid-water complexes measured by cluster beam deflection, AIP Conf. Proc., 1197, 57, 2009]). Although, it ought to be mentioned that in the $HCl(H_2O)_N$ case the theoretical calculations showed that the change in the cluster dipole moment upon the acidic dissociation was relatively small and could be overlapped by dynamic effects. In our present investigation of the mixed $H_2SO_4(H_2O)_N$ clusters, the calculations show very broad range of dipole moments (e.g., from 0.3 D to 4.6 D for N = 5 clusters) which depend rather on the cluster structure than on the acidic dissociation (see **Fig. 2** –also added in SI now). Most likely, not only the energy minimum structure but many different cluster structures are generated in the supersonic expansion.

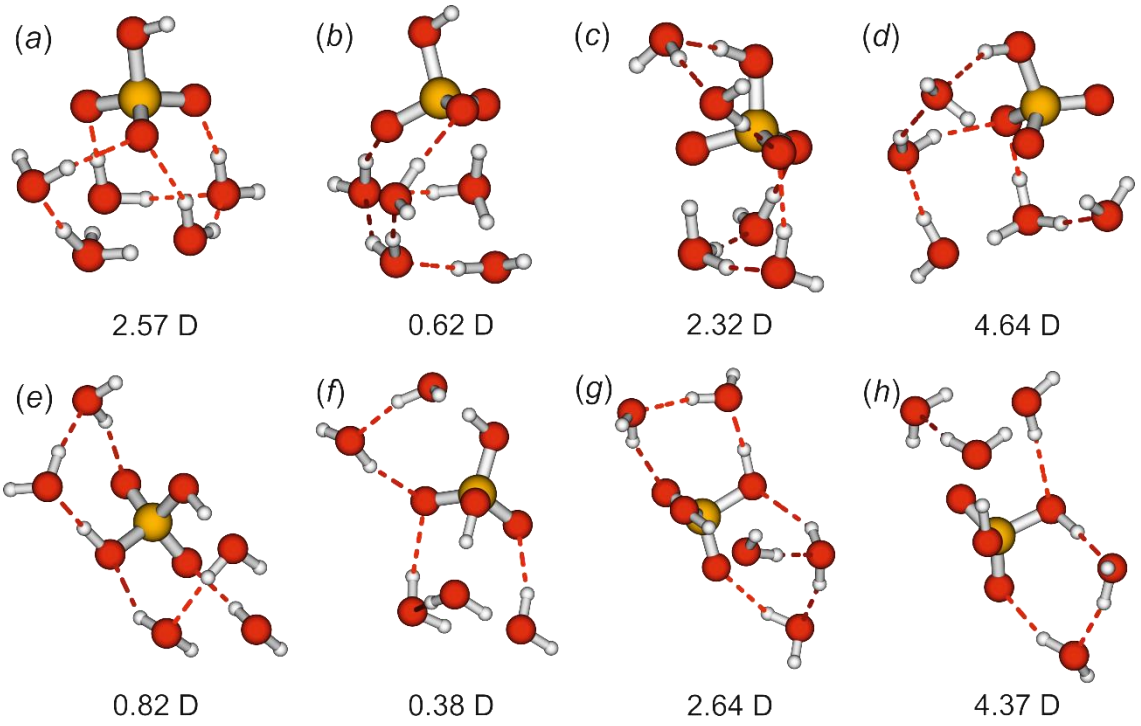

Figure 2. Selected local minima of neutral, $H_2SO_4\cdots H_2O$, (a-d) and ion-pair, $HSO_4^-\cdots H_3O^+$, (e-h) structures in $H_2SO_4(H_2O)_5$ clusters and the corresponding dipole moments.

However, the increase of the peak intensities in mass spectra as a function of the number of water molecules *n* in the clusters is an unambiguous experimental observation. This increase has to be connected with a change in some physical properties of the clusters with *n*. The obvious property which changes with *n* is the occurrence of the ion pair from a certain *n* on –please, see [Kay, B. D., Hermann, V., and Castleman Jr., A. W.: Studies of gas-phase clusters: The solvation of HNO_3 in microscopic aqueous clusters, Chem. Phys. Lett., 80, 469, 1981] for more detailed argumentation. In the present case it can be the presence of the H_3O^+ in the cluster which leads to the more efficient electron attachment and generation of the negative $(H_2O)_nHSO_4^-$ clusters, rather than a larger dipole moment of the zwitterionic clusters (which does not have to be larger as the present calculations suggest).

Thus, thanks to this referee's comment, we have actually discovered an interesting issue, which might have been not quite correct in the past and recent literature and might require some attention in the future. Therefore we have modified our arguments correspondingly (two sentences: page 7 line 10; page 10 line 17).

4) On page 9, the authors mention the "polarization of the second H2SO4 molecule when the HSO4- ion is generated" as the reason for the very exothermal formation of HSO4- H2SO4 (and neutral free H) from (H2SO4)(H2SO4)-. 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)(H2SO4) cluster.

We have changed the corresponding sentence according to referee's suggestion.

5) Line 2 of section 2: "home-build" should be "home-built".

The phrase has been corrected.

6) 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)

The referee is correct, we apologize for this confusion and change the corresponding text.

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 [(H2O)nH.HSO4-] species forms, before the neutral hydrogen atom is released. This mechanism applies probably only in cases where H2SO4 is charged directly by an e-. However, to my knowledge thermal electrons will most likely attach first to more abundant species. H2SO4 would then react with those ions and form HSO4-. If the authors have any references to more recent work that indicate direct charging of H2SO4 by free electrons in the Earth atmosphere they should cite them. H2SO4 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 (≳1 eV) via multiple inelastic collisions (Campbell and Brunger, 2016) . At these low energies, they are rapidly captured by abundant molecules, in particular* O_2." However, we focus on the mixed H_2SO_4/H_2O 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 than fly in the vacuum without further interactions. Typically the molecules undergo ~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 be 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 H_2SO_4 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 μs (based on the cluster velocity ~1.0-1.5×10^3 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 μs.

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 μs during which the clusters can interact with the electrons. After the electron pulse there is a delay of 0.5 μs 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 intracluster 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 μs (taking into account also the ionization pulse duration, the maximum time available for this fragmentation could be 2.5 μs).

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 ~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 μs delay between the electron pulse and the ion extraction (at most 2.5 μs 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 μs. 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 HNO_3 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 H_2SO_4-H_2O 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 H_2SO_4-H_2O 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 ($(H_2SO_4)_{1-2}(H_2O)_{0-5}$, $(H_2SO_4)_{0-1}(H_2O)_{0-5}HSO_4^-$) including the hydrogen-bonded, $H_2SO_4\cdots H_2O$, and ion-pair, $HSO_4^-\cdots H_3O^+$, 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 H_2SO_4/H_2O 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 H_2SO_4 and HSO_4^-. 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:

$$H_2SO_4(H_2O)_{n-1} + H_2O \rightarrow H_2SO_4(H_2O)_n \qquad \Delta_rG^0(1)$$

$$H_2SO_4 + nH_2O \rightarrow H_2SO_4(H_2O)_n \qquad \Delta_rG^0(2)$$

In the present paper, we calculate the free energy $\Delta_rG^0(1)$ 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 $\Delta_rG^0(2)$. The former way of calculation, $\Delta_rG^0(1)$, is more illustrative for our discussion. When we calculated $\Delta_rG^0(2)$, 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=298K and p^0=1atm) of binary nucleation of H_2O/H_2SO_4 clusters

n =	$\Delta_rG^0(1)$ our results	$\Delta_rG^0(1)$ Kurtén, et al.	$\Delta_rG^0(2)$ our results	$\Delta_rG^0(2)$ Henschel, et al.	$\Delta_rG^0(2)$ 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 5×10^{3} 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 O_2. 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 HSO_4^- ions are most likely formed in reaction of gas-phase sulfuric acid and various molecular anions, such as O_2^-. 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 H_2SO_4/H_2O 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 NO_3^-. 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 H_2SO_4/H_2O 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.

Electron-induced chemistry in microhydrated sulfuric acid clusters

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Abstract. We investigate the mixed sulfuric acid-water clusters in a molecular beam experiment with electron attachment and negative ion mass spectrometry, and complement the experiment by DFT calculations. The microhydration of $(H_2SO_4)_m(H_2O)_n$ clusters is controlled by the expansion conditions, and the electron attachment yields the main cluster ion series $(H_2SO_4)_m(H_2O)_nHSO_4^-$ and $(H_2O)_nH_2SO_4^-$. The mass spectra provide an experimental evidence for the onset of the ionic dissociation of sulfuric acid and ion-pair ($HSO_4^-\cdots H_3O^+$) formation in the neutral $H_2SO_4(H_2O)_n$ clusters with $n \geq 5$ water molecules, in excellent agreement with the theoretical predictions. In the clusters with two sulfuric acid molecules $(H_2SO_4)_2(H_2O)_n$ this process starts already with $n \geq 2$ water molecules. The $(H_2SO_4)_m(H_2O)_nHSO_4^-$ clusters are formed after the dissociative electron attachment to the clusters containing the ($HSO_4^-\cdots H_3O^+$) ion-pair structure, which leads to the electron recombination with the H_3O^+ moiety generating H_2O molecule and the H atom dissociation from the cluster. The $(H_2O)_nH_2SO_4^-$ cluster ions point to an efficient *caging* of the H-atom by the surrounding water molecules. The electron energy dependencies exhibit an efficient electron attachment at low electron energies below 3 eV, and no resonances above this energy, for all the measured mass peaks. This shows that in the atmospheric chemistry only the *low-energy electrons* can be efficiently captured by the sulfuric acid-water clusters and converted into the negative ions. Possible atmospheric consequences of the acidic dissociation in the clusters and the electron attachment to the sulfuric acid-water aerosols are discussed.

1 Introduction

Gas-phase sulfuric acid (H_2SO_4) is a key precursor influencing atmospheric aerosol nucleation (Weber et al., 1997; Weber et al., 1999; Sihto et al., 2006; Kulmala et al., 2007). Efficient uptake of water molecules leads to its hydration and the ionic dissociation (Hanson and Eisele, 2000). Progressive hydration of sulfuric acid increases the probability for proton transfer from the acid to water. Theoretical calculations predict the covalently-bonded H_2SO_4 as the global minima for $H_2SO_4(H_2O)_n$ clusters with $n \leq 4$, while for $n = 3$ and 4 the hydrogen-bonded, $H_2SO_4\cdots H_2O$, and ion-pair, $HSO_4^-\cdots H_3O^+$, structures are energetically very close and both structures coexist for these clusters (Re et al., 1999; Temelso et al., 2012a). Upon further hydration $H_2SO_4(H_2O)_n$ for $n \geq 5$ the ion-pair structures become the global energy minima. The ion formation can significantly increase the nucleation rate due to the long-range dipole-charge interactions between the core ions and the polar

molecules (Raes and Janssens, 1985, 1986; Yu and Turco, 2000; Lovejoy et al., 2004). The ions can be also formed by the cluster ionization by cosmic radiation. 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 (≳1 eV) via multiple inelastic collisions (Campbell and Brunger, 2016). At these low energies, they are rapidly captured by abundant molecules, in particular O_2. Recently, we have shown that the low-energy electrons can be also efficiently captured by hydrated acid clusters generating negative ions and induce a cascade of ion-molecule reactions (Lengyel et al., 2017a).

Ion-induced nucleation was invoked to explain the correlation between the global cloudiness and the cosmic rays intensity (Carslaw et al., 2002; Harrison, R. G., Carslaw, K. S., 2003). The temperature-dependent aerosol chamber measurements on the binary H_2SO_4-H_2O nucleation showed that the neutral particle formation is preferred at low temperatures, while ion-induced particle formation dominates at higher temperatures (Duplissy et al., 2016). A significant contribution of the ion-induced nucleation to the sulfuric acid aerosols was observed experimentally using a particle beam under atmospheric conditions (Enghoff et al., 2011). Field measurements indicate that the ions are strongly involved in the atmospheric nucleation events (Hirsikko et al., 2007; Hirsikko et al., 2011). However, the ion-induced nucleation alone could not explain the observed nucleation rates (Kirkby et al., 2011). Therefore, other compounds, such as bases (e.g., ammonia and amines) and organic acids, were proposed to contribute to the sulfuric acid aerosol formation (Zhang et al., 2004; Kirkby et al., 2011; Zhang et al., 2012; Almeida et al., 2013; Kürten et al., 2014; Schobesberger et al., 2015; Kürten et al., 2016).

The gas-phase reactions between thermalized electrons and H_2SO_4 molecules proceed rapidly yielding the bisulfate anion HSO_4^- (Adams et al., 1986). However, hydration dramatically change the nature of the electron driven processes (Lengyel et al., 2017a; Lengyel et al., 2017b) in particular via the strong influence of hydration on ion-pair formation. The surrounding water molecules can also stabilize anions, which are otherwise electronically unstable in the gas-phase (Pluhařová et al., 2012). Therefore the electron induced chemistry in sulfuric acid-water clusters is fundamental to our molecular-level understanding of the cluster ion formation and reactivity of aerosol particles.

Recently, a new method for microhydration of molecules has been developed in our laboratory (Kočišek et al., 2016). It enables the generation of the mixed clusters with water where the cluster composition can be relatively well controlled, e.g., clusters of single molecules solvated by one or a few water molecules could be prepared (Kočišek et al., 2016). By this method, we generate the mixed sulfuric acid-water clusters where the sulfuric acid microhydration is controlled. It ought to be mentioned, that it is difficult to control the particle hydration in aerosol experiments of the condensation chamber type, and often dehydrated sulfuric acid particles are obtained. Thus our experiments offer a unique opportunity to investigate the electron induced processes in the binary sulfuric acid-water systems.

We investigate the low-energy electron attachment to $(H_2SO_4)_m(H_2O)_n$ clusters in a crossed-beam experiment where the cluster beam in ultrahigh vacuum is crossed by an electron beam of well-defined adjustable low energies. The formed negative ions are monitored via a time-of-flight (TOF) mass spectrometry. In addition, the small neutral complexes $(H_2SO_4)_m(H_2O)_n$ are characterized by DFT calculations, and the energetics of the initial dissociation step is calculated.

2 Experimental and theoretical methods

The experiments were performed on the CLUster Beam (CLUB) apparatus in Prague (Kočišek et al., 2016; Lengyel et al., 2017a). The mixed $(H_2SO_4)_m(H_2O)_n$ clusters were generated in a home-build source via continuous supersonic expansion of the sulfuric acid/water vapor in helium buffer gas through a divergent conical nozzle (100 μm diameter, 2 mm long, and ~30° full opening angle) into the vacuum. The clustering conditions were controlled by heating the H_2SO_4 solution in reservoir and by the stagnation pressure of the buffer gas. Reservoir temperatures 180 °C and buffer gas pressures between 1 and 2 bar were employed. The nozzle was heated independently to a higher temperature (185-190°C) to avoid any condensation. To further increase the water content in the vapor, the humidification of the He buffer gas was performed using a commercially available Elemental Scientific Pergo gas humidifier, where the He-gas passes through a Nafion tube submerged in water reservoir kept at a constant temperature (25°C in the present experiments) and water permeates through the tube and humidifies the buffer gas (Kočišek et al., 2016).

The cluster beam was skimmed and passed through three differentially pumped chambers before entering the ion source of the perpendicularly mounted reflectron TOF mass spectrometer. The voltages on the extraction plates were set for the negative ion detection. The clusters were ionized in the extraction region of the spectrometer using pulsed electron gun at 8 kHz frequency with pulse duration of 2 μs. The electron energy was scanned from 0 to10 eV in 0.2 eV steps and the mass spectra were recorded at each step. The mass spectra presented here were integrated over the entire energy range, since there were no significant qualitative differences in the spectra measured at different electron energies. The extraction pulse to accelerate the negative ions was applied with 0.5 μs delay after the electron pulse to exclude effects of any free electrons in the ionization volume. The ions were detected on the Photonics MCP detector in the Chevron configuration. The electron-energy scale was calibrated using the 4.4 eV and 8.2 eV resonances in the O^- production from CO_2 molecule (Denifl et al., 2010). The energy spread of the electron beam was approximately 600 meV. Test measurements with SF_6 revealed that below 1.5 eV the electron current passing the ionization region quickly drops, and the current recorded on the Faraday cup does not reflect the actual current in the ionization region. This is caused by the construction of the electron gun which was optimized for operation at energies of several tens of electronvolts for positive ionization. The ion yields below the 1.5 eV can be biased when normalized on the electron current, and large error bars are expected at these low electron energies. The ion yield curves were therefore plotted just at energies above 1.5 eV.

Our experimental observations were supported with quantum chemistry calculations. The calculations were performed for the following clusters: $(H_2SO_4)_m(H_2O)_n$, m = 1-2, n = 0-5, $(H_2SO_4)_m(H_2O)_nHSO_4^-$, m = 0-1, n = 0-5 to describe the thermochemistry of the experimentally observed dissociative electron attachment process in which an H-atom left the cluster. We used previously observed energetic minima from literature as the initial structures (Zatula et al., 2011; Husar et al., 2012; Temelso et al., 2012a; Temelso et al., 2012b; Henschel et al., 2014) and equilibrated them in molecular dynamics runs to find the most stable isomers. Molecular dynamics was run on the BLYP/6-31+g* potential energy surface, nuclei were propagated according to classical equations of motion; the constant temperature of 298 K was maintained with Nosé-

Hoover thermostat. The total length of the simulations was 5 ps, with a time step of ~1 fs (i.e. 5000 steps). From the trajectory, several structures were taken and re-optimized at the M06-2X/aug-cc-pVDZ level of theory including zero-point-energy corrections (all structures represented local minima). Altogether 8 different isomers on average were optimized from various initial structures for each cluster type ($(H_2SO_4)_{1\text{-}2}(H_2O)_{0\text{-}5}$, $(H_2SO_4)_{0\text{-}1}(H_2O)_{0\text{-}5}HSO_4^-$) including the hydrogen-bonded, $H_2SO_4\cdots H_2O$, and ion-pair, $HSO_4^-\cdots H_3O^+$, structures in neutral clusters. Only the most stable isomers were considered for further calculations. We chose the M06-2X functional because of its performance for related systems (Walker et al., 2013; Lengyel et al., 2017a). Localized structures, including hydrogen-bonded, $H_2SO_4\cdots H_2O$, and ion-pair, $HSO_4^-\cdots H_3O^+$, structures, are in excellent agreement with literature (Re et al., 1999; Henschel et al., 2014). All calculations were performed with the Gaussian 09 software package (Frisch et al., 2013), ABIN code was used for molecular dynamics (Hollas et al., 2015).

3 Results and discussion

To investigate the formation of mixed sulfuric acid/water clusters, different concentrations of water and sulfuric acid were exploited in the expansions. Fig. 1 shows the negative ion mass spectra for three different water concentrations. Essentially, the same cluster ions of the types $(H_2SO_4)_m(H_2O)_nHSO_4^-$ and $(H_2O)_nH_2SO_4^-$ could be identified in all three mass spectra (and in other spectra recorded under different expansion conditions, not shown here). However, their relative intensities vary significantly, reflecting the changes in the neutral cluster composition with water concentration in the expansions. At low water concentrations (molar fraction, $x_{H_2O} \leq 1.5\times10^{-3}$; Fig. 1a), the mass spectrum is dominated by anhydrous $(H_2SO_4)_mHSO_4^-$ (m = 0-7) series. The hydrated analogues $(H_2SO_4)_m(H_2O)_nHSO_4^-$ are less populated and observed only up to m = 3. Apart from these series, there is the minor series $(H_2O)_nH_2SO_4^-$. It ought to be mentioned that an uptake of H_2SO_4 molecule by H_2SO_4/H_2O clusters is energetically more efficient than an addition of H_2O molecules (Table 1). The efficient sticking results from H_2SO_4 forming multiple hydrogen bonds in mixed clusters, as revealed by vibrational spectroscopy (Yacovitch et al., 2013). Upon hydration, the free energy of the addition of a single sulfuric acid molecule to the hydrated cluster is gradually increasing (1), while the free energy for the addition of a single water molecule is essentially decreasing (2). Probably saturation of sulfuric acid by the surrounding water molecules causes this trend. Nevertheless, the negative values of the free energies still favor the nucleation. Our calculated values are in a good agreement with previously published data (Kurtén et al., 2007; Loukonen et al., 2010; Henschel et al., 2014), which is shown in Table S2.

$$H_2SO_4(H_2O)_n + H_2SO_4 \rightarrow (H_2SO_4)_2(H_2O)_n, \quad (1)$$

$$H_2SO_4(H_2O)_n + H_2O \rightarrow H_2SO_4(H_2O)_{n+1}. \quad (2)$$

Table 1: Free energies (in kJ mol^{-1}, at T=298K and p^0=1atm) of binary nucleation of H_2SO_4 (1) and H_2O (2) to small $H_2SO_4(H_2O)_n$ clusters calculated at the M06-2X/aug-cc-pVDZ level of theory.

	H_2O	H_2SO_4
H_2SO_4	–11.2	–26.3
$H_2SO_4(H_2O)$	–7.2	–31.4
$H_2SO_4(H_2O)_2$	–3.4	–32.6
$H_2SO_4(H_2O)_3$	–9.7	–45.8
$H_2SO_4(H_2O)_4$	–4.8	–38.3

With increasing water vapor pressure (Fig. 1b, $x_{H_2O} = 2.5\times10^{-3}$), the larger clusters with $m > 3$ from the $(H_2SO_4)_mHSO_4^-$ series disappear and the mass spectrum contains $(H_2SO_4)_m(H_2O)_nHSO_4^-$ ions with m = 0-3 and n = 0-4. The series $(H_2O)_nH_2SO_4^-$ increased in relative intensity compared to the spectrum in Fig. 1a. Further, the water vapor concentration was increased to $x_{H_2O} = 2.0\times10^{-2}$ by the helium buffer gas humidification. The mass spectrum corresponding to this increase of water content by almost an order of magnitude is shown in Fig. 1c. It is dominated by the hydrated $(H_2SO_4)_m(H_2O)_nHSO_4^-$ (m = 0-3, n =0-8) cluster ions. Qualitatively, all the spectra exhibit essentially the same major series, which differ only by their relative intensities. Therefore we will analyze the last spectrum containing the most of the mixed water-sulfuric acid species.

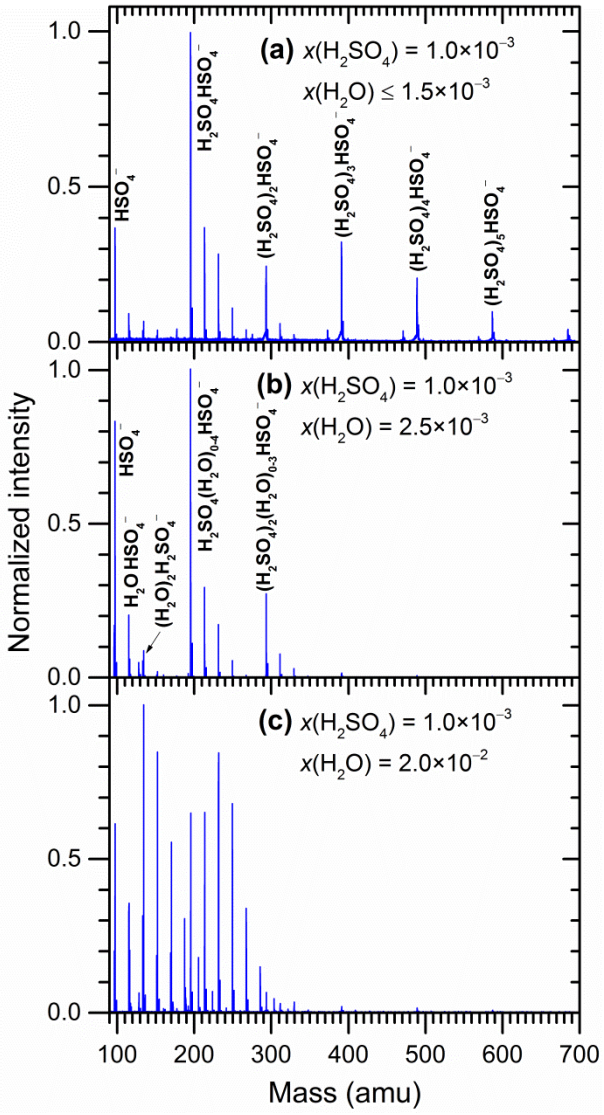

Figure 1: Negative ion mass spectra integrated in the electron energy range 0-10 eV. Panels (a)-(c) show a decreasing H_2O mole fraction in the vapor coexpanding with constant H_2SO_4 mole fraction in helium. See Figure 2 for analysis of the spectrum (c).

Fig. 2 shows an analysis of the mass spectrum in Fig. 1c). There are three pronounced cluster ion series: $(H_2O)_nH_2SO_4^-$ (n = 0-6), $(H_2O)_nHSO_4^-$ (n =0-8) and $H_2SO_4(H_2O)_nHSO_4^-$ (n =0-8). In addition, there are also weak $(H_2SO_4)_m(H_2O)_nHSO_4^-$ series with m = 2 and 3 discernible in the mass spectrum (the m = 2 series is indicated in Fig. 2). It is important to realize that the mass spectra reflect fingerprints of two different processes separated in space and time: (*i*) the neutral cluster generation in the supersonic expansion in the nozzle, and (*ii*) the cluster ionization via electron attachment in the mass spectrometer ionization region. Keeping this in mind, we can start analysing the mass spectra in Fig. 2.

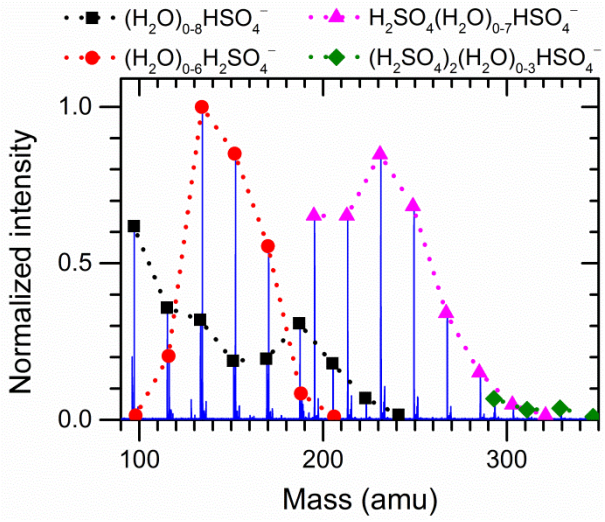

Figure 2: Negative ion mass spectrum of humidified He/H_2SO_4 (x=1.0×10^{-3})/H_2O (x=2.0×10^{-2}) gas mixture.

First, we consider the major $(H_2O)_nH_2SO_4^-$ series. The electron attachment to the pure water clusters is inefficient (Knapp et al., 1987; Lengyel et al., 2017a) thus we can see only the electron attachment to the mixed clusters. The ionization of an isolated sulfuric acid (Adams et al., 1986) proceeds via dissociative electron attachment (DEA):

$$H_2SO_4 + e^- \rightarrow HSO_4^- + H, \quad (3)$$

yielding the relatively strong HSO_4^- ion peak and the $(H_2O)_nHSO_4^-$ series. Nevertheless, we observe also the $(H_2O)_nH_2SO_4^-$ series with the covalently-bonded sulfuric acid molecule. This can be due to the H-atom caging by the water molecules after the DEA process (3), which has been described in our recent paper (Kočišek et al., 2016). In the present case of the DEA process (3) in the cluster, the departing H-atom meets the H_2O molecule and bounces back to remain within the $(H_2O)_nH_2SO_4^-$ complex:

$$H_2SO_4(H_2O)_n + e^- \rightarrow [(H_2O)_nH\cdots HSO_4^-] \rightarrow (H_2O)_nH_2SO_4^-. \quad (4)$$

The calculated structures of $H_2SO_4(H_2O)_n$ clusters, Fig. 3, suggest that from n = 2 both acid hydrogens are shielded by the H_2O molecules from the direct departure after the DEA process, while in case n = 1 one hydrogen points to the water molecule and the other one can freely leave the cluster. Therefore the intensity of $(H_2O)_nH_2SO_4^-$ series increases steeply from n = 1 to 2. The decrease of intensity for $n \geq 3$ is probably due to the neutral $H_2SO_4(H_2O)_n$ cluster size distribution which has an exponentially decreasing character with n, typical for small clusters in general (Lengyel et al., 2012; Lengyel et al., 2014). The caging might be also accompanied by subsequent evaporation of water molecule(s). Such evaporative process could contribute to the mass peak at m/z = 98 generating $H_2SO_4^-$ ion. However, the negligibly small intensity of this peak (less than 3% of the peak at m/z = 97) suggests insignificant contribution of the evaporative processes.

The DEA (3) can lead also to the processes where the H-atom leaves the clusters yielding the $(H_2O)_nHSO_4^-$ series. This series exhibits interesting dependence on n with a secondary maximum at n = 5. We assign this maximum to the ion-pair generation in the neutral clusters. According to the theoretical calculations, the molecular structures of sulfuric acid in

the clusters for $n \leq 4$ either correspond to the global energy minima or are energetically very close to the ion-pair structures (Re et al., 1999). Thus, for the small clusters with covalently bound H_2SO_4 molecule, we assume the DEA process with hydrogen departure from the clusters:

$$H_2SO_4(H_2O)_n + e^- \rightarrow [(H_2O)_nH\cdots HSO_4^-] \rightarrow (H_2O)_nHSO_4^- + H, \quad (5)$$

The intensities of the corresponding $(H_2O)_nHSO_4^-$ mass peaks then reflect the neutral $H_2SO_4(H_2O)_n$ cluster size distribution, decreasing with the size as outlined above. However, upon hydration with sufficient number of water molecules, the HSO_3O–H becomes polarized and heterolytic dissociation occurs yielding the ion-pair $H_3O^+(H_2O)_{n-1}HSO_4^-$ structure. The global minimum for ion-pair structure was reported for $H_2SO_4(H_2O)_n$ clusters with $n \geq 5$ (Re et al., 1999). The electron attachment to these clusters with ion-pair has different character for two reasons. First, the incoming free electron can interact with the H_3O^+ moiety or with the dipole of the ion-pair structure of the cluster increasing the electron attachment cross section (Fabrikant et al., 2017). Second, the attached electron will most likely recombine with the H_3O^+ in the cluster generating H_2O and H atom. The H-atom can subsequently depart from the cluster, carrying away the excess recombination energy, leaving behind the $(H_2O)_nHSO_4^-$ ion:

$$H_3O^+(H_2O)_{n-1}HSO_4^- + e^- \rightarrow (H_2O)_nHSO_4^- + H. \quad (6)$$

Photodissociation studies of mixed water-hydrogen halide clusters with similar ion-pair structures demonstrated that the dissociating H-atom exits from the clusters efficiently (Poterya et al., 2007; Ončák et al., 2011; Poterya et al., 2014). Therefore it is plausible to assume, that in the present case the H-atom leaves the cluster after the recombination, and carries away the excess energy without any need for further water evaporation from the cluster. Thus the increase of the electron attachment cross section at $n = 5$ due to the ion-pair structure of the clusters leads to the increase of the ion intensity for $(H_2O)_5HSO_4^-$. The further intensity decrease for $n > 5$ is again due to the decreasing neutral cluster size distribution.

Finally, there is the $H_2SO_4(H_2O)_nHSO_4^-$ series with the intensity maximum at $n = 2$. This is again consistent with the ionic dissociation of the acid in the clusters. Shields and co-workers (Temelso et al., 2012b) observed the ion-pair formation for clusters containing two sulfuric acid molecules, in which one sulfuric acid molecule is ionically dissociated already in the presence of two water molecules. Thus the maximum at $H_2SO_4(H_2O)_2HSO_4^-$ is in agreement with the ion-pair structure of the neutral $(H_2SO_4)_2(H_2O)_2$ precursor (i.e. $H_3O^+(H_2SO_4)(H_2O)HSO_4^-$) and with the model outlined above, Eq. (6).

Thus the observed intensity maxima for $(H_2O)_nHSO_4^-$ and $H_2SO_4(H_2O)_nHSO_4^-$ cluster series can be induced by the chemical reactions in the corresponding neutral clusters. The agreement with theoretical predictions (Re et al., 1999; Temelso et al., 2012a; Temelso et al., 2012b) suggests that the acidic dissociation occurs. To our best knowledge, the H_2SO_4 dissociation has not been studied in the mixed water-sulfuric acid clusters experimentally, yet. Therefore our study represents the first experimental observation which confirms the theoretical calculations of how many water molecules are necessary to induce the ionic dissociation of H_2SO_4 molecules.

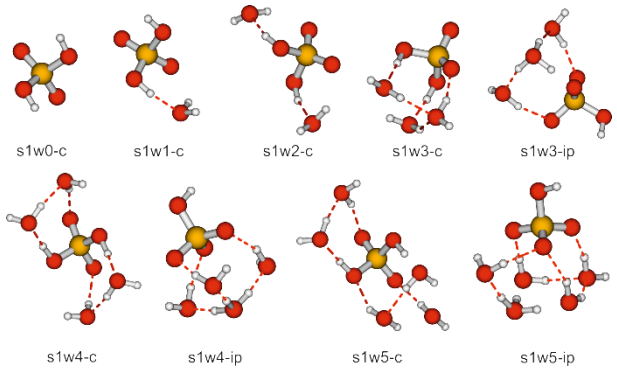

Figure 3: The observed most stable energy isomers of $H_2SO_4(H_2O)_n$ (n= 0-5) clusters with both hydrogen-bonded, $H_2SO_4\cdots H_2O$, (c) and ion-pair, $HSO_4^-\cdots H_3O^+$, (ip) structures optimized at the M06-2X/aug-cc-pVDZ level of theory.

Since the mass spectra were measured at different electron energies between up to 10 eV in 0.2 eV steps, the ion-yield curves could be constructed for all the mass peaks in the spectra. However, they were essentially the same for all the ions as exemplified by a few ion yield curves in Fig. 4. The negative ion formation is observed at low electron energies up to 3 eV, which is independent of the composition and degree of hydration of all measured ions. As outlined in the experimental section, we could not determine the position of the ion yield maximum exactly due to the larger error bars on our measurements at the energies below approximately 1.5 eV. Nevertheless, the important point for atmospheric chemistry is that only the secondary electrons with low energy below 3 eV can be directly attached to the mixed sulfuric acid-water clusters. There are no resonant contributions at the higher energies above 3 eV.

The present attachment of low-energy electrons to hydrated sulfuric acid clusters can be compared to other atmospherically abundant particles, namely the nitric acid hydrates. Those also exhibited a relatively high cross section for electron attachment at low energies measured in range of 0-10 eV. The DEA to HNO_3/H_2O clusters induced three different dissociation channels, namely NO_3^-, NO_2^-, and OH^- formation. The opening and closing of these reaction channels were specific to cluster size, composition, and degree of hydration (Lengyel et al., 2017a). In contrast to HNO_3, the dissociation of hydrated H_2SO_4 clusters leads exclusively to HSO_4^- formation. However, some similarity in the electron attachment can be found between these two cases, namely the $H_3O^+ + e^-$ recombination reaction of ion-pair and the caging of the dissociating molecules by the surrounding cluster environment. As already mentioned, the ion-pair formation efficiently increases the cross section for electron attachment and the electron attachment cross sections are very sensitive to the electron energies (Fabrikant et al., 2017; Lengyel et al., 2017a). Therefore, even if there are only few electrons available for the electron attachment reactions with the cluster particles in atmosphere, the interaction can be very efficiently enhanced by the high cross section, and these reactions may actually contribute to the total budget of the atmospheric HSO_4^-.

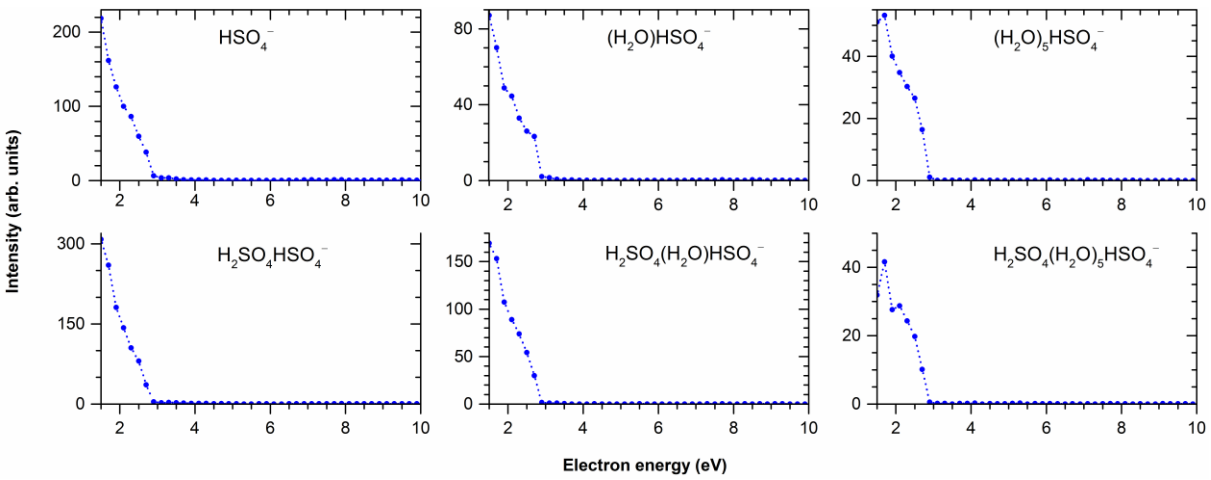

Figure 4: Ion-yield curves for ionic fragments of $(H_2O)_nHSO_4^-$ and $H_2SO_4(H_2O)_nHSO_4^-$ with different degree of hydration.

To support the experimental observation, the energetics for the reactions (5) and (6) was evaluated at the M06-2X/aug-cc-pVDZ level and both hydrogen-bonded, $H_2SO_4\cdots H_2O$, and ion-pair, $HSO_4^-\cdots H_3O^+$, structures were considered in our calculations. Note that the breaking of a specific bond upon the electron attachment primarily depends on the direction of the gradient of the anion potential energy hypersurface at the initial structure, and does not necessarily depend on the asymptotic energetics (Fabrikant et al., 2017). However, the overall thermochemistry gives an overview of how much energy could be released upon the reaction. Our calculations in Fig. 5 show that even the reaction of bare H_2SO_4 with free electron yielding bisulfate anion (blue dots) releases the energy of about 8.6 kJ mol^{-1}. Upon the hydration of H_2SO_4, the energy release gradually increases with the number of water molecules due to the interaction of HSO_4^- with water. Similar behavior was found in the low-energy electron collision with the nitric acid hydrates (Lengyel et al., 2017a). Thus our calculations clearly show that the reactions (5) and (6) above can be driven energetically in the clusters.

Sulfuric acid dimer forms $H_2SO_4HSO_4^-$ upon the electron attachment quite efficiently with the energy release of 132.2 kJ mol^{-1} (green dots) due to the higher binding energy of $H_2SO_4HSO_4^-$ compared to $(H_2SO_4)_2$ dimer. With an increasing degree of hydration the energy release somewhat decreases, yet the reaction retains its exothermic character. Thus the reactions (5) and (6) in the clusters with more than one sulfuric acid can also be driven energetically.

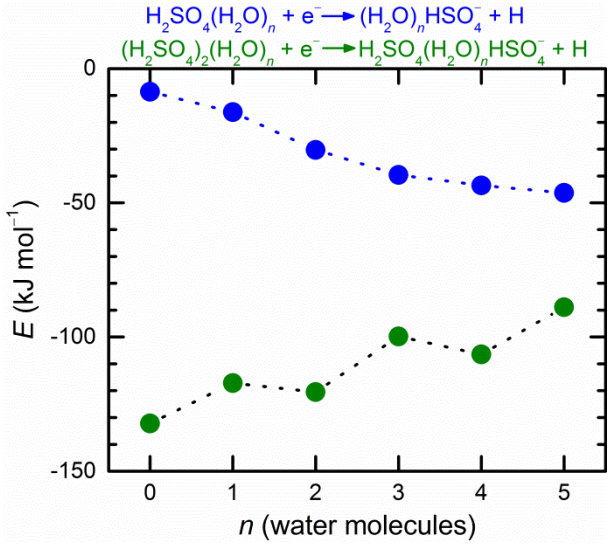

Figure 5: Reaction energies for the HSO_4^- dissociation channels after electron attachment to H_2SO_4/H_2O clusters optimized at the M06-2X/aug-cc-pVDZ level of theory.

4 Conclusion

We have investigated mixed sulfuric acid-water clusters in a molecular beam experiment where the cluster beam was crossed with an electron beam at different energies and electron attachment to the clusters was probed with the mass spectrometry of the negatively charged cluster ions. By the precise control of the sulfuric acid reservoir temperature and the buffer gas humidification we were able to produce the mixed clusters with *different water content*. In all the spectra the main cluster ion series appear: $(H_2SO_4)_m(H_2O)_nHSO_4^-$ and $(H_2O)_nH_2SO_4^-$. Their relative intensities depend on the degree of humidification

By the analysis of these series as a function of the number of surrounding water molecules, we have obtained experimental evidence for sulfuric acid ionic dissociation to form the ion-pairs in the clusters. This occurs in neutral $H_2SO_4(H_2O)_n$ clusters with $n \geq 5$ water molecules, in excellent agreement with the theoretical predictions. Similarly, in the clusters with two sulfuric acid molecules $(H_2SO_4)_2(H_2O)_n$ this process seems to start already with $n \geq 2$ water molecules again in agreement with theory. We introduce the first experimental measurements of the sulfuric acid ionic dissociation in dependence on the controlled stepwise microhydration in the mixed clusters. In relevance to the atmospheric processes the acidic dissociation in small clusters will lead to the increase of the probability that the cluster will capture further molecules from the ambient air. The presence of charge in the cluster containing the ion-pair can increase the interaction between the cluster and the polar (or polarizable) molecules.

Our theoretical investigations of the structure and energetics support the experimental results in several ways: The ion-pair structures are obtained as the energy minima at the degrees of hydration which correspond to the experimental observations. These structures exhibit solvent-separated ion-pairs with the H_3O^+ moiety at the cluster exterior. This gives an opportunity for the H-atom to leave the cluster after the electron attachment to these clusters and subsequent $e^- + H_3O^+$

recombination, yielding the experimentally observed clusters with bisulfate anions HSO_4^-. For the small $H_2SO_4(H_2O)_n$ clusters with the covalently bound sulfuric acid, the calculated structures suggest the possibility of an efficient H-atom *caging* after the dissociative electron attachment, which is demonstrated experimentally by the presence of $(H_2O)_nH_2SO_4^-$ cluster ions. The calculations also provide support for the proposed reactions (5) and (6) which can be driven energetically in the clusters.

Finally, the energy dependencies of the measured mass peaks exhibit an efficient electron attachment at low electron energies below 3 eV, and there are no resonances above 3 eV. Therefore in the atmospheric chemistry only the low-energy electrons below 3 eV can be efficiently captured by sulfuric acid-water aerosols and converted into the negatively charged ions. It is also interesting to note, that the electron attachment efficiencies qualitatively exhibit the same energy dependencies for all the species independently of the degree of hydration (at least for electron energies above 1.5 eV).

Data availability. All of the presented data are available from the corresponding authors upon request.

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Supplement of

Electron-induced chemistry in microhydrated sulfuric acid clusters

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S1 Experimental setup

The experiments were performed on a versatile and unique experimental apparatus CLUB (cluster beam apparatus) which allows a variety of different experiments with a molecular beam of isolated clusters in vacuum. The apparatus and experiments have been described in numerous publications previously (e.g., mass spectrometry: (Lengyel et al., 2012; Kočišek et al., 2013a; Kočišek et al., 2013b); electron attachment: (Kočišek et al., 2016a; Kočišek et al., 2016b; Lengyel et al., 2016); etc.) and the details can be found in these references. The sketch of the CLUB apparatus is shown in Fig. S1 below. In the present work, the clusters were produced in the first vacuum chamber by supersonic expansion of the sulfuric acid vapor with buffer gas He, i.e. a mixture of H_2SO_4, H_2O and He gas phase molecules. The present mass spectrometry was performed in the 4th vacuum chamber TOFMS, where the cluster beam was crossed by a low-energy electron beam. Further details are given in the experimental section of the present paper. The other options and features of the CLUB apparatus shown in Fig. S1 were not exploited in the present experiments.

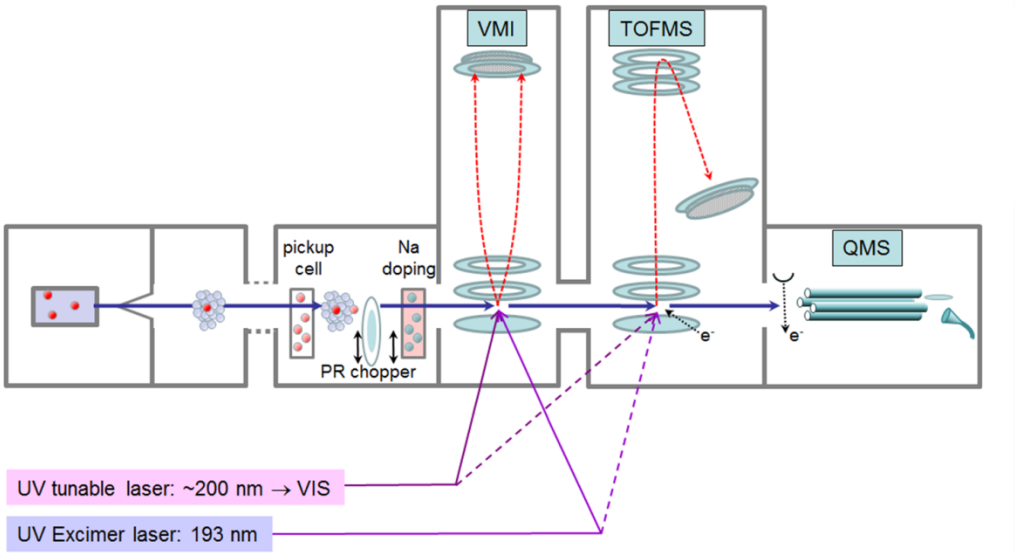

Figure S1: Schematic overview of the CLUB apparatus: VMI –velocity map imaging for photodissociation of molecules in clusters; TOFMS –reflectron time-of-flight mass spectrometer with various ionization methods, e.g., electron ionization, electron attachment, photoionization; QMS –quadrupole mass spectrometer with electron ionization.

S2 Dipole moment of $H_2SO_4(H_2O)_5$ clusters

Our M06-2X/aug-cc-pVDZ calculations exhibit only a small change in the cluster dipole moment upon the acidic dissociation of the sulfuric acid molecule on water cluster and could be overlapped by dynamic effects. The calculated dipole moments summarized in Figure S2 were in very broad range from ~0.3 D to ~4.6 D for $H_2SO_4(H_2O)_5$ clusters which depend rather on the cluster structure than on the acidic dissociation. Most likely, not only the energy minimum structure (see Figure S2 (a) for ion-pair and (e) for covalently-bonded H_2SO_4) but many different cluster structures are generated in the supersonic expansion.

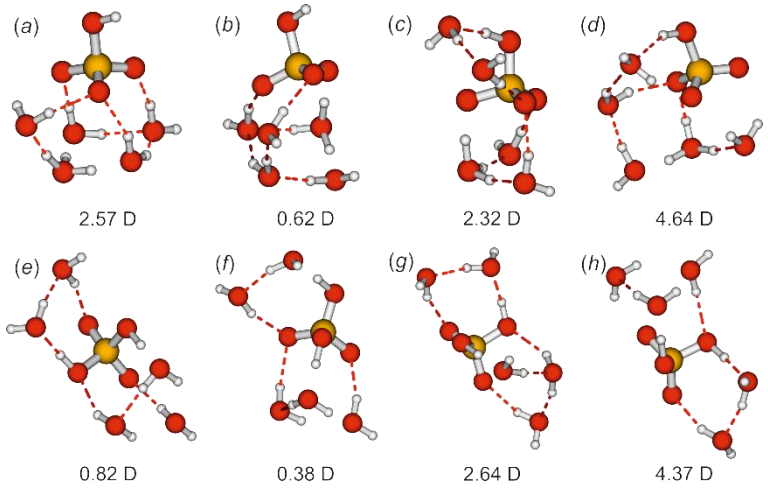

Figure S2: Selected local minima of neutral, $H_2SO_4\cdots H_2O$, (a-d) and ion-pair, $HSO_4^-\cdots H_3O^+$, (e-h) structures in $H_2SO_4(H_2O)_5$ clusters and the corresponding dipole moments calculated at the M06-2X/aug-cc-pVDZ level of theory.

S3 Thermochemistry

Table S1: Reaction energies (in kJ mol^{-1}) for the HSO_4^- dissociation channels after electron attachment to H_2SO_4/H_2O clusters optimized at the M06-2X/aug-cc-pVDZ level of theory.

N	$H_2SO_4(H_2O)_N$	$(H_2SO_4)_2(H_2O)_N$
0	–8.6	–132.2
1	–16.2	–117.2
2	–30.3	–120.5
3	–39.6	–99.8
4	–43.5	–106.5
5	–46.3	–88.9

Table S2: Free energies (in kJ mol^{-1}, at T=298K and p^0=1atm) of binary nucleation of H_2O/H_2SO_4 clusters

$H_2SO_4(H_2O)_{n-1} + H_2O \rightarrow H_2SO_4(H_2O)_n$ $\Delta_rG^0(1)$

$H_2SO_4 + nH_2O \rightarrow H_2SO_4(H_2O)_n$ $\Delta_rG^0(2)$

n =	$\Delta_rG^0(1)$ our results	$\Delta_rG^0(1)$ (Kurtén et al., 2007)	$\Delta_rG^0(2)$ our results	$\Delta_rG^0(2)$ (Henschel et al., 2014)	$\Delta_rG^0(2)$ (Loukonen et al., 2010)
1	–11.3	–11.76	–11.3	–10.88	–12.26
2	–7.1	–7.82	–18.4	–18.41	–26.19
3	–3.3	–9.92	–21.8	–24.39	–29.75
4	–9.6	–3.77	–31.4	–29.50	–33.93
5	–5.0	–	–36.4	–28.49	–41.88

S4 Ion-yield curves for selected ionic fragments

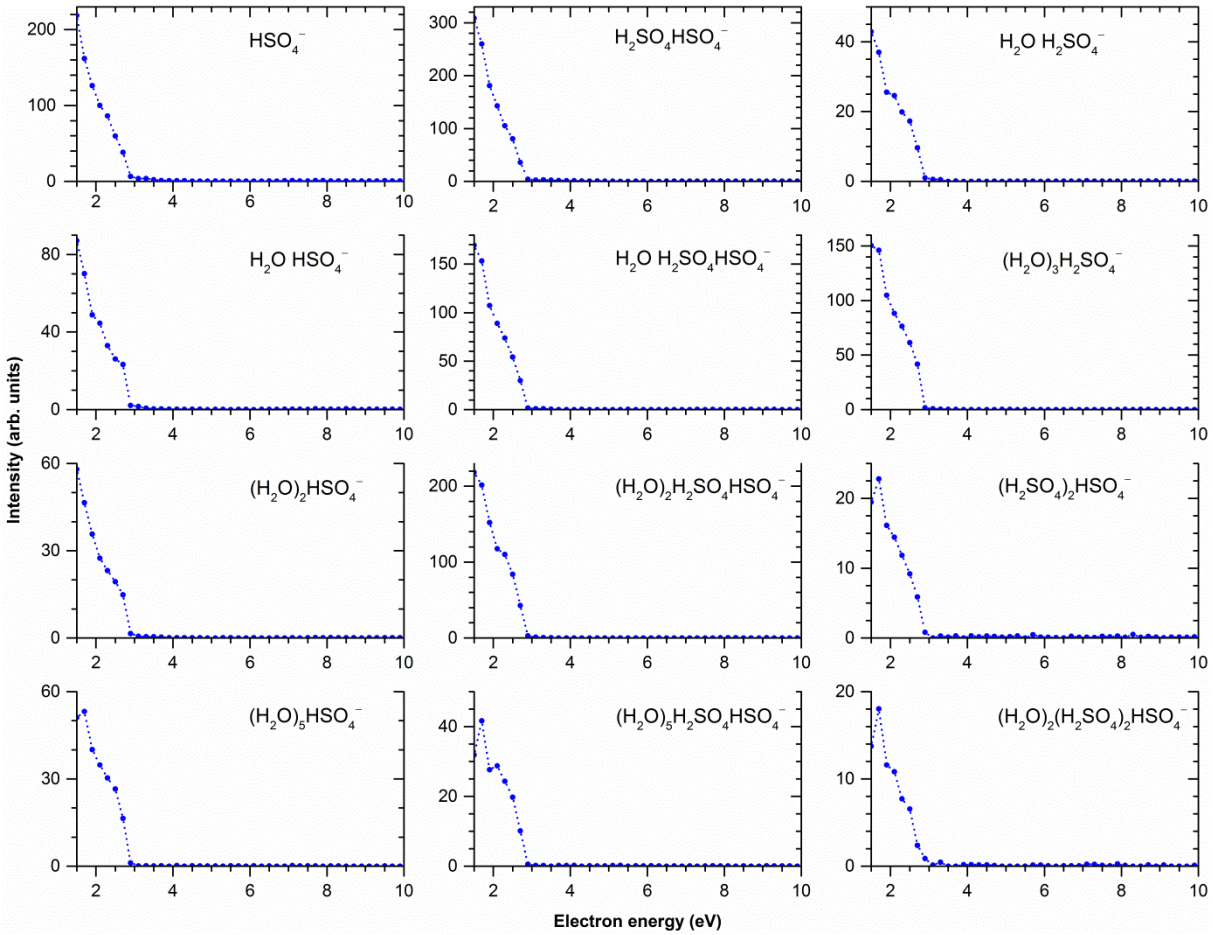

Figure S3: Ion-yield curves for selected ionic fragments with different degree of hydration.

S5 Benchmarking the electronic structure calculations

Table 1 summarizes the benchmark calculations of electron affinity of HSO_4, ionization potential of H_2SO_4, and reaction enthalpies for deprotonation of gas-phase H_2SO_4 calculated at different levels of theory. The M06-2X/aug-cc-pVDZ energies are comparable with the CCSD/aug-cc-pVDZ values with the exception of the IP(H_2SO_4). The comparison of double-zeta with triple-zeta basis sets of the M06-2X functional shows that there is essentially constant shift from the experimental values and therefore we do not expect any significant shift in reaction energies even upon hydration. The calculated reaction enthalpies for deprotonation of gas-phase H_2SO_4 are in good agreement with the experimental value. The error of the DFT method is 0.1-0.2 eV. Please note that, in the present work, chemical trends with respect to hydration are of the main concern, and a possible systematic shift of few tenths of eV does not influence our conclusions.

Table S3: Electron affinity of HSO_4, ionization potential of H_2SO_4, and enthalpy of deprotonation at various levels of theory (all in kJ mol^{-1}). DZ and TZ represent aug-cc-pVDZ and aug-cc-pVTZ, respectively. Enthalpies were calculated at 298.15 K within the harmonic approximation.

	B3LYP/DZ	M06-2X/DZ	M06-2X/TZ	MP2/DZ	CCSD/DZ	Experiment
EA(HSO_4)	453	474	483	503	478	458±10 (Wang et al., 2000)
IP(H_2SO_4)	1103	1117	1137	1195	1209	1196±5 (Snow and Thomas, 1990)
ΔH($H_2SO_4 \rightarrow H^+ + HSO_4^-$)	1318	1304	1300	1294	1309	1295±23 (Wang et al., 2000)

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Structures optimized at the M06-2X/aug-cc-pVDZ level of theory (coordinates in Å)

H2SO4,

S	0.000064	-0.000011	0.150574
O	-0.008803	1.287414	0.823392
O	0.008537	-1.287472	0.823344
O	-1.253357	-0.047337	-0.873079
O	1.253426	0.047310	-0.873222
H	-1.477412	0.867560	-1.107276
H	1.477544	-0.867564	-1.107433

H2SO4.H2O,

S	-0.002092	0.478526	0.019730
O	-1.122963	1.157172	-0.631673
O	1.114572	1.190582	0.618755
O	-0.562309	-0.538977	1.107359
O	0.584738	-0.519520	-1.120247
H	-1.483379	-0.811275	0.821010
H	1.486119	-0.765134	-0.858585
O	-2.970064	-0.852470	0.101511
H	-3.213990	-1.565378	-0.497780
H	-2.837433	-0.066926	-0.451981

H2SO4.2H2O,

S	0.000000	0.467392	0.000000
O	-1.127912	1.182899	-0.598603
O	1.127912	1.182899	0.598603
O	-0.544571	-0.525972	1.126354
O	0.544571	-0.525972	-1.126354
H	-1.457398	-0.819564	0.845467
H	1.457398	-0.819564	-0.845467
O	-2.952264	-0.863317	0.087315
H	-3.167318	-1.556293	-0.545456
H	-2.804014	-0.059401	-0.435852
O	2.952264	-0.863317	-0.087315
H	3.167318	-1.556293	0.545456
H	2.804014	-0.059401	0.435852

H2SO4.3H2O,

O	1.534809	1.462137	-1.001570
H	1.781577	0.721103	-1.570209
H	2.010710	1.291324	-0.171101
S	-1.254013	-0.027940	0.145515
O	-2.676737	-0.212944	0.334029
O	-1.037139	1.389948	-0.533069
O	-0.755988	-1.052734	-0.979924
O	-0.331366	-0.161830	1.295309
H	-0.055388	1.501559	-0.728110
H	0.213448	-1.230135	-0.856840
O	1.907043	-1.412438	-0.785868
H	2.255817	-1.097554	0.069469
H	2.246433	-2.302996	-0.917273
O	2.326583	0.197862	1.379342
H	2.786076	0.330487	2.212974
H	1.369934	0.132151	1.580426

H2SO4.4H2O,

O	0.369118	1.579893	-0.259299
H	1.202090	1.605634	0.346984
S	0.347838	0.202507	-1.049951
O	1.673499	-0.093974	-1.603650
O	0.109356	-0.873963	0.093257
H	-0.835252	-0.743440	0.484336
O	-0.815844	0.274657	-1.940218
O	3.128602	-1.008646	0.656279
H	2.514904	-1.630884	1.062595
H	2.800389	-0.920750	-0.255144
O	-2.695346	1.776866	-0.432679
H	-2.179271	1.430809	-1.181062
H	-2.166168	2.514883	-0.109840
O	2.413802	1.506984	1.243770
H	2.769558	0.589206	1.141609
H	3.139971	2.102662	1.033068
O	-2.207302	-0.418736	1.025772
H	-2.499986	0.413818	0.577955
H	-2.891058	-1.073226	0.850620

H2SO4.5H2O,

O	2.530094	-0.488264	0.456179
O	2.766862	1.149864	-1.439462
O	1.747942	-2.556670	-1.273177
O	-0.058200	0.544141	0.545237
S	-0.833135	-0.036079	-0.582157
O	-0.673560	0.720459	-1.870133
O	-0.672560	-1.504548	-0.771780
O	-2.372431	0.198128	-0.113351
O	0.908546	2.840738	-0.960190
H	1.624235	-0.272759	0.750816
H	2.451809	-1.361197	0.030348
H	1.818091	-3.515374	-1.300637
H	0.205597	2.354613	-1.433529
H	0.670757	2.675538	-0.036384
H	0.813063	-2.344304	-1.056790
H	-2.948688	-0.173522	-0.798367
H	2.094086	1.898372	-1.246379
H	2.755855	0.515316	-0.617185
H	2.352817	0.566049	-2.187776
H	1.724621	-1.281620	-2.713774
O	1.610395	-0.384716	-3.074888
H	0.679306	-0.153067	-2.895336

2H2SO4,

S	1.745825	0.029839	-0.059980
O	3.329326	0.099758	-0.237040
O	1.225540	1.341119	-0.440342
O	1.681857	-0.172605	1.515730
O	1.235030	-1.168892	-0.740880
H	3.685237	-0.804701	-0.247897
H	0.719563	-0.220633	1.736599
S	-1.924079	-0.019868	0.098364
O	-1.563209	-1.143575	-0.981219
O	-3.351604	-0.059240	0.306312
O	-1.584903	1.348763	-0.655891
O	-0.981346	-0.160287	1.227890
H	-0.592141	-1.293207	-0.969850
H	-0.616274	1.506078	-0.611788

2H2SO4.1H2O,

S	-1.353553	-0.511414	-0.087013
O	-1.227393	-0.561068	1.499813
O	-1.128619	0.883270	-0.538941
O	-2.864381	-0.884391	-0.260993
O	-0.530691	-1.558253	-0.696590
H	-0.279978	-0.347271	1.693110
H	-3.405755	-0.031417	-0.155546
S	2.251621	0.254920	0.108457
O	2.223385	-1.111167	-0.718891
O	1.345124	0.113600	1.267819
O	1.594297	1.312963	-0.894274
O	3.636755	0.618520	0.292603
H	1.294006	-1.430291	-0.763406
H	0.613364	1.264162	-0.813656
O	-3.918220	1.453703	-0.075381
H	-3.105060	1.963084	-0.204107
H	-4.331662	1.791292	0.726718

2H2SO4.2H2O,

S	1.133014	-0.781556	-0.436442
O	1.107072	-0.548213	1.139465
O	2.498648	-1.195467	-0.751781
O	0.831395	0.660660	-1.022179
O	0.001521	-1.622536	-0.845083
H	0.188558	-0.231213	1.368849
H	1.648914	1.315414	-0.812327
S	-2.450541	0.296644	0.340762
O	-1.979223	1.026965	-1.004861
O	-1.338323	0.400646	1.313497
O	-2.605880	-1.226151	-0.102257
O	-3.764970	0.783930	0.683121
H	-1.000647	0.985115	-1.071389
H	-1.718447	-1.558502	-0.372102
O	4.165046	0.366943	0.940214
H	3.793831	-0.421900	0.511638
H	3.970992	0.264946	1.878140
O	2.749942	2.106272	-0.451276
H	3.281491	2.434290	-1.184733
H	3.352697	1.559276	0.121564

2H2SO4.3H2O,

S	1.911406	0.302172	1.004299
O	2.002457	-0.519031	-0.354128
O	3.251986	0.516643	1.497074
O	1.163196	-0.684751	2.002934
O	1.013037	1.465973	0.766709
H	1.082924	-0.652053	-0.723374
H	0.231275	-0.829764	1.678738
S	-1.640653	-0.938902	-0.382259
O	-0.465014	-0.686075	-1.281778
O	-2.024913	-2.497877	-0.553992
O	-2.837837	-0.154923	-0.791105
O	-1.312562	-0.843515	1.068651
H	-2.305329	-2.646579	-1.470978
O	-2.325283	2.390213	-0.373368
H	-2.018102	2.289516	0.620738
H	-1.448985	2.403053	-0.944100
H	-2.714090	1.496154	-0.584884
O	-0.187319	2.160939	-1.662509
H	0.493477	2.109950	-0.966892
H	-0.257542	1.239238	-1.962555
O	-1.484569	1.913077	1.941515
H	-1.722947	0.978659	2.051025
H	-0.517672	1.880340	1.817961

2H2SO4.4H2O,

S	1.784275	0.547719	-0.487643
O	0.376649	1.048498	-0.879104
O	-0.981482	-1.044910	-1.422991
H	-0.520105	-0.142336	-1.325710
O	2.488009	-0.033265	-1.644329
O	1.504115	-0.718557	0.461352
O	1.067604	-2.379082	-2.044191
H	-0.208564	-1.691632	-1.666255
O	-0.628815	2.820358	0.642983
H	-1.347252	2.233968	1.056338
S	-1.585857	-0.132154	1.888293
O	-0.168479	0.160378	2.261477
O	-1.715621	-1.338022	1.009703
O	-2.321114	1.068096	1.404662
H	0.921306	-0.429200	1.224166
O	2.489556	1.589776	0.284729
H	1.374637	-2.963366	-1.340778
H	1.718500	-1.643959	-2.049245
H	-1.320159	-1.237200	-0.482771
H	-0.185312	2.196170	-0.033581
H	0.100541	3.046060	1.335600
O	-2.369059	-0.507824	3.251984
H	-2.013358	-1.347082	3.583243
H	1.775657	4.057102	2.168376
O	1.340476	3.198028	2.166567
H	1.931806	2.593921	1.671787

2H2SO4.5H2O,

S	2.463316	-0.007738	-0.264464
O	1.490393	-0.370175	0.797581
O	3.883207	-0.484662	0.361638
O	2.600433	1.455901	-0.521683
O	2.285757	-0.790802	-1.528680
H	4.582422	-0.267420	-0.274512
S	-2.346417	-0.293625	0.162067
O	-1.629343	-0.359861	-1.151363
O	-3.794822	-0.921159	-0.223972
O	-2.596308	1.106970	0.615838
O	-1.768006	-1.142111	1.232780
H	-4.357598	-0.882783	0.564910
O	0.165337	-2.193356	-1.420715
H	1.026470	-1.660524	-1.541397
H	0.229414	-2.605931	-0.459033
H	-0.579199	-1.512094	-1.369709
O	0.612327	2.885592	0.249474
H	1.428177	2.386092	-0.074238
H	0.269836	2.362126	1.089286
H	-0.121548	2.805885	-0.467326
O	-0.201685	1.490133	2.156993
H	-1.136652	1.294638	1.972911
H	0.271242	0.659281	1.979821
O	-1.311766	2.570989	-1.373026
H	-1.984887	2.240590	-0.746780
H	-1.170761	1.803888	-1.945146
O	0.302146	-2.945633	0.961722
H	-0.519241	-2.509320	1.258325
H	0.989487	-2.323997	1.251641