

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 HNO₃ in microscopic aqueous clusters, *Chem. Phys. Lett.*, 80, 469, 1981]: the number of water molecules needed to acidically dissociate an HNO₃ molecule in HNO₃(H₂O)_N clusters was derived from the shape of the HNO₃(H₂O)_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 HNO₃ molecule, *J. Phys. Chem. Lett.*, 3, 3096, 2012]). Recently, we have shown that for the (HNO₃)_M(H₂O)_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 HNO₃/H₂O 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
$\Delta H(\text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^-)$	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 $\sim 10^4$ 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 H₂O: H₂SO₄ 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 $(\text{H}_2\text{SO}_4)_N$ 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 $(\text{H}_2\text{SO}_4)_N$ 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 $(\text{H}_2\text{O})_N$ 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 $(\text{H}_2\text{O})_n\text{H}_2\text{SO}_4^-$ 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 $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ moiety), the $(\text{H}_2\text{O})_n\text{H}_2\text{SO}_4^-$ 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 $(\text{H}_2\text{O})_n\text{H}_2\text{SO}_4^-$ clusters system with $n = 1-5$. **Fig. 1** represents the most stable energy isomers of $(\text{H}_2\text{O})_n\text{H}_2\text{SO}_4$ ($n = 0-5$) 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 $\sim 158^\circ$ to $\sim 75^\circ$ 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.

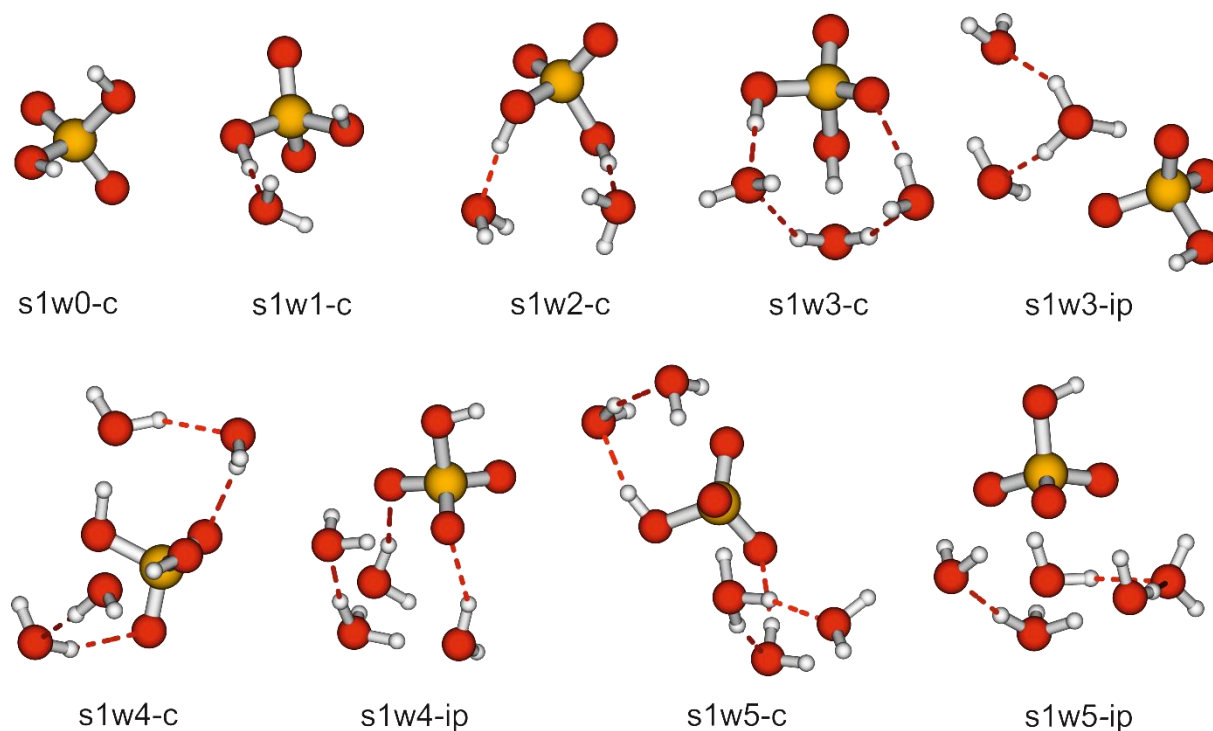


Figure 1. Re-optimized neutral most stable energy isomers of $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ ($n = 0-5$) clusters with both covalent-bonded (c) and ion-pair (ip) structures as anions. The clusters were optimized at the M06-2X/aug-cc-pVDZ level of theory. The corresponding neutral structures 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 $(\text{H}_2\text{O})_n \text{H}_2\text{SO}_4^-$ species sufficiently. Yet, the observation of these ions in the mass spectra is an unambiguous experimental fact, therefore the $\text{H}_2\text{SO}_4 + e^- \rightarrow \text{HSO}_4^- + \text{H}$ dissociation after the DEA process has to be hindered and the hydrogen must be caged by the solvent in order to observe the $(\text{H}_2\text{O})_n \text{H}_2\text{SO}_4^-$ series in the spectrum. We do not wish to speculate what kind of structural arrangement the $(\text{H}_2\text{O})_n \text{H}_2\text{SO}_4^-$ clusters assume, since there are probably numerous possibilities (there will be also a distribution of the neutral starting $(\text{H}_2\text{O})_n \text{H}_2\text{SO}_4$ 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 $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n \text{HSO}_4^-$ clusters are formed after the dissociative electron attachment to the clusters containing the $(\text{HSO}_4^- \cdots \text{H}_3\text{O}^+)$ 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 $(\text{HSO}_4^- \cdots \text{H}_3\text{O}^+)$ 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 $\text{HNO}_3(\text{H}_2\text{O})_N$ 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 $\text{HCl}(\text{H}_2\text{O})_N$ clusters were deflected in electric fields [Guggemos, N., Slaviček, 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 $\text{HNO}_3(\text{H}_2\text{O})_N$ 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 $\text{HCl}(\text{H}_2\text{O})_N$ 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 $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_N$ 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.

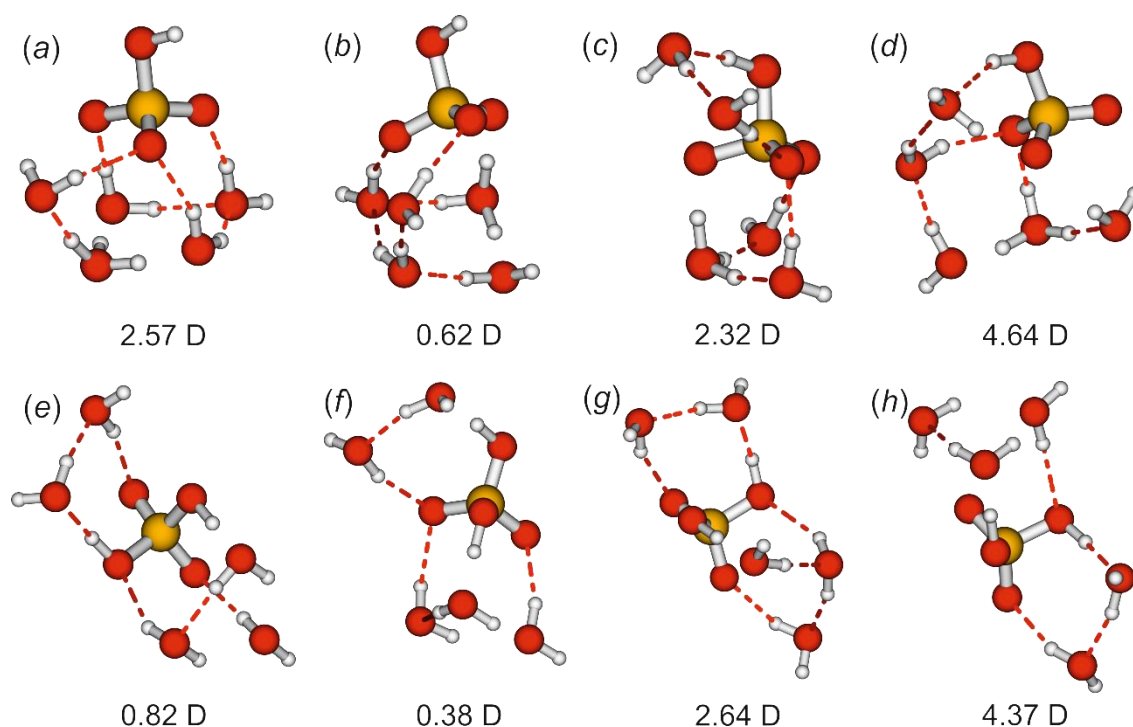


Figure 2. Selected local minima of neutral, $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$, (a-d) and ion-pair, $\text{HSO}_4^- \cdots \text{H}_3\text{O}^+$, (e-h) structures in $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_5$ clusters and the corresponding dipole moments.

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 $(\text{H}_2\text{O})_n\text{HSO}_4^-$ 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 H_2SO_4 molecule when the HSO_4^- ion is generated” as the reason for the very exothermal formation of $\text{HSO}_4^- \cdots \text{H}_2\text{SO}_4$ (and neutral free H) from $(\text{H}_2\text{SO}_4)(\text{H}_2\text{SO}_4)^-$. This is not in itself wrong, but a more

informative/illustrative way to phrase it would be that the $\text{HSO}_4\text{-(H}_2\text{SO}_4\text{)}$ cluster has a much higher binding energy (by tens of kcal/mol) than the $(\text{H}_2\text{SO}_4)(\text{H}_2\text{SO}_4)$ 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 H_2O mole fraction" should presumably be increasing (as we go from a to b to c, $x(\text{H}_2\text{O})$ goes up)

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