Authors' response to editor's comments for "Pre-deliquescent water uptake in deposited nanoparticles observed with *in situ* ambient pressure X-ray photoelectron spectroscopy"

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January 11, 2021

We thank the editor, Thorsten Bartels-Rausch, for his time and careful reading of the manuscript and helpful suggestions. We address his comments below.

"My main remaining comment also addresses the uncertainty. May I ask you to elaborate in slightly more detail on the BE shifts that you observe and on the peak-ratio with water vap[o]r and rule out the following hypothesis. Please don't get me wrong, I think this is a very clever and novel analysis with a clear finding. However, the I believe the manuscript would be stronger if the following arguments are tackled explicitly:"

1. What is the origin of the shift you observe? I must confess, that I find the presentation of the results slightly confusing. I tend to understand that "Shift" is defined as change in observed or apparent binding energy relative to that at 0 mbar in the manuscript While this is correct; I'm used to a definition of "shift" relative to un-charged samples (or literature values). NaCl appears to have a N[a]1s BE of 1071-1072 eV; I would therefore argue that the 0mbar samples in Figure 1 are shifted, but the 2 and 5 mbar are not (or less). So, there is less (or no) shift with increasing water vapor pressure – as opposed to my understanding of lines 199-201. As your write, this shift is caused by charging of the sample in UHV and is reduced in presence of gas-phase water. The importance of this, I think, becomes evident, when looking at Figure 5 which describes the C1s of Sucrose. The C-H is precisely where one would expect it at 285eV. Apparently this sample is not charged even at 0 mbar. Then, is my point, this would explain why the BE does not change in presence of water as the sample has already been dis-charged at 0 mbar. This brings me to some questions that I ask you to discuss in your manuscript.

   Since we are primarily interested in changes in our samples with respect to the addition of water vapor, we do use "shift" to mean relative to the

measurements at 0 mbar. We understand that this may be confusing to those used to thinking of a shift in different terms. We have clarified what we mean by shift in the manuscript.

At 0 mbar, the adventitious carbon C-H peak is at 285.90 and 285.75 eV for sucrose and malonic acid, respectively, so they are not exactly at 285 eV. The binding energies from all the peak fits may be found in the supplement. For sucrose, the shift in binding energy is less than 0.5 eV up to 5 mbar water vapor pressure, which leads us to conclude that there is very little water uptake to the sucrose particles. For malonic acid, there is a shift of just over 0.5 eV at 1 mbar water vapor pressure. Along with other changes in the malonic acid C 1s and O 1s spectra with RH, we conclude that there is some water adsorption onto the malonic acid particles.

(a) Can you quantify how much dis-charging you would have expected by gas-phase water alone as compared to adsorbed water? That is an interesting finding, does this explain why and result in water gas being so much more efficient in discharging than nitrogen gas or even oxygen gas.

In their measurements of NaCl charge state, Verdaguer et al. (2008) controlled the relative humidity by keeping the water vapor pressure constant and changing the ambient temperature. Since the water vapor pressure was constant throughout the measurements, changes in the NaCl charge state were attributed to the adsorption of water. Since we see similar behavior as a function of RH to Verdaguer et al. (2008), we expect adsorption to similarly play a larger role in our measurements. However, since we control our relative humidity by changing the water vapor pressure, it may not be possible to exactly quantify the relative contribution to discharging from gas-phase water compared to adsorbed water from this set of data.

(b) How well are the samples electrically conductive? I assume that gold is very conductive, but have no experience with silicon wafers. Could it be that those are less conducting and therefore you observe a charge with the NaCl samples at 0 mbar and not with the organic samples on gold?

We do not have any quantitative numbers, but yes, we do expect the silicon wafers to be less conductive than gold. This could lead to different amounts of charging between the substrates, but we must stress again that we examine shifts in BE for a given compound on a given substrate relative to the BE at 0 mbar water vapor pressure.

(c) How did your sample look like? Could it be that you sample adventitious carbon mostly at the gold surface -without any charging even at 0 mbar - and sucrose as deposits with are charged at 0 mbar and with reduced charging at 1 mbar? I think this point might be stressed more in the manuscript to explain the different behavior of

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the individual features in the C1s spectra with respect to changes of the BE at varying RH.

We are not entirely sure what the editor means here. Visually speaking, the gold substrates with organic compounds deposited onto them are indistinguishable from clean substrates to the naked eye. It could very well be that adventitious carbon is mostly at the gold surface and does not experience charging while the sucrose particles are on top of the adventitious carbon and do experience charging at 0 mbar water vapor pressure. However, we cannot rule out additional adventitious carbon accumulation after the deposition of the sucrose particles. We do not have sufficient sensitivity in our current measurements to comment with any certainty about the layering of the deposited particles and adventitious carbon.

(d) How certain are you about the BE of the C1s features. What is the impact on fitting (width, peak ratio, position contains as well as background treatment) on the BE for each feature and its change with RH?

We are confident in the BE of the C 1s features. We have used literature values from XPS measurements in vacuum conditions– Ferreira Jr. et al. (2017a,b) for malonic acid and Stevens and Schroeder (2009) for sucrose–to initialize our fits and subsequent Monte Carlo error analysis shows small uncertainty estimates in the binding energy.

(e) Adventitious carbon often also has some oxidized functionalities (Barr, 1998). Would one not need to differentiate more clearly between the CO peaks of your sample and those from the adventitious carbon (line 350). I agree that this gives too much freedom to the fits though.

In our fitting of the C 1s spectra of malonic acid and sucrose, we have followed Ferreira Jr. et al. (2017b) and Stevens and Schroeder (2009), respectively, in only assigning C-C/C-H bound carbon as adventitious carbon. It may be possible to account for oxidized functionalities of adventitious carbon in our measurements, but we agree that the overlap with the C-O peaks from the sample would probably give too much freedom in the fits.

2. Was there no adventitious carbon on the NaCl samples? By the way, why is O1s not shown for the NaCl samples to quantify the water uptake? Might masking by carbon also explain the trend seen in Fig. 4 and line 286-290 – assuming that carbon built up with time or that the data are from different sample spots?

This is an excellent point about adventitious carbon on the NaCl samples. Unfortunately, we did not check for C 1s on the NaCl samples, although it is almost certainly present. We do not believe that time or position-dependent masking by carbon explains the trend seen in Fig. 4 and lines

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286-290. We do not expect any build up of adventitious carbon on the sample once the sample is in the measurement chamber, and we have kept the sample position fixed once we have found a suitable position for measurement.

As for O 1s for the NaCl samples, the contribution from the native oxide of the silicon wafer dominates the signal preventing any quantification of water uptake using the O 1s spectra. This is discussed in lines 209-212 of the manuscript.

Further comments (that you may or may not consider). I add a few references from our work because I think they might interest you. As editor it is not my intention to make you cite them.

1. Line 35: I could not agree more on the importance of the surface to volume ratio (Artiglia, Nat. Commun. 2017)

2. Line 50: Again, very important point. The presence of organics indeed may have profound impacts on heterogen[e]ous chemistry, in particular the solubility of ozone in the liquid aerosol phase and thus the reaction rate of halogen oxidation by gas-phase ozone (Edebeli, Env. Sci. Process Impacts 2019).

   We are glad that you agree with the importance of the two preceding points, and thank you for bringing the two papers to our attention.

3. Line 65: Here, I wonder how much aerosol deposits as you elegantly used differ from experiments with slurry considering that one exposed the samples to UHV and then humidifies again. Probably a topic to discuss during a conference – I hope we have the chance soon. (Lampimäki, J. Phys. Chem. 205; Orlando J Phys Chem Lett, 2019; Orlando Top. Catalysis 2016)

   Unfortunately we do not have any experience with slurries to make a comparison, but we would indeed be interested to discuss this further in the future.

4. Line 95: sampling nano-scale particles I have a practical question: How did you find the sample for a good XPS signal? Was it covering the whole sample holder at the measurement spot?

   Coverage on the sample substrate was sufficient that finding the sample was generally not a problem. We tried to optimize the position of the sample in order to maximize counts seen in Na 1s for NaCl particles on O 1s for the organic compounds.

5. Line 139: please define ESP

   The nanometer aerosol sampler (NAS) introduced in line 136 is a type of electrostatic precipitator (ESP). We now refer to NAS instead of ESP in line 139.

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6. Table 1: Please define mü, sigma, etc in the caption.

The caption now reads: "Aerosol sampling data including generated size distribution information (geometric mean number μ_N, geometric number standard deviation σ_g, total number N, and geometric mean surface area μ_{SA}) and sample collection parameters (sampler flow rate Q, collection time t, substrate, and coverage)."

7. Line 200 ff: Water uptake before deliquescence has been observed before. Please cite Wise 2008, Aerosol Sci Technol 42, 281-294

We have added the findings of Wise et al. (2008) to the introduction in the paragraph beginning with "A number of spectroscopic techniques ..."

8. Figure 1: mention and explain blue peak in caption.

The caption now reads: "Na 1s XPS spectra of NaCl aerosol particles recorded at different water vapor pressures (relative humidities, RH). The point markers show the recorded data and the solid lines the fit envelope curve. The spectra are fit using a single, symmetric Voigt peak shown in red with an additional peak in blue necessary to explain the spectrum at 0 mbar after water exposure. The dashed vertical line shows the binding energy of Na 1s at 0 mbar pressure (0 % RH) at the beginning of the experiments. Error bars show the estimated uncertainty in the peak position from Monte Carlo analysis. Photon energy was 1486.6 eV from the Al anode."

9. Line 293 "This behavior" are you referring to the ratio at 0 mbar or the shift with RH?

We are referring to the ratio of Na to Cl calculated from the peak area ratios. We have clarified the sentence: "As the spectra for all RH are recorded with a constant excitation energy from the Al Kα anode, different transmission through the electron analyzer at different electron kinetic energies cannot explain the difference between the Na to Cl peak area ratio and the NaCl stoichiometric ratio."

10. Line 310: Maybe it is worth to compare the surface coverage also to the findings by Ewing 2005 (H2O on NaCl: From single molecule, to cluster, to monolayer, to thin film, to deliquesence. In chapter 12, springer-Verlag, 2005

We cite Peters et al. (1997); Peters and Ewing (1997); Foster and Ewing (2000) for the surface coverage of water on NaCl (100), which are the same sources cited in Ewing (2005).

11. Line 338 that $\rightarrow$ than (?)

Yes. This has been corrected.

12. Line 358. Do you observe a difference in peak wi[d]th for gas-phase and condensed phase peaks? If so, I would add this information as strong argument.

For sucrose, the peak widths for gas-phase and condensed-phase water are different. However, for malonic acid, both gas-phase and condensed-phase water were assumed to have the same width. We have made these decisions in order to obtain the best fit to the measured data given the assumptions were could make to constrain the fit.

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