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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Pre-deliquescent water uptake in deposited nanoparticles observed with *in situ* ambient pressure X-ray photoelectron spectroscopy" *by* Jack J. Lin et al.

Anonymous Referee #1

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This is an interesting article describing the application of a new technique to study pre-deliquescence water uptake and the changes in the chemical environment near surface based on changes of XPS peak characteristics of model aerosol compounds as a function of relative humidity. The work is novel. The paper is heavy on discussing spectral characteristics and less on atmospheric implications. Much of the discussions rely on spectral fitting of the spectra, which at times are quite noisy. In general, the authors need to provide more information on how uncertainties due to the experiments as well as fittings would affect the results.

In the Introduction, the authors did a good job in identifying the need of surface analysis

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as well as pre-deliquescence water uptake. However, they seem to have missed some useful literature relevant to this paper. 1. XPS has been used to examine ambient particles collected by a MOUDI. Cheng et al. (2013, 2014) analyzed particles from various stages, including the last stage of 0.056 to 0.1 microns. 2. Gen et al. (2017, 2019) have used SERS to detect the presence of surface adsorbed water and the formation of BrC on particle surface. 3. Pre deliquescence water adsorption/absorption of NaCl has been indirectly discussed in HTDMA measurements, albeit at much higher RH than the range studied in this paper. I also encourage the authors to look into the literature of the changes of the shape factors as indication of pre-deliquescence water uptake.

Line 148: The authors discussed the shift in binding energy and the intensities of the peaks as two independent variables. I wonder if the intensity of the peak changes as a result of changes in the chemical environment. If this is the case, some of the discussions on peak ratios later need to incorporate this dependency.

Figure 3: It is necessary to give more evidence to convince this reviewer that the 0.2eV memory effect is real, from the perspective of experimental uncertainty and peak fitting. Have they reproduced the results? Much of the discussion in that paragraph seems to be more on the results of NaCl(001) single crystals than of the particles. It is interesting to note the NaCl (001) data show another increase in shifts after reaching a plateau. Any reasons?

Line 190-210: The authors discussed that peak broadening of the particles is less than that of single crystals. I don't have a good sense of the discussion because there was no quantitative information for comparison. In Figure 1, compared to 0 mbar peak, the 5 mbar peak did occur to me that there was broadening. It would be good to again have some sensitivity analysis on how fitting and experimental uncertainty would potentially affect the extent of broadening or the lack of it. Are we talking about results that are statistically significant? Line 209-213: I cannot follow the logic. It was suggested earlier that "the decrease in peak broadening observed for single crystals is ultimately attributed to adsorbed water reducing inhomogeneities in the surface potential". Do you mean that particles have more inhomogeneities and therefore the same amount of water will have a less effect in reducing inhomogeneities, when compared to single crystals? I am also confused by the term "immediately" in the sentence "The KPM experiments show that the inhomogeneities are removed immediately after water is adsorbed on the surface." What does it mean in terms of the amount of water needed to remove the inhomogeneities?

Line 217: How confident are the authors on these ratios, in light of the experimental uncertainty, especially that for Na 1s at high RH? Also, it is useful to include data of the UHV experiment and 0 mbar after dosing for comparison.

Line 268: The C-C/C-H peak dominates all the spectra of sucrose and may significantly affect the fitting of the C-O and O-C-O peaks in C1s. The authors need to do a better job in defending the validity of these fitted results.

Line 283: The O1s peak dominates in Figure 6 and the author attributed it to water vapor. I am surprised that whatever interactions between water vapor and the particles can lead to energy shift of the water vapor peak. Do you mean Adsorbed water? Did you see the same in NaCl experiments? Again, I am not sure how the uncertainty would affect the fitting results.

Line 292: I found the discussion " the changes in relative ratios between C-O and O-C-O bound carbon C 1s and oxygen O 1s signals are small" somewhat arbitrary. From eyeballing the peaks, I feel that there are some changes in the ratios of the intensities of the two peaks. If these changes are considered small, I would argue that the changes in Na/Cl ratios are small too.

Line 295: I found the use of EDB data to support their results not convincing, at least not consistent with the earlier claims that EDB, optical levitation and a host of other techniques do not provide adequate sensitivity in pre-deliquescence water uptake.

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Line 340: Is the comparison of absolute intensities across different spectra (C1s and O1s) valid? I guess ok for observing a trend but may need more justification to compare with the stoichiometric ratio of malonic acid.

The authors may want to comment on the application of this technique at high RH values, which are more atmospherically relevant.

References: Cheng et al. (2013) Surface Chemical Composition of Size-fractionated Urban Walkway Aerosols Determined by X-ray Photoelectron Spectroscopy, Aerosol Science and Technology, 47, 1118-1124. DOI:10.1080/02786826.2013.824066. Gen M. and Chan C.K. (2017) Electrospray-surface enhanced Raman spectroscopy (ES-SERS) for probing surface chemical compositions of atmospherically relevant particles. Atmospheric Chemistry and Physics. https://doi.org/10.5194/acp-17-14025-2017. Gen M., Kunihisa R., Matsuki A., Chan C.K.* (2019) Electrospray surface-enhanced Raman spectroscopy (ES-SERS) for studying organic coatings of atmospheric aerosol particles. Aerosol Science and Technology. https://doi.org/10.1080/02786826.2019.1597964

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