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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Electrospray-Surface Enhanced Raman Spectroscopy (ES-SERS) for probing surface chemical compositions of atmospherically relevant particles" *by* Masao Gen and Chak K. Chan

Anonymous Referee #1

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Overview This manuscript describes a novel approach to SERS analysis of aerosol particles, where the nanoparticles are deposited onto the aerosol surface, as opposed to aerosol particles being deposited onto a more conventional SERS substrate. The manuscript thoroughly considers the prior Raman and SERS literature and makes a significant step forward in the spectroscopic analysis of aerosol particles. There are some significant shortcomings that need to be addressed, but overall this is manuscript has many positive features. Major Comments - SERS is often most enhanced when two metal nanoparticles are at a specified distance from each other with a predeter-

mined geometry. How ordered are these nanoparticles? What methods have been used to image the silver nanoparticles are the aerosol particle surface? Is the assumption that the enhancement is coming entirely from individual silver nanoparticles? - The size of the particles used calls some of the relevance of the findings into question. For example in Figure 3 the particles are 23 and 47 microns. It would be very helpful to have Raman of AS particles on top of silver nanoparticles for comparison. At these sizes it would not be surprising to see nanoparticles on top making a difference versus nanoparticles underneath, but no data on is given to support this claim. Also an optical image in the main text of AgNPs on top of the AS particles would be helpful are for particles 10s of microns in size, should be relatively easy to image. - Calculation of enhancement factors? Relative enhancement of specific modes? - Optical and electron microscopy imaging of particles with and without nanoparticles on top would strongly improve the authors claims that the particles are sitting on top. - Only a few particles are analyzed throughout the entire paper. Some details on the reproducibility, consistency of enhancements, and overall quantification are needed to truly show that this is a method that can be extrapolated to other aerosol studies. As of right now with so few spectra there could be concerns that only the best examples were chosen, which more statistics would help alleviate. - The use of the gold coating on the Si wafer needs to be described in more detail. It is unclear the purpose of this and whether it plays a role in the enhancements. If the enhancements are from the gold or partially gold and partially silver, this is important for the overall findings. More information would be helpful to evaluate this possibility. Do AS particles on just Si with Gold sputtered coating give any enhancements? It seems like an expensive choice if there is no specific reason for doing it, so a more convincing description would be helpful. - Lines 153-160: For the nanoparticles no information is given about the size distribution and physical characteristics. The methods used are listed, but not the values for the silver nanoparticle synthesized. Given the importance of the silver nanoparticle properties for generating an enhanced response, more details are needed about what is being deposited on the atmospheric or model system particles. The journal EnvSci:Nano has a nice list of sug-

gested nanoparticle characterization criteria that all papers using nanoparticles should us, this might be a good guide as to the detail that should be included in the manuscript. Similarly since the size distribution after electrospraying with the DMA and CPC would be helpful to evaluate whether particles are individual particles or aggregates after ESI. - Lines 140-148: The aerosol size distribution also needs to be described in more detail. What was the size distribution of aeorsols. All of the information given is that the aerosols are generated and deposited (in the methods). Information like the mode, any size selection, etc would be very helpful in understanding the particle properties. Are the AS particles are assumed to be effloresced crystals since they are stored at < 10% RH and then analyzed at 60% (below the deliquescence RH of AS)? This could impact the enhancement of the SERS by determining nanoparticle/ammonium sulfate interactions. - For the enhancement (162) reported on line 354, what size particles does this refer to? Is it possible that a larger particle versus a smaller particles is playing a role? This is part of why more details are needed for the aerosol sizing. - Minor Comments - Line 80: The Ofner paper referenced is of TERS, which while similar to SERS, should be specifically noted as such. - Line 329-331: The depth of focus section is not clear and should be discussed in more detail. - More details on Gen and Lenggoro method need to be added. - Figure 4: It would be nice to see the rest of the Raman spectrum (perhaps as an inset) to evaluate any nanoparticle effects. - Figure 6: Why does the peak shift to lower frequencies? More information on this would be helpful. - Figure 7: For the particles that is very weak signal for very large particles. What is the RH of the particles when analyzed? Is it really safe to assume they are aqueous? Many prior Raman aerosol paper show much sharper sulfate features for ambient particles, why does the SERS struggle here so much? - Figure 8: Why is the v(O-H) stretching region not shown? - This is a minor point, but the figures take a very long to load, which I would guess is related to the resolution used. Please check that the figures load easily for a future draft (hopefully this is not just my computer having issues).

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