Reply to Reviewer 1, Juan Fernandez de la Mora:

This study describes in considerable detail a powerful instrument that has already produced valuable experimental data on new particle formation in the carefully controlled CLOUD experiment (Wang et al. 2020). The instrument is able to generate with fine sensitivity and resolution a size distribution in the 1.5-25 nm range in 60 s, which is apparently faster than previously achieved. Additionally, the article provides extensive information on design criteria, which should be most valuable in future studies aimed at making comparable measurements with improved performance. The experimental and interpretive challenges overcome are great in many fundamental dimensions, including sampling, charging, transmission, size resolution, sensitivity of detection, speed of measurement, etc. Handling all these problems in a single instrument has required a difficult strategic thinking on components choices, and this is also carefully discussed with extensive knowledge of related literature. Globally considered this is an outstanding contribution to the field of atmospheric measurement, which should by all means be published. The choice of journal is also excellent, as the article provides an ideal venue for discussion of the many challenges involved in these measurements, as well as on the many possible alternative experimental tools that were not chosen.

In my discussion I will focus on these other alternatives. I realize that the authors have contributed their own practical solution to their global measurement problem, including a fair amount of justification for their strategic choices. They have accordingly no duty to engage in the more extensive discussion I propose. Nevertheless, given their wide experience, their response would be exceedingly useful to the many colleagues familiar with the various components of this instrument, but not necessarily with their optimal integration into a functioning system.

Response:

We thank the reviewer for his kind words. He correctly notes in his opening comments that the design of an instrument and the interpretation of the data that it generates has posed many challenges. Indeed, these challenges introduced conflicting demands on its design, and the specification of its operating conditions. The objectives of this design included measurement ranging from clusters of sizes probed by mass spectrometers to stable particles that can continue to grow to become cloud condensation nuclei with the time and size resolution needed to quantify the dynamics of these new particles. The questions raised are constructive points about alternate choices that could have been made. We note that the instrument on which we report was designed measurements either in the atmosphere or in chamber studies that simulate the atmosphere. Thus, we address those suggestions in light of the experiments for which this instrument was designed.

As a general point on our responses, we note that the primary focus, and unique feature of the instrument that we report, the nano scanning electrical mobility spectrometer (nSEMS), is the voltage-scanning radial opposed migration ion and aerosol classifier (ROMIAC). The measurement system comprising the nSEMS must include a detector and a charge conditioner; other designs of those components of the integrated instrument, could be substituted for the ones that we report without changing the essential features of the nSEMS.

We feel that the new capability enabled by the scanning ROMIAC warrants publication of this paper; some of the questions raised will be addressed in future papers.

1. The two-stage condensation detector is justified as follows: *Some single-stage CPCs have been operated at sufficiently high supersaturation to activate particles as small as 1 nm diameters, but in the experiment for which this instrument has been developed, where measurements must be made in a high-radiation environment, this can lead to nucleation within the CPC. Therefore, we took a more conservative approach that has proven robust and effective for sub-10nm particle detection, namely a two-stage CPC, in which the first stage employs a low vapor pressure working fluid, typically diethylene glycol (DEG) that can activate small particles with minimal risk of homogeneous nucleation (Iida et al., 2009).* Assuming that the nucleation region cannot be shielded, the effect of radiation would be to create small ions in air, similar to those produced in the X-ray chamber, but not removable by the DMA. One must then select a vapor able to discriminate between small ions produced by radiation and 1.5 nm particles. But why would this be precluded in common CPC vapors? In theory (say in Thomson's classical model for nucleation on charged particles) all vapors have critical activation curves that depend on size, which theoretically enables the exclusion of small air ions. Furthermore, Tauber et al. (ChemPhysChem 2018, 19, 3144– 3149) have recently found significant differences between the critical supersaturation for various atomic ions in butanol vapors. Similarly, Attoui and colleagues (doi: https://doi.org/10.1016/j.jaerosci.2021.105772) report that Kanomax's fast CPC can detect 2 nm particles. My point is that there may be single CPC solutions to the detection problem that, in addition to being simpler, would be faster. If these solutions are presently unknown or insufficiently reliable, please state so, as this would provide a healthy stimulus for developing them.

Response:

A single-stage condensation particle counter (CPC) detector could be used instead of the two-stage CPC that has been employed in the nano scanning electrical mobility spectrometer (nSEMS). The reviewer is correct in noting that the two-stage CPC slows the instrument response since each of the activation and growth stages within the two-stage CPC has its own finite time response. A number of investigators have demonstrated single-stage CPCs that can detect particles approaching 1 nm in size, and several working fluids have been shown to work (e.g., butanol and diethylene glycol: Kuang et al., 2012, Aerosol Sci Tech 46: 309–15; water: Hering et al., 2017, Aerosol Sci Tech 51: 354–62). For many applications, these instruments would perform well.

The CLOUD experiment at CERN, where nSEMS was first deployed, employs a 3 GeV pion beam to generate ion concentrations comparable to those in the upper troposphere. The instrument cannot be shielded from the pions. Ion generation within the supersaturated volume of the CPC led to false counts during beam events in some early experiments. In the two-stage CPC, the initial activation is achieved in a high supersaturation, but the rate of nucleation within the instrument is constrained by the high surface tension and relatively low vapor pressure of diethylene glycol. Growth to optically detectable size is achieved with a lower supersaturation of a more volatile working fluid, minimizing the risk of nucleation within the CPC and the associated false counts, even if ions are generated. We, therefore, took the conservative approach of using the two-stage CPC as the detector for the experiments for which the nanoSEMS was designed, in spite of its slower response than the single-stage CPC.

We did, however, replace the TSI butanol CPC that we employed as the second stage in initial experiments with the nSEMS with a faster response, water-based, Aerosol Dynamics MAGIC CPC to speed the detector response. As the reviewer suggests, other experiments may benefit from the faster response of the single-stage CPCs.

2. DMA selection. The selection of the DMA used is justified because "*radial opposed migration ion and aerosol classifier (ROMIAC), can classify nanometer-sized particles with minimal degradation of its resolution or diffusional losses.* Another advantage of ROMIAC noted is that it achieves resolving powers comparable to those of conventional DMAs, though at substantially reduced flow rates. Nevertheless, given that a key advance in the new instrument is to reduce measurement time, it would seem that a larger gas flow rate would be preferable. For instance, the Half-Mini DMA has a residence time typically below 1 ms in the analyzer. Anotherimportant issue we have recently noted is that high resolution is directly relevant to measurement speed because the residence time in the analyzer is almost identical for all ions of a given mobility, and therefore appears as a pure delay easily corrected in a fast measurement. study we argue that a full mobility scan can be completed within a few seconds by combining a detector with a response faster that 20 ms with the half-mini DMA. Although such a fast CPC exists, that claim remains to be experimentally substantiated.

Figure 8 of the article shows that the resolution of the ROMIAC is excellent even for the sophisticated nucleation studies pursued. However, the figure also shows that the width of the spectrum of all monomobile particles used spans several seconds in the 60 s temporal spectrum. A DMA of higher resolution would not only resolve perfectly the 3.4 and 2.9 particles (partially overlapping in Figure 8). Even more usefully, much narrower peaks would enable much faster scans without loss of resolution.

One could be led to conclude from the nucleation event illustrated in Figure 11 that a temporal resolution of 1 minute is adequate. This may be true for events lasting several minutes, but perhaps not in situations where the reservoir of vapor available for particle growth is more limited. Given that the improved time resolution of the instrument of Kong et al. enabled the capture of nucleation events that would have been missed with slower prior equipment, one may surmise that currently undetectable events will be capturable by future devices having more temporal resolution.

There is another potential advantage of higher resolution in nucleation studies, as well as in other situations with a natural mechanism to produce narrow size distributions. If the signal is concentrated into a narrow range of sizes, being able to resolve them would increase the signal. In Figure 8 of Kong et al. one sees that the peak corresponding to 3.4 nm particles spans a size range from 2.9 to about 3.9 nm. The atmospheric nucleation spectrum shown in Figure 11 includes mobility peaks of comparable width, suggesting that perhaps the real size distribution along the growth curve is considerably narrower and taller than can be captured with the available resolving power. In other words, higher resolution would enable detecting lower intensity as well as shorter nucleation events. It would also provide a more precise measurement of the growth rate.

Response:

Operating the mobility classifier at higher flow rates than those of the ROMIAC reported here would reduce the time required by reducing the residence time within the instrument. The reviewer has demonstrated instrument scans as rapid as 1.2 s, using a "half-mini" DMA with a sheath flow rate of ~488 L/min, 40 times that used in the ROMIAC, and an aerosol flow rate of 3 L/min. This enables the fast response that the reviewer describes. For chamber experiments, the high sheath flow rate would require either operating the DMA with a recirculating sheath flow, or supplying the sheath flow from a different source than the sample to avoid depleting the aerosol from the chamber. Either of these modes could perturb the aerosol, though the short residence time might make the effect of the thermodynamic perturbations small for some aerosols and measurement scenarios. The reviewer correctly notes that improved size resolution may better reveal the fine structure of the particle size distribution. Both of these potential benefits come at a cost of reduced counts, and correspondingly increased statistical uncertainty. Each measurement scenario involves compromises. The ROMIAC allowed resolution comparable that employed in a wide range of atmospheric and simulated atmospheric measurements. Time response and resolution are not the only considerations in atmospheric measurments.

The reviewer further notes that the data shown in Fig. 11 might benefit from both improvements identified. That intense nucleation event produced large number concentrations, but many of the events that we studied produced lower number concentrations; ambient atmospheric concentrations are also often much smaller. The number of particles detected is further reduced by the low charging probability for particles in the low nanometer size range, i.e., O(1%) for a bipolar diffusion charge conditioner as is commonly used in mobility size distribution measurements. Furthermore, an experiment that operates nearly continuously (seven days per week, 24 hours per day) for more than a month does not lend itself to fine tuning of operating parameters that may be appropriate for laboratory experiments that can readily be repeated. The finite chamber volume further constrains the sample flow rates that can be tolerated without depleting the air in the chamber.

3. Soft X-ray ionizer. This element does not receive as detailed a description as other components of the system. The choice of a bipolar source is defended based on the freedom it offers to examine positive and negative polarities. This is indeed a most useful feature, especially for particles of such small sizes, whose charging probability has not been yet well studied. Soft X-rays have an evident regulatory advantage over radioactive sources. However, all ionization sources relying on energetic particles pose a danger of converting organic volatiles into involatile species, causing artificial nucleation events in sufficiently polluted atmospheres. The details of how this tendency is moderated by Kong et al. would be of interest to the reader. In this realm, it is worth noting that the advent of electrospray ionization did change this situation long ago in the case of unipolar sources. One relevant feature of electrospray ionization at atmospheric pressure is that, in contrast to electrical discharges, ions are created under strictly thermal conditions. Vapors are certainly introduced through the evaporation of a solvent. However, in high conductivity electrosprays, solvent flow rates may be as small as 10^{-7} g/s. For this reason, electrosprays of pure volatile solvents containing volatile salts such as ammonium acetate have had an increased use in chemical analysis as a clean and efficient ionization source for vapors. More recently, bipolar electrospray sources combining a positive and a negative emitter have provided a clean substitute for bipolar sources based on ionizing radiation. There is some literature on the ionization probability of unipolar ES sources with vapors, and some untested calculations of how this probability would depend on particle size. on the size dependence of the

charging probability of nanoparticles in bipolar ES sources, but a similar ambiguity exists for bipolar sources of ionizing radiation. Hopefully these two gaps will be filled soon.

Response:

As noted above, the unique component of this measurement system is the scanning ROMIAC, other charge conditioners (chargers), even other soft x-ray charge conditioners, or the ones that the reviewer proposes, could be used in a nSEMS. Due to laboratory shutdowns during the COVID-19 pandemic, the characterization of the charge conditioner used in this study could not be completed in time to be included in this paper. That characterization will be completed, and will be reported along with the design details in a separate paper. We therefore propose to state in this paper indicate that we characterize that portion of the nSEMS downstream of the charge conditioner. This level of characterization is needed since an important class of applications is its use as the analyzer in TDMA-type measurements (e.g., replacing the analyzer SMPS of a tandem differential mobility analyzer).

Though we are removing the charge conditioner employed from the instrument that we describe, the comments by the referee still warrant discussion. Differential mobility analysis of environmental aerosols requires a known charge distribution if one is to determine the particle size distribution. To that end, most DMA measurements employ a bipolar charge conditioner. The reviewer suggests that choice of the bipolar charge conditioner is based upon the ease of selection of positive or negative ions. While we take advantage of having both polarities, the reason that bipolar charge conditioning is standard in mobility-based size distribution measurements of aerosols lies in the consistency of the charge distribution that results. Exposing the aerosol to a cloud of ions of both polarities that is overall neutral leads to a steady-state charge distribution provided the concentration of particles is not so high that the ions are depleted during charge conditioning. The neutral cloud of ions is typically produced by irradiating the sample with energetic particles, often those emitted by radioactive decay, but increasingly and, in this study, soft x-rays. Detail on the soft x-ray source that we have employed is, admittedly, limited, since planned experimental characterization of it was delayed by the COVID-19 restrictions. That work is beginning now, and will be the subject of a future paper.

The reviewer cautions that the energetic particles can lead to transformations of organic vapors that lead to particle formation, and false particle counts. Whether we use a radioisotope or soft x-rays to generate the ions, we do detect "charger ions" in the 1-1.4 nm mobility equivalent diameter size range. We have not resolved whether the charger ions might be particles as the reviewer suggests. Since we cannot definitively discriminate these ions from the particles that we seek to measure, we only report size distributions for particles larger than 1.5 nm. Estimations of the nucleation rate in the CLOUD experiments and elsewhere are inferred from the particle flux through size space at a specific size (e.g., 1.7 nm) that is sufficiently large compared to the charger ions to allow confidence that those clusters or particles were present in the sampled air.

The reviewer further proposes using a pair of electrospray sources to produce ions of both polarities that would then be introduced into the aerosol to avoid new particle formation by energetic particles. That might work, provided the electrospray sources are sufficiently robust to maintain charge balance and sufficient ion concentrations within the charge conditioner continuously for the duration of the experiment. In the case of measurements at CLOUD or

atmospheric measurement campaigns, continuous operation for weeks or months is required, and the instrument must be able to operate unattended. The present methods of charge conditioning serve our purpose well, but do complicate measurements in the range where the charger ions are found. New approaches to charge conditioning that overcome this limitation would be welcome.

We agree with the reviewer that a broad discussion of the many design constraints that need to be considered in designing this or other types of instruments would be valuable, but this would require a comprehensive review of these many dimensions of instrument design in the context of different use scenarios. This paper describes an instrument that was designed for measurement of ultrafine particles in the atmosphere and in chamber studies that simulate the atmosphere, we limit our discussion to constraints that were considered for this specific instrument.

References cited:

Kuang, C, M Chen, PH McMurry Aerosol Science and, 2012. n.d. “Modification of Laminar Flow Ultrafine Condensation Particle Counters for the Enhanced Detection of 1 Nm Condensation Nuclei.” *Taylor & Francis*.

Hering, Susanne V, Gregory S Lewis, Steven R Spielman, Arantzazu Eiguren-Fernandez, Nathan M Kreisberg, Chongai Kuang, and Michel Attoui. 2017. “Detection Near 1-Nm with a Laminar-Flow, Water-Based Condensation Particle Counter.” *Aerosol Science and Technology* 51 (3): 354–62. doi:10.1080/02786826.2016.1262531.