Discussion of: **Characterization of the planar differential mobility analyzer (DMAP5): resolving power, transmission efficiency and its application to atmospheric cluster measurements**, by: Zhengning Xu, Jian Gao, Zhuanghao Xu, Michel Attoui, Xiangyu Pei, Mario Amo-González, Kewei Zhang, Zhibin Wang

by Juan Fernandez de la Mora, Yale University, Mechanical Engineering Department.

The article describes an instrument combination previously used in laboratory studies, but, to my knowledge, not in atmospheric studies. I see merit in that approach, and consider this exploratory article a valuable contribution to the field of atmospheric measurements. It covers prior work fairly, and adheres to high scientific standards. I support its publication, pending some desirable improvements. There is the important issue of whether the instrument will be sufficiently sensitive for relevant atmospheric studies. Whether or not this is the case, the article already shows clearly that the instrument can be very fruitful at least in laboratory studies of atmospherically relevant clusters. In this I believe there are precedents that ought to be cited.

1. Abstract. It would be preferable to avoid the abbreviations TMAI, TBAI, THAB and TDAB. Also the term "*newly developed*" seems inappropriate for an instrument that has existed for considerable time.

2. DMA Transmission. The transmission study is most valuable, as I am not aware of prior quantitative studies of this important metric for planar DMAs that would be directly relevant to atmospheric measurements. There are studies with electrospray sources directly facing a planar DMA inlet slit, showing many orders of magnitude gains in transmitted ion signal versus cylindrical DMAs. However, an electrospray is an intense unipolar ion source injecting several hundred nA of current into an area typically smaller than $1\mu m^2$. In this case, the major source of ion loss is beam broadening by space charge, which would not be relevant in most atmospheric measurements. In a planar DMA the electrospraying capillary can be brought arbitrarily close to the inlet slit. Under such conditions, Javaheri et al. (2008) have shown that almost all molecules of an electrosprayed dilute species in solution can be transmitted as ions through the atmospheric inlet orifice of a mass spectrometer. Similarly, over 1 nA of the dominant electrosprayed ion can be transmitted to the outlet slit of a planar DMA (Fernandez de la Mora, 2019). This exceptional transmission has been exploited by Tauber et al. (2018) to introduce DMA-purified highly concentrated atomic ions into a nucleation chamber to study ion induced nucleation. Their study suggests that the same is not possible with any cylindrical DMA. Similarly, in our first tandem DMA-MS study involving a Time of Flight (TOF) mass spectrometer, it took us over an hour with a high resolution cylindrical DMA (passing 10 L/min of aerosol) set at a fixed voltage to accumulate a single mass spectrum with useful information on $(THABr)_n(THA^+)_z$ clusters (Fernandez de la Mora et al. 2005). This is the main reason why most successful couplings of DMAs with MS systems (mainly using electrospray sources) have involved planar DMAs. There are nevertheless exceptions involving quadrupole MS systems set at a fixed mass, while a cylindrical DMA scans over the voltage (Ude et al., 2004). Steiner et al. (2014) have successfully coupled a cylindrical DMA of relatively high resolution to a TOF-MS to investigate small ions from radioactive bipolar sources.
The present transmission study uses a tandem setup with a cylindrical first DMA. In this case the vast majority of electrospray ions are lost by space charge in the aerosol inlet tube and in the

annular region preceding the inlet slit to the analyzing region of the first (cylindrical) DMA. Consequently, there is little space charge left when these ions reach the second (planar) DMA. Therefore, the losses measured by Xu et al. are primarily diffusive losses, which is what would be relevant in atmospheric sampling. These losses are not negligible for the small ions investigated by Xu et al., and the observed substantial advantage of planar over cylindrical DMAs (Figure 5b) is apparently also due to lack of an extended annular region upstream of the injection slit. This dominant region of diffusive losses is evidently reduced in cylindrical DMAs using a small outer radius R_2, which explains the advantage of the Half-Mini DMA (R_2=7 mm) reported in figure 5b over other cylindrical DMAs.
It would be useful if the authors would report the geometry in the cubic chamber used in the planar DMA upstream of the injection slit, since this might be the major source of the observed 46% ion loss. Most relevant to these losses is how far from the slit is the end of the tube bringing in the aerosol into this cubic chamber.

3. Mass spectrometer selection. Xu et al. use a TOFWORK AG mass spectrometer. In this they follow the lead of many widely cited atmospheric studies by Kulmala and colleagues. However, most other past DMA-MS couplings have relied on other commercial time of flight mass spectrometers developed broadly for electrospray mass spectrometry studies, many of them having much higher resolving power and mass range than the TOFWORK MS. These other instruments have achieved high reliability and ion transmission efficiency, and would at first sight seem to be ideally fitted for coupling with a DMA for atmospheric studies. It would be of considerable interest to those intending to pursue related atmospheric DMA-MS studies to learn about the considerations that have led Xu et al. to their MS choice.

4. Cluster fragmentation
Given that the clusters forming as precursors to atmospheric nucleation are physically bound and often fairly labile, the important issue arises as to whether the clusters observed in the mobility and the mass analyzers are the original species present in the atmosphere, or rather their fragmentation products artificially generated during their relatively violent transfer to the vacuum system. The matter is briefly alluded to in line 270 "*Since the voltage configurations can affect the fragmentation of the cluster inside the API-ToF-MS (270 Passananti et al., 2019), the DMA-MS spectrum is highly instrument dependent*". Nevertheless, more discussion on fragmentation would be indicated in relation to an instrument put together to investigate atmospheric nucleation. Fragmentation is certainly strongly affected by the choice of the mass spectrometer and its voltage settings, and this may relate to point **3** above. There are excellent commercial instruments able to measure both mobility and mass in tandem. Most of them use either intense potentially fragmenting electric fields in the mobility analyzer, or carry the mobility analysis in a region of reduced pressure. What is special about the DMA is that it operates at atmospheric pressure and has little tendency to fragment even weakly bound clusters. It is accordingly possible to establish which ions detected in the MS are the original ions selected in the DMA, and which are fragments. This possibility is much more limited in situations when fragmentation may arise prior to or during the mobility measurement. This important advantage of the DMA is well illustrated in the work cited by Hogan and colleagues. It is also nicely demonstrated in the rather interesting DMA-MS spectrum included in Figure 9b of Xu et al. This lovely figure seems to me to deserve far more discussion than currently provided. For instance, if the bisulfate dimer ion had fragmented into a monomer during its transit to the vacuum system, an ion with the mobility of the dimer and the mass of the monomer would appear in Figure 9b. It is not clear in that figure if this fragmentation product is present or not, but

the same deconvolution used in Figure 9a would clarify the issue. On the other hand, it is certain from Figure 9b that the bisulfate trimer does not decompose into either a dimer or a monomer. Yet the tetramer does undoubtedly decompose partially into the trimer during its vacuum transit. This new experimental tool is therefore already telling us a lot about how the stability of these clusters changes with their size. It would be most helpful if the authors would refer to prior literature on the stability of sulfate or bisulfate clusters.

There are a number of other transitions revealed by figure 9b, whose less obvious potential relevance would call for additional input from the authors. For instance, a mass a little larger than that of the dimer (perhaps a solvated dimer) arises at voltages of about 1800 and 2250 Volts. These two ions decompose partly into the monomer on their way to the MS, providing some additional basis to the guess that they are indeed solvated bisulfate dimers. Similarly, an ion slightly heavier than the tetramer (perhaps a solvated tetramer) decomposes into the tetramer.

Another potentially interesting feature in Figure 9a is the presence of an ion at approximately half the monomer mass. Please, clarify if this is the doubly charged sulfate.

5. Minor remarks

*Following equation (1), *U* should rather be the velocity in the symmetry plane going through the center of the slit.

*The article states that "*The reason for the difference of resolving power between the two recirculation modes and the deviation from the theoretical calculation is the turbulence effect.*" I have my doubts about this interpretation. What would be its basis?

*Line 244 states "*the resolving power of planar DMA is directly related to V_{DMA} and Ne.*" Does *Ne* refer to the negative spray? Please clarify the relevance of this, as it is not at all clear.

*Line 165: The program *Igor* is quoted for mobility peak analysis. Would you please provide a little more background for those unfamiliar with this tool?

* The authors note that their recirculation circuit is not part of the commercial system, perhaps to warn readers of the possibility that DMA performance may depend on this component of the system. I doubt that the flow control part will be much effect on DMA performance, though I may be wrong. One original component in this recirculating flow system perhaps deserves some comment. This is the planar commercial HEPA filter, apparently sandwiched between two surfaces with NW-40 connectors. Would the authors please provide some more detail of this design?

* The reference to Fernandez de la Mora and Kozlowski given in Figure 5b must be incorrect, as their study did not include transmission measurements. The correct reference must be a later study by Attoui and colleagues.

6. Conflict of interest statement.

JFM collaborates frequently with authors Michel Attoui and JFM's former graduate student Mario Amo-Gonzalez.

JFM and his wife owned half of the now bankrupt company SEADM where Mario Amo Gonzalez led the development of the planar DMA P5. JFM remains keenly interested in the continuation of SEADM's efforts by others, including the company MION SL.

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