Referee #3

Discussion of: **Characterization of the planar differential mobility analyzer (DMA P5): 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.

We thank the reviewer for the comment. We have removed the abbreviations in the abstract in the revised manuscript. We agreed with the reviewer that it is inappropriate to described DMA P5 as newly developed, since Amo-González et al. have coupled DMA P5 with mass spectrometer in 2018. We have removed the "*newly developed*" in the revised manuscript.

Reference

Amo-González, M. and Pérez S.: Planar Differential Mobility Analyzer with a Resolving Power of 110, Analytical Chemistry, 90, 6735–6741, 10.1021/acs.analchem.8b00579, 2018

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 R2, which explains the advantage of the Half-Mini DMA (R2=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.

We thank the reviewer for the comment. The reviewer has listed numbers of outstanding works from the precedents about the ion transmission study of planar DMA and the comparison with cylindrical DMAs. Moreover, the reviewer also well illustrated the benefit of applying TDMA on studying the ion transmission of DMA P5 for atmospheric relevant study. We have cited these works in the revised manuscript.

Moreover, as being pointed out, the geometry of cubic chamber is related to the reported ion transmission efficiency. The inner geometry of cubic chamber was cylinder-shaped, with the diameter of 32 mm, and the height of 6.5 mm. A straight conductive silicone tube is inserted into the center of the cylinder-shaped space thorough the hole on the top of the chamber. The space between the conductive silicone tube and the hole is sealed with silicone glue. The injection end of the tube is connected to the beam splitter, while the exit end is at the same plane with the lower end of the chamber. When the chamber is sealed to the inlet electrode of DMA P5, the distance between the exit end of tube and the inlet slit of DMA P5 is about 5.2 mm. In the revised manuscript, the geometry of cubic chamber was reported. The detailed description of how the monodispersed THA^+ ions are injected to the inlet slit was also added in the revised manuscript. The added sentences are shown as following "….. *Downstream to the Half Mini DMA, DMA P5 operated at scan mode was connected between the flow splitter and the second electrometer. A 3D-printed cubic chamber was used was used to connect the inlet tube and DMA inlet slit. The inner geometry of cubic chamber was cylinder-shaped, with the diameter of 32 mm, and the height of 6.5 mm. The inlet tube was inserted straightly into the centre of the cylinder-shaped space thorough the hole on the top of the cubic chamber. The space between the conductive silicone tube and the hole was sealed with silicone glue. The injection end of the inlet tube was connected to the beam splitter, while the exit end was at the same surface with the lower end of the chamber. When the cubic chamber was sealed to the inlet electrode of DMA P5, the distance between the exit end of inlet tube and*

the inlet slit of DMA P5 is about 5.2 mm. …..". We hope other group using DMA P5 can find useful information from our work.

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.

We thank the reviewer for the comment. There were two main reasons that we chose the APi-TOF from TOFWORK AG to couple with DMA P5 for atmospheric relevant clusters study: *(1) Low detection limit*: the APi-TOF consists of a time-of-flight mass spectrometer (TOF) coupled to an atmospheric pressure interface (APi). The Api has three differentially pumped chambers, the first two containing short segmented quadrupoles used in ion guide mode, and the third containing an ion lens assembly. The APi-TOF has a very low background noise level and detection limit. Junninen et al., (2010) reported that the detection limit of the APi-TOF within the mass range of 80-900 was below 1 ion/cm^3. Taking the high ion transmission of DMA P5 into consideration, we think coupling DMA P5 with the APi-TOF have the potential for the measurement of atmospheric clusters. Moreover, both Api-TOF and Api-TOF coupling with a chemical ionization source (CI-API-TOF) have been successfully applied for atmospheric cluster measurement in laboratory and field, exhibiting the capability of detecting different atmospheric clusters, such as cluster complexes of sulfuric acid with ammonia (Kirkby et al., 2011; Lehtipalo et al., 2016), amine (Almeida et al., 2013; Yin et al., 2021), and organics (Riccobono et al., 2014). *(2)* **Adjustable APi configuration:** Fragmentation of molecular clusters inside MS is a significant source of uncertainty in a wide range of chemical applications. Different clusters fragmented differently inside MS due to the different binding energy (*Lopez-Hilfiker et al., 2016; Passananti et al., 2019*). The voltage configuration, combination of the voltages applied to the APi-TOF, can significantly affects the transmission and

fragmentation of clusters. By the combination of API-TOF and DMA-P5, we aim to study the physiochemical properties of the selected atmospheric (relevant) clusters (based on their ion mobility) by adjusting the voltage configuration, scanning the electric field strength within the transfer optics in real time while measuring a steady-state distribution of the selected clusters. With this function, we can experimentally determine the electric field strength required to break apart atmospheric (relevant) clusters, which are directly related to the binding energy of the clusters. The related experimental results are not within the scope of this work, and will be reported in another paper, currently under preparation. In the revised manuscript, we have added the consideration of why we choose API-TOF to couple with DMA P5. The revised sentences are shown as following "……. *API-ToF-MS has a very low background noise level and detection limit (< 1 ion/cm3, Junninen et al., 2010). Moreover, both Api-TOF and Api-TOF coupling with a chemical ionization source (CI-API-TOF) have been successfully applied for atmospheric cluster measurement in laboratory and field, exhibiting the capability of detecting different atmospheric clusters, such as cluster complexes of sulfuric acid with ammonia (Kirkby et al., 2011; Lehtipalo et al., 2016), amine (Almeida et al., 2013; Yin et al., 2021), and organics (Riccobono et al., 2014). By the combination of API-TOF and DMA-P5, it is also possible to study the physiochemical properties of the atmospheric relevant clusters scanning the electric field strength within the transfer optics (Lopez-Hilfiker et al., 2016). ……..*".

Reference

Passananti, M., Zapadinsky, E., Zanca, T., Kangasluoma, J., Myllys, N., Rissanen, M. P., Kurtén, T., Ehn, M., Attoui, M., Vehkamäki, H., How well can we predict cluster fragmentation inside a mass spectrometer? Chemical Communications 2019, 55 (42), 5946-5949.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., et al. (2011). Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. Nature 476 (7361), 429–433. doi:10.1038/nature10343.

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Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., D'Ambro, E. L., Kurtén, T., and Thornton, J. A.: Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, Atmos. Meas. Tech., 9, 1505–1512, https://doi.org/10.5194/amt-9-1505-2016, 2016.

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.

We thank the reviewer for the comment. We have added more discussion on the cluster fragmentation. The revised manuscript is shown as following "……. *Since the voltage configurations can affect the fragmentation of the cluster inside the API-ToF-MS (Passananti et al., 2019), the DMA-MS spectrum is highly instrument dependent. Cautions should be paid on the comparison between different experiments. Given that the clusters forming as precursors to atmospheric nucleation are physically bound and often 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 the transfer to the vacuum system. The situations are even more complicated if fragmentation*

arise prior to or during the mobility measurements. Therefore, it is important to consider the fragmentation when interpreting the DMA-MS measurements. Ions with smaller mass but appearing at the same mobility of parent ions are originated from dissociation or decomposition. Under the condition that not all parent ions are fragmented into smaller ions within the mass analyzer, we can determine which ions detected in the MS are the original ions selected in the DMA, and which are fragments. As shown in Fig. 9b, except for SA multimers, cluster of methyl sulfate with $(SA)_1^-$ $(CH_4SO_4HSO_4^-)$ was observed at the different mobility (VDMA of about 1800 V and 2250 V). Cluster of ammonia molecule adducted on $(SA)_4^-$ was also identified at VDMA of about 2450V. The first three peaks identified in the mobility spectrum (Fig 9a) were NO_2^-, CO_3^- and CHO_4^-. To further interpret the fragmentation, the ion mobility spectrum at the mass to charge ratio of the main observed ions/cluster-ion adducts was discussed (Fig S6): both $(SA)_1^-$ and $CH_3SO_4^-$ showed two peaks, with the latter one being fragments originated from $CH_4SO_4HSO_4^-$. The mobility of $(SA)_1^-$ and $(SA)_2^-$ was close, making the separation of $(SA)_1^-$ and $(SA)_2^-$ fragments difficult. Hower, it is unlikely that $(SA)_2^-$ fragmented contributed largely to $(SA)_1^-$, due to an obvious difference in centroid mobility. The latte two peaks of $(SA)_2^-$ were the fragments from $(SA)_3^-$ and cluster of methyl sulfate with $(SA)_2^-$ $(CH_4SO_4 (H_2SO_4) HSO_4^-)$. $(SA)_4^-$ would fragment into $(SA)_3^-$ via losing one sulfuric acid molecule and originate from the fragmentation of NH_3-$(SA)_4^-$ and larger clusters. Under our experimental configuration, the interference of fragmentation on the intensity of SA clusters is minor (<10%). When the (CI)-API-TOF was deployed for atmospheric measurements, the instrument configuration should be checked by using similar experimental set up to avoiding underestimate of the clusters due to large de-cluster ratio.".

5. Minor remarks

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

We thank the reviewer for the comment. We have corrected the description of U in the revised manuscript.

*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?

We thank the reviewer for the comment. Firstly, we used the corrected formula to calculated the resolving power. The new formula is corrected from Amo-González et al. (2018). The derivations are added in the revised SI. The current resolving power, similar with the pre-delivery test at SEADM, is lower than the theoretical values. As shown in Eq. (4), except for the flow rates of mono/ploy-dispersed aerosol, and the geometry of DMA P5, the term affects the resolving power is the Reynolds number. We have compared with the reported experimental results with Amo-González et al. (2018), our results were approximately the same with the reported results (R=79, under V_{DMA}= 5500, for THA$^+$ monomer) without adding prelaminarizers into the recirculation system, which supports the Eq. (4). Moreover, the main difference between the two recirculation modes is that under suction mode polydiserpersed aesosol (at the flow rate of 2L/min) was injected from ESI chamber into the separation region from the inlet slit, while under counter flow mode countflow (at the flow rate of 0.5-1L/min) flow out of the separation region through the inlet slit. We think the way the ions inserted, which leads to different laminar condition of the sheath flow, results in the difference of the resolving power. As the decreased laminar condition is likely due to the extra turbulence effect for the flow injection. Consequently, we made the statement that it is the laminar condition that lead to the lower resolving power.

References

Amo-González, M. and Pérez S.: Planar Differential Mobility Analyzer with a Resolving Power of 110, Analytical Chemistry, 90, 6735–6741, 10.1021/acs.analchem.8b00579, 2018

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

We thank the reviewer for the comment. Ne represents the net charge of the aerosol. We have added the description of Ne in the revised manuscript.

*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?

We thank the reviewer for the comment. We have added the description of the analysis package used for multipeak fitting. We used Multi-peak Fitting 2 package embedded in Igor program for the peak fitting. This package was designed to provide curve fits to multiple, overlapping peaks of any sort

of measurement that results in localized peaks or lines. The program can also give you an estimate of the peak heights, widths, locations and areas.

* 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? *

We thank the reviewer for the comment. The original intension of mention the home-build recirculation system is that all components can be purchased from the local market. Our reported transmission and resolution are expected to be reproduced under suction mode or counter flow mode of DMA P5 with any recirculation system providing temperature-constant, aerosol-free, stable sheath flow. We agree with the reviewer that emphasizing home-build recirculation system can lead to the misunderstanding that the reported results may not be able to apply to other P5 DMA systems due to the difference in the recirculation system, which is not our original intention. In the revised manuscript, we have removed the descriptions of "*the home-build*", emphasizing the universal characteristics of the recirculation system that should be applied within DMA P5 system in section.

We have provided more details of the design how we put the HEPA filter into the recirculation in the revised manuscript. The provided description is shown as following "*The particle filter consists a planar commercial HEPA filter (Ref 34230010, Megalem MD143P3, Camfil Farr) and two stainless assembly. Top side of the assembly is a NW40 connector, while the bottom side fits the geometry of the planar HEPA filter. The HEPA filter is sandwiched between the two bottom surfaces of the two assembly, sealed with O-ring and screws.*"

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.

We thank the reviewer for the comment. We have corrected the reference in the revised manuscript. The reported transmission efficiency for HalfMini (p) is the internal data from SEADM.

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.

References

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