Interactive comment on "Characterisation of the transfer of cluster ions through an Atmospheric Pressure interface Time-of-Flight mass spectrometer with hexapole ion guides" *by Markus Leiminger et al.*

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We thank referee #3 for his comments. Those will help us to improve our manuscript. In the following, we present our reply. The reviewer's comments (RC) are marked in *italic*, our replies (AC) follow in Times New Roman and the updated text is shown in blue.

RC: 1. Why hexapoles not octupoles or higher order multipoles are employed in the instrument? What are the advantages by using the hexapoles as the ion guide compared to those high multipoles? There are also some literatures available in modelling ion trajectory for the multipoles. It will be of interest to the readers if the authors can add a brief literature overview in this aspect

AC: We thank referee #3 for his questions regarding our choice of the hexapole. In general, it would also be interesting to see if higher multipoles would yield even more advantageous properties for the transfer of weakly bound cluster ions. In this study, we chose the hexapole ion guide as the next logical step after the quadrupole because of its properties. These are increased mass range, lower effective potential close to the centre and an enhanced focusing compared to the octopole. The higher mass range of the hexapole might already be sufficient for the study of a broad range of atmospheric ions and clusters without a low-mass cut-off as known from the quadrupole. Other applications could of course profit from higher mass ranges or higher charge capacities using higher multipoles. We added a brief overview about ion trajectory simulations.

Line 127: Ion trajectory simulations through a quadrupole, a hexapole and an octopole by Hägg and Szabo (1986) showed that higher multipoles ($n \geq 3$) are more suited for guiding ions while only the quadrupole can be used as a mass analyser. In an accompanying study, the authors found that the transmission through higher multipoles depends on the initial conditions of the ion beam, e.g. initial position or velocity (Hägg and Szabo, 1986a). The reason for this is that the x- and y-coordinates are no longer independent compared to the quadrupole. An overall lower transmission efficiency of ions could be a likely consequence. Hägg and Szabo (1986) found in another study

that the multipoles of even-order like the octopole have more stable trajectories because the opposing electrodes have the same sign whereas multipoles of odd-order like the hexapole have opposing electrodes of opposite sign. This would be one benefit using an octopole over a hexapole despite otherwise similar transfer properties. For further ion trajectory simulations in multipole ion guides with focus on phenomena like collisional cooling and radial stratification of different m/z ions due to ion-ion and ion-neutral interactions we refer the reader to Tolmachev et al. (2003) and references therein.

RC: 2. Figure 4 shows the overall transmission efficiency of the instrument. It would be beneficial to the readers if the authors provide detailed supplementary material information to illustrate the detailed process how to come up with the transmission efficiency curve since this is a very important part of the instrument calibration, e.g., what flow value was used, how to account for the fragmentation etc.

AC: We thank referee #3 for this suggestion. We created supplementary material information and added more details about the way we determined the transmission efficiency.

Line 191: An exemplary ion mobility spectrum is shown in the supplement Fig. S1.

Line 197: For the same reason, the flow rates to both the FCE and the ioniAPi-TOF are set equally to 6 L/min resulting in an overflow of 2 L/min.

Line 262: Additionally, minor peaks of impurities or fragments were observed, see Fig. S2.

RC: 3. The distribution of the hydronium ion clusters with various voltage gradients between the skimmer and the second hexapoles shown in Fig. 7 is apparently dependent on many factors including the initial energy of the cluster (determined by the voltage applied in the entrance aperture), the voltage on the skimmer (currently grounded), the voltages on the lenses after the second hexapole. It is hence that the distribution may look differently under other settings. Did the authors try any other settings? How those voltages may affect the distribution, especially how those voltages affect the detection sensitivity of the instrument?

AC: We agree with referee #3 that the distribution may look differently under other settings e.g. m/z dependent transmission effects by varying the RF settings of the first hexapole. In the current configuration of the ioniAPi-TOF, no voltages can be applied in the entrance aperture besides the RF voltage on the first hexapole. Therefore, no axial DC electric fields can have an impact on the tested hydronium cluster distribution. The voltage on the lense after the second hexapole plays an important role regarding transmission effects and fragmentation. We tried other settings and we provide the results of these experiments in the supplement.

Line 358: The initial cluster distribution may look differently depending on the conditions in the first pressure stage like pressure or electric fields, e.g. different RF settings on the first hexapole can alter the mass dependent transmission.

Line 420: It has to be noted that the ion transmission shows strong responses for even small voltage differences between ion optic parts. A DC offset of only 0.2 V on the second hexapole for example can significantly improve the ion transmission compared to no offset. To maintain a satisfying detection sensitivity the electric potentials of the second hexapole and the following lens should be set closely.

RC: 4. In section 3.2.3, the authors assume that the binding energy is linear with the voltage gradient between the skimmer and the second hexapole and estimate a threshold binding energy of about 8-10 kcal/mol for the hydronium ion clusters. The question is: how good is this assumption? It seems that the proposed binding energy is rather subjectable.

AC: We agree with referee #3 that this threshold binding energy is only an estimation of the results from the dV scanning procedure and not experimentally determined. Nevertheless, these values are given to present an orientation to the reader to classify the performance of the ioniAPi-TOF compared to one exemplary APi-TOF from the literature.

Line 409: The results from section 3.2.2 allow establishing an approximate threshold cluster binding energy for a fragment-free transfer through the mass spectrometer as an example for the applied conditions. These results may vary under different conditions.

RC: 5. In Fig. 9, it is difficult to tell that the higher sensitivity from the ioniAPi-TOF in the higher mass range is real or just due to higher background noise since the signals are almost flat above 700 m/z for the instrument compared to the APi-TOF. In addition, the comparison will be in a better view if the scale of the upper and bottom panels is set to the same physical height.

AC: We thank referee #3 for his comment on Fig. 9. The apparent higher sensitivity of the ioniAPi-TOF is probably not that real. The lower mass resolution comes along with slightly higher background noise. In addition, the correction for inlet line losses yielded a higher correction factor as the inlet line of the ioniAPi-TOF was much longer. The scale could be changed to a more technical unit like ions per extraction. As we compare a medium sized TOF mass analyser (H-TOF, Tofwerk) and a compact TOF mass analyser (ioniTOF1000, Ionicon Analytik), differences in the analyser lengths will automatically result in different extraction frequencies. The extraction

frequencies are given in Fig. 8 and show that a scaling on the extraction frequency will reduce the signals of the ioniAPi-TOF by a factor of roughly 3.

Line 488: The apparent higher sensitivity of the ioniAPi-TOF for high mass ions can be explained with a higher background noise due to the lower mass resolution. The correction for inlet line losses and the threefold higher extraction frequency, values given in Fig. 8, of this compact TOF mass analyser compared to the medium-sized APi-TOF contribute as well.

RC: 6. 1) Some figures mentioned in the text were not in order. Please follow the correct order for the figure mention; 2) Consistency: for example, sometimes "at ground level" is used and "at ground levels" is used in other occasions; line 400, 406, 411 on p.13, First, Secondly, Thirdly: : :, please rephrase them to be consistent.

AC: 1) We corrected the order in lines 169 and 184. 2) We changed line 29 to "at ground level". 3) We rephrased all lines with "firstly, secondly, thirdly" to "first, second, third" for consistency.

Additional references

Hägg, C. and Szabo, I.: New ion-optical devices utilizing oscillatory electric fields. II. Stability of ion motion in a two-dimensional hexapole field, Int. J. Mass Spectrom. Ion Process., 73(3), 237–275, doi:10.1016/0168-1176(86)80002-7, 1986.

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