Authors' response to referee comment RC1
on manuscript
"Development of an Automatic Linear Calibration Method for High Resolution
Single Particle Mass Spectrometry: Improved Chemical Species Identification
for Atmospheric Aerosols"

We thank Referee #1 for the comments and suggestions. We have addressed every comment and made significant changes to the paper to improve the paper. Again, the referee's comments are greatly appreciated.

Referee Comments in black bold.

Authors' Response **in** blue.

Changes in manuscript **in** *Red italic.*

Major comments

This paper develops an automatic linear calibration method to calibrate the mass spectra for individual particles measured by newly developed HR- SPAMS. The method improves the current accuracy of mass-to-charge (m/z) measurement for single aerosol particles, based on the testing of laboratory-generated sea spray aerosol and atmospheric ambient aerosol. The authors provided the time series of peaks with small m/z differences and a comparison of particle classification between LR-SPAMS and HR-SPAMS. While this method may be applicable to the scientific community, there are still some limitations. The main criticism is the limited discussion of the analysis of newly generated mass spectra by the HR-SPAMS, and the lack of discussion on why only sea spray aerosols were selected. It is certainly TRUE that applying high-resolution data with enhanced mass calibration can significantly affect particle classification (identification). However, it is more important if there is new information obtained from the classification.

Response:

We agreed that the discussions of the analysis of newly generated mass spectra by the HR-SPAMS are limited and the new information obtained from the classification is not enough in the original manuscript. In the revised manuscript, we have added the more detailed discussions of the HR-SPAMS mass spectra and illustrated why we selected sea spray aerosols as a case study, which considers the sea spray aerosol chemical compositions are relatively simple, compared to the ambient aerosol chemical compositions. The calibration method was evaluated to apply both in simple and more complicated systems. Meanwhile, based on the referee's comments, some new information, obtained from the classification, is added.

Changes in manuscript:

Line 99-107:

"In this study, we report a calibration method for single particle high resolution mass spectra data. Based on the assumption that the sea spray aerosol has relatively simple chemical composition while the ambient aerosol has more complex chemical composition, the performance of the calibration method had been evaluated in detail for these two aerosol systems with different complexity. In addition, the impact of using high resolution SPAMS data on particle classification by ART-2a algorithm was assessed. An open source code specific for

HR-SPAMS was made and we proposed the principle of this calibration method can be applied into some similar instruments, such as single particle mode Aerosol Mass Spectrometer (AMS)."

Line 273-280:

"More importantly, $139[C_2H_3O_5S^-]$ (the theoretical m/z value: -138.97) can be clearly distinguished from other possible assignments, such as $139[C_{11}H_7^-]$ with the m/z value of -139.55 and $139[AsO_4^-]$ with the m/z value of -138.90. Moreover, $153[C_3H_5O_5S^-]$ with theoretical m/z value of -152.986 can be distinguished from other possible assignments, such as $153[C_{12}H_9^-]$ with m/z value of -153.070 and $153[Na_2Cl_3^-]$ with m/z value of -152.883. These two important organic ion peaks have been suggested to be the characteristic ion peaks for the organosulfates in secondary organic aerosols (Surratt et al., 2010; Surratt et al., 2007)."

Line 319-347 :

"The ART-2a classification of the HR-SPAMS results (Fig.S6) show that the signal at $23[Na^+]$ in Type 2HR was stronger than Type 1HR while the signals at $26[CN^-]$ and $42[CNO^-]$ were weaker in Type1 HR. Meanwhile the averaged mass spectra of the Type 2HR showed the presence of $206[Pb^+]$, $207[Pb^+]$ and $208[Pb^+]$, which are known to be harmful to human health (Das et al., 2018; Peng et al., 2020). Furthermore, particles of Type 2HR containing abundant secondary inorganic components like $[NO_2^-]$, $[NO_3^-]$ and $[SO_4^-]$, which originated from the aerosol aging processes (Dall'Osto and Harrison, 2012; Ma et al., 2016). In contrast, these two first particle types were lumped together into Type 1LR in the LR-SPAMS classification results (Fig.S5). Due to the merge of these two particle types, [Pb+] ions were not significant. Meanwhile, Type 3,4, 5HR classification results contain strong signals at $26[CN^-]$, $42[CNO^-]$, $46[NO_2^-]$, $62[NO_3^-]$ and $97[HSO_4^-]$, suggesting that these three types were from biomass burning or residential cooking burning. $[K^+]$ is also another feature of this type particle emission(Bi et al., 2011; Hudson et al., 2004). There were obvious relative ion intensity differences at $26[CN^-]$, $42[CNO^-]$, $46[NO_2^-]$ and $62[NO_3^-]$ among these types, which implied that these three particle types might be from different burning sources or experienced different levels of aging (Luo et al., 2020). While these three particle types were lumped together as Type 2LR. This critical information which could be potentially used to distinguish particle sources and aging processes was lost. Additionally, Type 7HR can be assigned as ECOC type, based on its strong signals at $[C_x^+]$, $[C_xH_y^+]$ and $[C_xH_yO_z^+]$. Particles of this type may come from the primary emission sources, and the emitted black carbon particles would also form this type particles after absorbing some low volatile organic compounds in the atmosphere(Sodeman et al., 2005). $97[HSO_4^-]$ can be observed to have a weaker signal than $62[NO_3^-]$ and $46[NO_2^-]$, which implied that the secondary reaction of SO_2 as the precursor of HSO_4^- was not significant in the particle surface for ECOC type particles in this study (SULLIVAN and PRATHER, 2007). In contrast, the classification results of the LR-SPAMS were not so clear and generated less particle types. Given HR-SPAMS spectra have much more detailed chemical information about particles, we would propose that the ART-2a classification of HR-SPAMS might be more accurate."

Specific comments：
1. Introduction: similar instruments, such as Aerosol mass spectrometer (AMS), also have

high-resolution versions. Is the calibration method identical to SPAMS? Inclusion of this in the introduction and discussion would be necessary for completeness.

We agree with the referee's opinion, and decided to make an additional instruction in the introduction and conclusion for paper completeness. Our open source code of calibration method was specific for high-resolution SPAMS, while the principle of this calibration method can be applied into some similar instruments such as AMS.

Changes in manuscript:

Line 104-107:

"An open source code specific for HR-SPAMS was made and we proposed the principle of this calibration method can be applied into some similar instruments, such as single particle mode Aerosol Mass Spectrometer (AMS)."

Line 373-376:

"All the automatic linear calibration method codes specific for HR-SPAMS are open access and can be found at https://github.com/zhuxiaoqiang- fdu/zhuxiaoqiang-fdu. And we proposed the principle of this calibration method can be adopted in other aerosol mass spectrometers."

2. Lines 80-85: In this section, it would be better to state the significance of why the calibration is required for each particle. While the authors noted that the ion peak position is still very susceptible to initial ion coordinate and speed, they did not provide details to show the significance.

We agree with the referee's opinion, and added an additional statement of the reason why the calibration is required for each particle and provide the details to show the significance of the initial ion coordinate and speed.

Changes in manuscript:

Line 85-94:

"Unfortunately, in spite of resolution enhancement with this new technique, ion peak position was still very sensitive to initial ion coordinate and speed. Chudinov et al., has demonstrated that the ion peak shifts of 208[Pb^+] and 147[$Na(NO_3)_2^-$] could be varied in the range of ± 10 ns and the ion start position could be varied in the range of $\pm 150 \mu m$. As a result, substantial peak jittering is observed when switching between mass spectra of each individual particle. This peak jittering leads to a fact that isotopic pattern identification becomes more difficult by averaged mass spectrum(Chudinov et al., 2019). Furthermore, the peak jittering is different in each single particle mass spectrum. In other words, the calibration parameter for each mass spectrum should be significantly different and calibration is required for each particle."

3. Line 192: "1,409 ambient particles were successfully calibrated". Why some fraction of particles cannot be calibrated? I think the discussion of such an issue in section 3.3 should be moved here to provide clear reasoning. Such an obvious deficiency should also be stated in the abstract or conclusion.

We agree with the referee's opinion that it's an obvious deficiency. This is mainly due to the reason that we set the threshold of absolute ion intensity 15 a.u for marker ions in the

ambient aerosols and 8 a.u in the sea spray aerosols. And a particle was discarded from the spectrum database if it did not have enough reference ions (the minimum number of reference ions was set to be 5) in either positive or negative mass spectrum. And now we have made a clear reasoning in the section 3.2 and also stated in the conclusion.
Changes in manuscript:
Line 210-213:
"And 4,624 sea spray particles and 1,409 ambient particles were successfully calibrated. As some fraction of particles had been filtered because their mass spectrum did not have 5 or more reference peaks to conduct the calibrations. To mitigate this problem, we proposed some adjustments in the next section."

Line 370-373:
"There is a deficiency of this HR-SPAMS calibration method, which has been showed that some fraction of particles cannot be calibrated due to the presence of weak signals of the marker ions. It can be mitigated by applying some additional marker ions."

4. What is the matrix size produced by the HR-SPAMS? Is there a limit for the ART-2a to classify the matrix of particle mass spectra? Such information should be included.
As there is 25,000 bins in either positive or negative single mass spectrum and we handled about 1,400 particles in this study. The matrix size is about $25,000 \times 2 \times 1400 = 7e7$. There was no absolute limit for ART-2a as long as the database was not extremely large, like the experiment data lasting for several months. And we have made the following additional statement to include this necessary information in our revised manuscript.
Changes in manuscript:
Line 305-306 :
"The previous ambient aerosol SPAMS dataset (1,400 particles) was used for the matrix size of the ART-2a is around 7×10^7."

5. Section 4.4: What kind of new information is provided when new matrix is included in the classification? I think it would be interesting if there is new information after the classification of newly calibrated mass spectra.
It is the same comment as the referee's major comments. We agree with the referee's comment that the discussions of our new classification results are not quite sufficient in our original manuscripts. And now we have made a more comprehensive discussions, as we responses to the referee's major comments above.

6. Some peak ions should be added to Fig S5 and Fig S6 for clearance.
We have added the necessary peak ions in the Fig S5 and Fig S6 for clearance in our revised supplement.
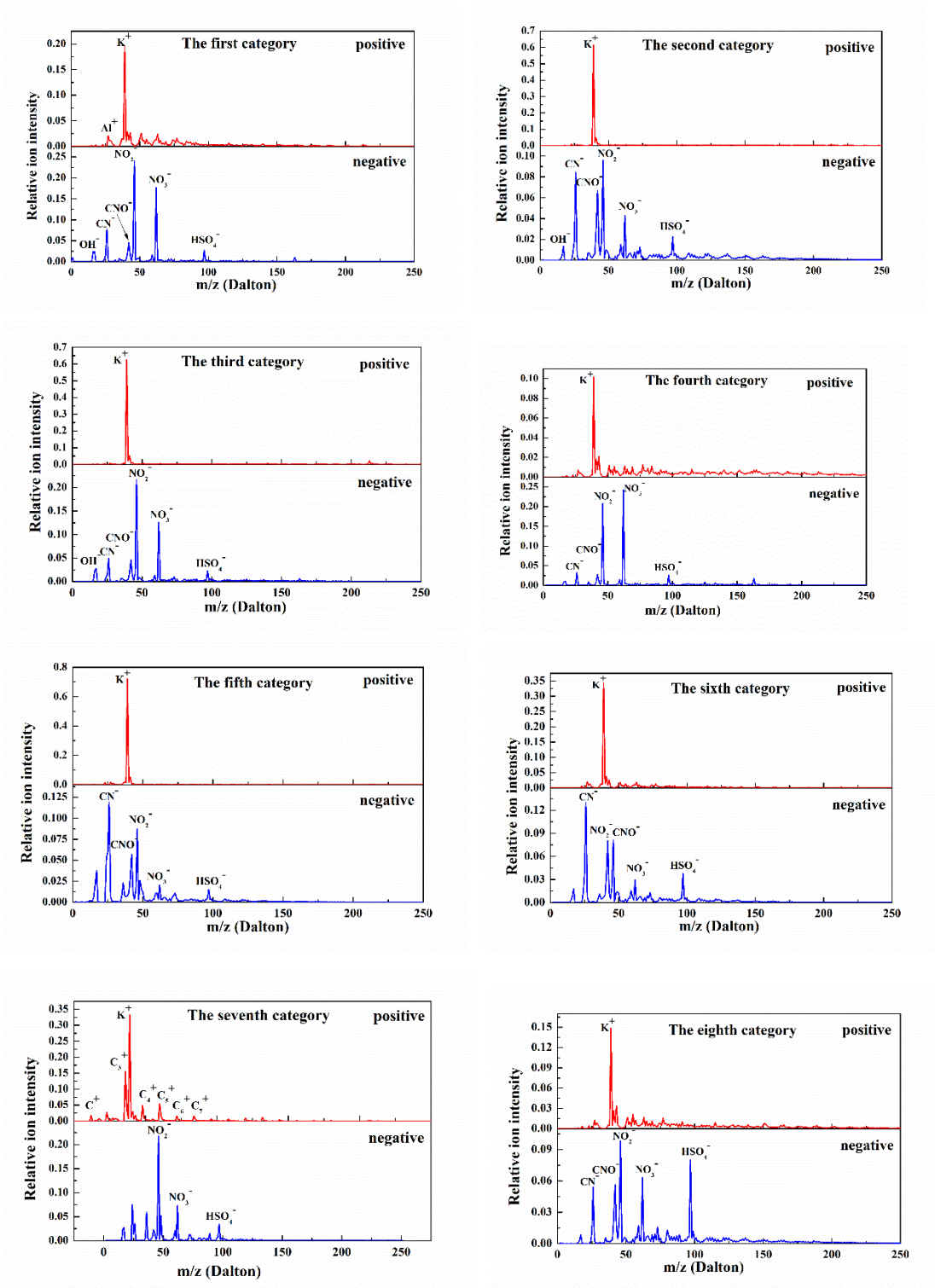Changes in supplementary material:

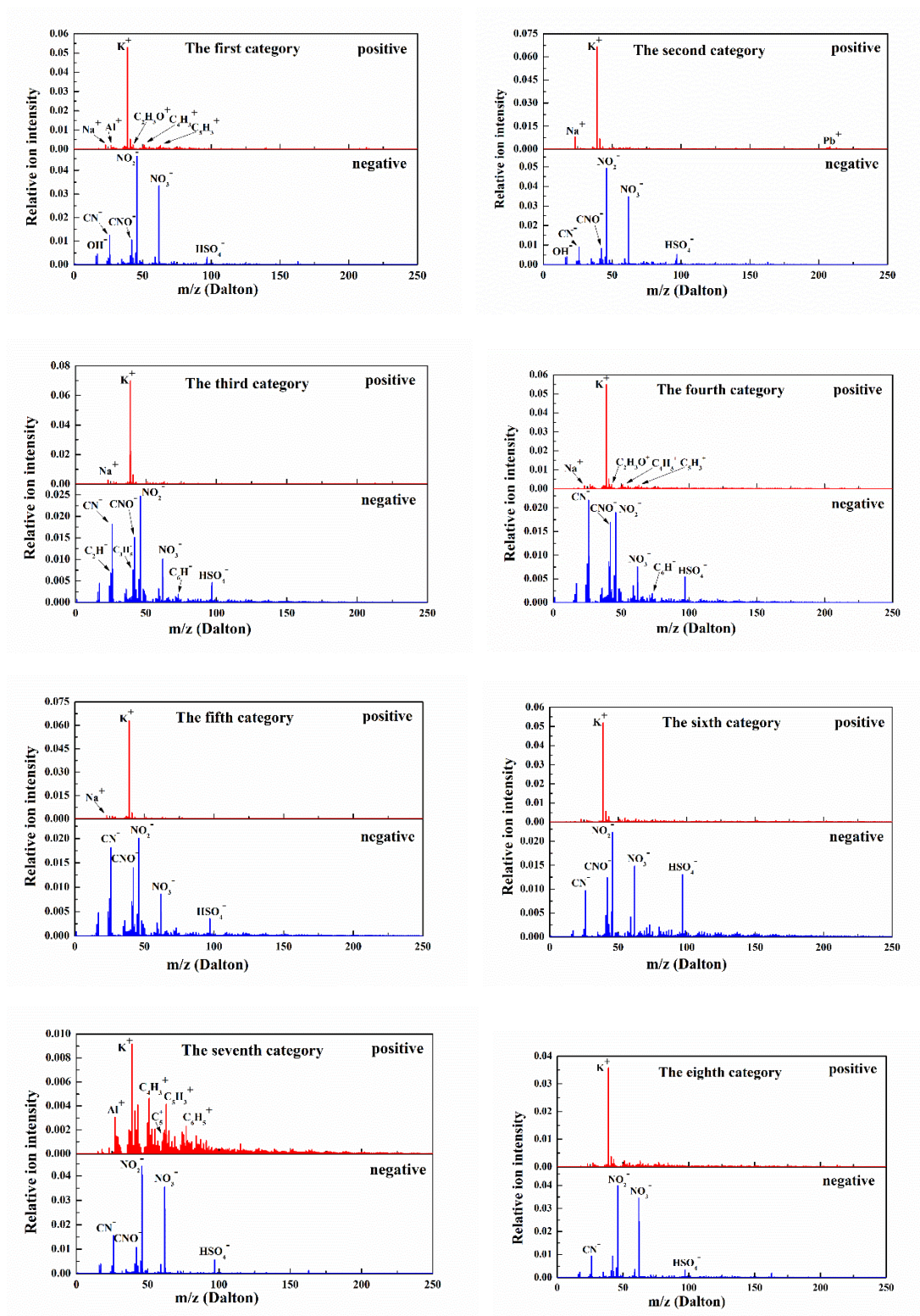Figure.S5 Classification results of the LR-SPAMS by ART-2a

Figure.S6 Classification results of the HR-SPAMS by ART-2a

7. Conclusion: It would be better to include some atmospheric implications for the identification of additional peaks, in particular, organic peaks. Currently, the authors showed that more particle types can be obtained, but it might not be meaningful enough for the scientific community.

We agree with the referee's comments and here is the revision:

Changes in manuscript:

Line 358-370:

"With this method, HR-SPAMS can also determine the time series of organic and inorganic peaks, whose m/z are very close to each other (e.g. $41K^+$ with the theoretical m/z value at 40.96182 and $C_3H_5^+$ with the theoretical m/z value at 41.03913). Important organic ion peaks, such as tracer peaks for secondary organic matter like $139[C_2H_3O_5S^-]$ and $153[C_3H_5O_5S^-]$, can be identified. More importantly, our ART-2a classification from HR-SPAMS dataset clearly showed a particle type containing heavy metals like Pb^+, which was obviously ignored in the ART-2a classification from the LR-SPAMS dataset. More particle types were generated by the ART-2a classification of HR-SPAMS data compared to that of LR-SPAMS data, as the original biomass burning particle type can be divided into three more detailed types based on the different signals of $26[CN^-]$, $42[CNO^-]$, $46[NO_2^-]$ and other organic species like C_xH_y and $C_xH_yO_z$, implying different aerosol aging processes or burning conditions. Such detailed information may be critical to study the aging processes and source appointment of atmospheric aerosols."

8.Grammar check
Line 70: LDI?
Line 77: "A SPAMS"
Line 99: "accessed"

We have made correction to the grammar issues.

Changes in manuscript:

Line 71-72:

"However, SPAMS with laser desorption/ ionization (LDI) method has several serious limitations (Manuel et al., 2006; Wenzel et al., 2003)."

Line 79:

"A higher mass resolution version of the SPAMS with better m/z accuracy is needed."

Line 103-104:

"In addition, the impact of using high resolution SPAMS data on particle classification by ART-2a algorithm was assessed."