Response to Editor

We sincerely thank the valuable comments and suggestions from the editor, and have extensively revised our manuscript accordingly. Here, we provide the point-by-point replies.

Editor

Thanks for answering the comments from both reviewers. After reviewing all the comments, replies and the revised manuscript, though I appreciate the fairly novel method by the authors to improve the accuracy of m/z determination for the single particle mass spectra, I found a few places need more information and explanation, besides the current replies from authors.

The main argument of the comments from one reviewer is about whether the separation between V+ and C4H3+ at m/z51Th is real or can be applied to the ambient air.

1) The raw and calibrated peaks at 51Th of single particles should be given. A few examples of single particle mass spectra around 51Th in both raw and calibrated forms will help, rather than only showing the averaged mass spectra in Fig. 5. This will answer referee's comments about whether both V and C4H3 may exist in the ambient air, and can also demonstrate how well your algorithm may work.

Response:

We sincerely thank the editor's suggestion. We have randomly chosen 10 V-containing particles and 10 C_4H_3-containing particles as examples for illustration, and plotted their raw and calibrated peaks at around ~51Th in our revised manuscript (Fig. 5e). The *m/z* of raw peaks are randomly distributed, which means the corresponding chemicals of these peaks could not be determined before the calibration. During the calibration, we tried all possible coefficients in the coefficient space, and the optimal coefficient was obtained using our value function. In other words, the calibrated m/z value of peak around 51 Th is determined by assessing the whole spectrum. We revised our manuscript in Lines 230-233 as:

For instance, we randomly chose 10 V^+-containing and 10 $C_4H_3^+$-containing particles, with single-particle mass spectra (raw and calibrated) provided (Fig. S4). The peaks, both raw and calibrated, at ~51 Th in these particles are illustrated in Fig. 5e. The corresponding species (V^+ or $C_4H_3^+$) of these peaks can easily be determined after our calibration (Fig. 5e, Text S4).
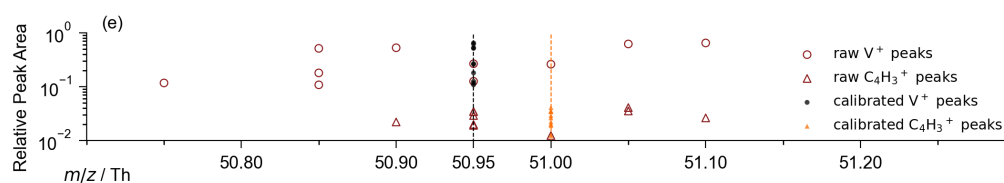
***Figure 5.** (e) Raw and calibrated peaks around 51 Th of 20 V^+-containing and 10 $C_4H_3^+$-containing particles.*

In addition, we provided the raw and calibrated single-particle spectra of the examples in Figure S4.

We believe the modification could help the reader's understanding of our calibration of the mass spectrum of single particles.

2) The authors should more explicitly explain why 50.95 should be assigned with V. The argument is about whether this has been proved in the laboratory. By tracking the literatures, I can see the original validation for V 50.95 is from the table 2. Du et al. has published the lab work where they generated particles with V mixing with other substances in single particle, and they found both peaks of 51 and 50.95 in single particle. I wouldn't think the authors need to repeat this lab work, but a full explanation (with clear reference supporting your results) should be given to explanation what 51 and 50.95 should be assigned with. This should come with the single particle mass spectra above to demonstrate how both compositions may separate or mix with each other in the ambient air.

Response:

We sincerely thank the editor's comment. When assigning peaks with the corresponding species, we first compare the calibrated mass to the exact mass. For instance, given the 500-ppm accuracy after calibration, m/z in the range of 50.925-50.975 Th are labeled 50.95 Th. Therefore, when assigning the corresponding chemicals of peaks at 50.95 Th, all possibilities whose exact m/z at 50.925-50.975 Th should be checked. We have calculated all possible species based on the mass of atoms and electrons. Here, we listed all species at ~50.95 Th in Table S2, and compared our result with the NIST database and the PubChem database.[1,2] Since all of the species are obtained by theoretical calculation, we only consider the species that can be found in the two databases.

Table S2. Possible ions around 50.95 Th under 500-ppm accuracy.

Ion	Exact m/z (Th)	NIST	PubChem
V^+	50.9434	Have data	Have data
SF^+	50.9699	Have data	Have data
ClO^+	50.9632	No data	No data
TiH_3^+	50.9709	No data	No data

However, for the remaining candidates, we should further check their stability and existence in the atmosphere. For instance, SF^+ is unstable and rarely encountered in the atmosphere. Instead, the existence of V^+ in atmospheric aerosols has been widely reported.[3–8] Therefore, we consider V^+ to be the corresponding species at 50.95 Th. Additionally, most 50.95-Th-containing spectra also contain peaks at 66.95 Th (the exact mass of VO^+), indicating the assignment of V^+ at 50.95 Th is self-consistent.

We applied the same method when assigning the possible species at 51.00 Th. Possible ions around 51.00 Th under 500-ppm accuracy (50.925-50.975 Th) are listed below (Table S3).

Table S3. Possible ions around 51.00 Th under 500-ppm accuracy.

Ion	Exact m/z (Th)	NIST	PubChem
AlC_2^+	50.9810	No data	No data
$CBSi^+$	50.9857	No data	No data
ClH_2N^+	50.9870	Have data	No data
$LiOSi^+$	50.9872	No data	No data
FO_2^+	50.9877	No data	No data
H_3OS^+	50.9900	No data	Have data
$H_3Mg_2^+$	50.9930	No data	No data

CH_4Cl^+	50.9996	No data	Have data
CHF_2^+	51.0041	Have data	Have data
$CLiO_2^+$	51.0053	No data	No data
C_3HN^+	51.0104	Have data	Have data
H_5NS^+	51.0137	No data	No data
$C_4H_3^+$	51.0229	Have data	Have data

The existence of most of these species has not been reported in previous studies. Elements in some species are in trace amounts in the atmosphere, including B, F, and Li. Species like ClH_2N^+ have more than one heteroatom, which makes the occurrence of these species in the mass spectra lower than simple species that contain only C, H, and N. For these reasons, we only consider $C_4H_3^+$ and C_3NH^+ as candidates at 51.00 Th. As shown in Figure 5 and Figure S4, spectra containing 51.00 Th also contain peaks at 12.00 Th (C^+), 36.00 Th (C_3^+), 37.00 Th (C_3H^+), 38.00 Th ($C_3H_2^+$), 39.00 Th ($C_3H_3^+$), 43.05 Th ($C_3H_7^+$), and 50.00 Th ($C_4H_2^+$). The combination of all these species is consistent with the distribution pattern of $C_mH_n^+$ fragments. Therefore, we assign 51.00 Th as $C_4H_3^+$ in our study. Further, the existence of $C_4H_3^+$ has been reported in previous studies (including both lab and ambient-measurement studies).[4,5,9,10]

In the revised manuscript, we have added a detailed explanation (Text S4) about determining the corresponding chemical species at 50.95 Th and 51.00 Th, which we think could help the reader's comprehension.

Reference

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