

Comment

Reply to the comment on ‘ Te_nS_4^+ ($n = 1-4$) clusters in the gas phase’ by Z. Špalt, M. Alberti, and J. Havel

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Abstract

Recently we reported the existence of TeS clusters, Te_nS_4^+ ($n = 1-4$) in the gas phase. The ions were detected in the laser desorption mass spectrum of bulk TeS powder. Špalt et al. have commented that there was ambiguity in that assignment and suggested that the peaks reported by us are due to Te clusters and not due to TeS clusters. Here in this reply, we show that there are unique features for the Te_nS_4 clusters which are manifested in the mass spectra, although most of the intense peaks do overlap with the Te_n clusters at the instrumental resolution investigated. The presence of TeS_4^+ can be confirmed on the basis of its unique features.

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1. Introduction

Alberti et al. [1] had reported the formation of tellurium, sulfur, and mixed tellurium–sulfur clusters. Four new cluster families of the composition, TeS_n ($n = 1-14$), Te_2S_n ($n = 1-10$), Te_3S_n ($n = 1-6$), and Te_4S_n ($n = 1-2$) were detected in the positive and negative ion modes, although the composition of the clusters was not determined as atomic weight of ^{128}Te is almost the same as $^{32}\text{S}_4$ [1]. These mixed clusters were seen from certain ‘sweet spots’ of the elemental mixtures of Te and S and spectrum in the negative ion mode was presented in [1]. In a recent report, we suggested the existence of the species, TeS_4 , Te_2S_4 , Te_3S_4 and Te_4S_4 in the positive ion spectrum by laser desorption from bulk TeS powder [2]. No ions of this kind were found in the negative ion mode. Experimental and computational studies showed that the clusters are stable.

In this report, we present certain clarifications in the light of the comment of Špalt et al. [3]. Additional experiments have been conducted to check various aspects and some of the recent data are presented. Experimental details are the same as the earlier report [2]. Spectra were opti-

mized by varying the laser intensity, delay time and number of laser shots.

2. Results and discussion

In the mass spectral region of TeS_4 , the other possibilities are Te_2 and S_8 , considering the source materials. As lower S_{8-n} clusters are not observed, one can disregard the possibility of S_8 , which occur along with the latter, especially at high laser powers. There are two mixed sulfide-oxide clusters, TeS_3O_2 and TeS_2O_4 possible in this mass region (as O_2 and S have the same mass), but these are less likely as simple oxides themselves are not detected in the positive ion spectrum.

The spectra were simulated using the Data explorer version 4.0.0.0 software provided by Applied Biosystems Inc. which uses the isotope database of IUPAC [4]. The clusters Te_2 and TeS_4 show similar mass distribution and it is difficult to assign them, especially using the peaks in the low mass region. However, in the high mass region, the TeS_4 cluster shows four unique peaks at m/z 256.7, 258.7, 260.7 and 261.7, although at reduced intensity.

A comparison of the theoretical peak positions and intensities of the clusters of interest are provided in Table 1. The unique features due to the TeS_4 clusters are given

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Table 1

A comparison of the theoretical peak positions and intensities of the clusters of interest

TeS ₄		Te ₂	
Mass	Relative abundance, %	Mass	Relative abundance, %
–	–	243.8	0.06
–	–	245.8	0.21
–	–	246.8	0.35
–	–	247.8	1.10
–	–	248.8	0.58
249.7	2.02	249.8	3.62
250.7	0.06	250.8	2.61
251.7	3.75	251.8	7.85
252.7	5.81	252.8	4.45
253.7	16.04	253.8	14.76
254.7	1.52	254.8	4.82
255.7	28.68	255.8	23.02
256.7	0.96	–	–
257.7	32.9	257.8	21.94
258.7	1.01	–	–
259.7	5.32	259.8	11.9
260.7	0.12	–	–
261.7	0.34	–	–

For clarity, the various isotope combinations have been omitted. The intensity cutoff was taken as 0.01%.

in italics. Although the relative abundances of these features are low, they are indeed observable. It may be pointed out that in reality these features are 20–30 times above the instrumental noise in regular measurements. Therefore, these can be used for assignment in cases where overlapping peaks become a problem. On the contrary, assignment on the basis of major peaks and their intensities alone would be practically difficult. It may also be noted that there are variations in relative peak intensities in routine measurements in LDI MS of a powdered solid sample.

In Fig. 1, we present a newly measured spectrum after optimizing the spectrometer parameters. The Te alone spectrum was taken using Te powder and the TeS cluster spectrum was taken using bulk TeS powder (after thorough ball milling, in both cases as reported in Ref. [2]). The peaks show clearly the existence of TeS₄ cluster with its

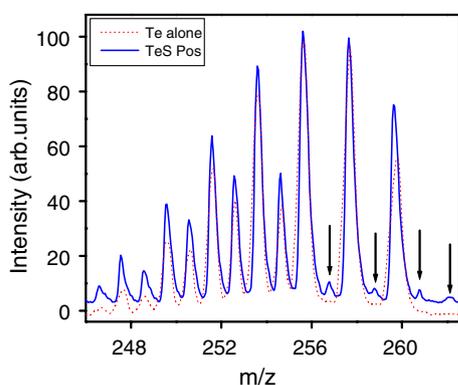


Fig. 1. Comparison of the experimental spectra obtained from Te and TeS. TeS cluster shows four unique features which are marked by arrows. Experimental spectra show minor shifts from the theoretical peak positions.

unique peaks. Note that in the spectrum of Te, these peaks are completely absent. Due to their prominence in the TeS spectrum and complete absence in the Te spectrum, the peaks at 256.7, 258.7, 260.7 and 261.7 were used for the identification of the TeS₄ cluster in the mass spectrum. All these peaks are present in the mass spectrum reported earlier [2]. Thus it is clear that the TeS₄ clusters are present in the laser desorption of TeS along with other clusters. From the 259 to 258 intensity ratio, it appears that a large fraction of the clusters is TeS₄, although we did not quantify it.

It may be mentioned that the peak maximum has 4.8×10^4 counts while the peak at m/z 256.7 has 4000 counts. In Fig. 2, we present an enlarged spectrum so that these unique features can be appreciated. Note that the spectrum has not been smoothed and no noise filter has been applied. These peaks are far above the noise level of the instrument which is typically in the range of 200 counts. Spectrum corresponding to 2,5-dihydroxybenzoic acid, which does not show any features in this mass region is shown in Fig. 2 to illustrate this point. Commercial MALDI-TOF spectrometers report a resolution ($m/\Delta m$) of 10000 and mass accuracy of 0.0001 Da [5–7] in this mass range. These points suggest that the four unique features observed are genuinely due to TeS₄⁺.

The unique peaks due to Te₂S₄ are clear in the Te₃ region also (see the supporting information for the spectra and theoretical peak listing). These peaks appear at m/z 386.7 and 388.7; two highest mass features are not clear due to their poor intensity. The number of unique peaks and their relative intensities decrease in larger clusters, although they appear in the spectra.

Regarding other points, we wish to clarify that,

1. We have shown that enhanced intensities for these clusters are seen only in the positive ion mode, while in negative ion mode other clusters are also seen. This is clear from Figs. 1 and 2 of Ref. [2].

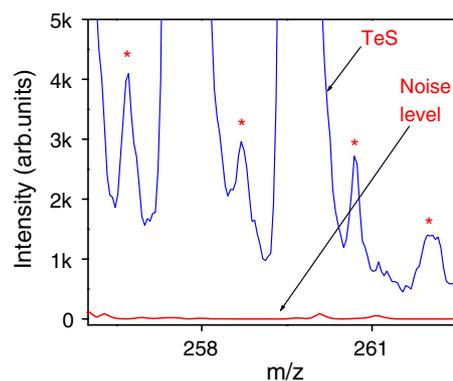


Fig. 2. Comparison of the experimental spectrum obtained from bulk TeS with the noise level in this mass range. The spectrum of 2,5-dihydroxybenzoic acid, which does not show any features in this mass range, measured at the same instrumental settings, is taken as the noise level. Peaks corresponding to TeS₄⁺ are marked.

- Several oxide-sulfide clusters are seen in the negative ion mode. They exist at a spacing of m/z 16 from the parent clusters and show the isotope distribution of Te. It is unlikely that they are due to other clusters, considering the chemical purity of the starting materials.
- Post source decay is an effective way of investigating stability of oxide and sulfide clusters. We have seen that several clusters dissociate in the PSD analysis, although no fragments were seen for Te_nS_4 clusters.

3. Conclusions

Although the spectra of two distinct species may be similar, there can be unique differences. These, especially in terms of new peaks can be used to make mass assignments, as in the case of TeS_4 . These unique peaks were present in the reported mass spectrum [2] as well. Mixed clusters of this kind co-exist with elemental clusters. In cases of ambiguity, it is better to compare the experimental spectrum derived from the elements. We note that PSD is an effective tool to understand the stability of the clusters.

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Appendix A. Supporting information

Possible peak positions and intensities for Te_n and Te_nS_4 clusters and comparison of the spectra of TeS and Te in the Te_3 region (two pages). Supplementary data associated with this Letter can be found, in the online version, at [doi:10.1016/j.cplett.2006.08.069](https://doi.org/10.1016/j.cplett.2006.08.069).

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