

Te_nS₄⁺ (*n* = 1–4) clusters in the gas phase

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Abstract

Positively charged ions, Te_nS₄⁺ (*n* = 1–4), are detected in the laser desorption mass spectra of bulk TeS. Enhanced intensities for these species are seen only for the positive ions. The clusters are formed as a result of the ion chemistry in the gas phase as elemental mixtures of Te and S also give the same clusters, albeit with different intensity distribution. Computational studies confirm the structural and electronic stability of these species. Te₃S₄⁺ and Te₄S₄⁺ clusters are observed for the first time in the gas phase.

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1. Introduction

Clusters in the gas phase have evolved into an important research area during the recent past. There have been reports of several inorganic compounds generating clusters in the gas phase. Various metal oxides [1–5] and sulfides [6–10] have been found to form clusters. These studies are important as they examine the ion chemistry, stability and reactivity of these prototypical species. Such studies have implications to catalysis in terms of understanding elementary chemical processes. Various methods can be used to generate clusters in the gas phase, in which evaporation of metals by heating and laser or ion bombardments are some of the widely followed methods. The generated clusters can be detected and analysed using a mass spectrometer, which provides information about the structure and stability [1–11]. Research in this area has been immensely benefited from advances in computational quantum chemistry which helps in understanding the structures and chemical reaction pathways.

Heteroatomic negatively charged clusters of the kind TeS_{*n*} (*n* = 1–14), Te₂S_{*n*} (*n* = 1–10), Te₃S_{*n*} (*n* = 1–6) and Te₄S_{*n*} (*n* = 1–2) have been formed in the gas phase from elemental tellurium and sulphur [12]. Units containing

TeS₄¹³, Te₂Se₄¹⁴ and Te₄S₄¹⁵ have been reported in the solid state as part of more complex structures. As part of our investigations of the structure and properties of chalcogenides in the gas phase [6], we explored the possibility of forming Te–S clusters. To our surprise, Te_{*n*}S₄⁺ clusters were found predominantly only in the positive ion mode, while various clusters of Te_{*n*}S_{*m*} stoichiometry were detected in the negative ion mode. Structures of these clusters were investigated using density functional theory. While for the TeS₄⁺ and Te₂S₄⁺ clusters, the calculated and experimental structures are comparable, there are no reports in the literature on the Te₃S₄⁺ cluster. The structure of Te₄S₄⁺ is similar to the experimental structure of Te₄S₄ moiety. From studies of elemental mixtures, we conclude that the clusters form as a result of the ion chemistry in the gas phase.

2. Experimental

Chemicals used for our work were purchased from Aldrich and were used without further purification. The mass spectrometric studies were conducted using a Voyager DE PRO Biospectrometry Workstation (Applied Biosystems) MALDI–TOF MS instrument. A pulsed nitrogen laser of 337 nm was used (maximum firing rate: 20 Hz, maximum pulse energy: 300 μJ) for desorption ionization and TOF was operated in the delayed extraction mode.

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For the mass spectrometric study, TeS was dispersed in acetone and directly spotted on the target plate. The sample was left to dry in air and inserted into the spectrometer. Typical delay times employed were of the order of 75–200 ns. The mass spectra were collected in both the negative and positive ion modes and were averaged for 100 shots.

Most of the measurements were done in the linear TOF mode. Laser desorption ionization (LDI) studies were carried out to understand the clustering behavior. We used both the negative and the positive ion modes for acquiring the spectra. For fragmentation as well as clustering studies, we used the timed ion selector, which is basically an electronic gate called “Bradbury–Nielsen gate” by which we can select a particular m/z and study its metastable decay [16]. The mass selection has an uncertainty of ± 4 Da. The clusters were assigned by comparing their experimental and calculated isotope patterns.

We have completely optimized all the structures discussed in this paper starting from the experimental X-ray structures. Computations used the GAUSSIAN '03 package [17]. DFT calculations were done using B3LYP/3-21G and B3LYP/LanL2DZ. Calculations were also done using effective core potentials, namely B3LYP/3-21G (Te) and 6-31G (S). The structures were completely optimized at various levels of theory. In the case of Te_3S_4^+ , no experimental structure was available and various initial guesses were tried.

3. Results and discussion

Spectra acquired in the positive and negative ion modes are shown in Figs. 1 and 2, respectively. In comparison to the negative ion mode of acquisition, in the positive ion mode we observed unique peaks corresponding to Te_nS_4^+ , where $n = 1-4$. Several ions of low intensity were observed

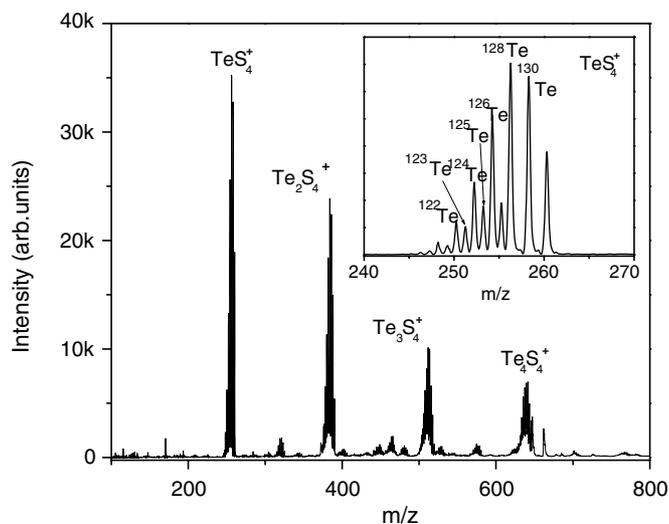


Fig. 1. LDI spectrum of tellurium sulfide in the positive ion mode. Inset shows an expanded view of the TeS_4^+ peaks showing the isotope distribution.

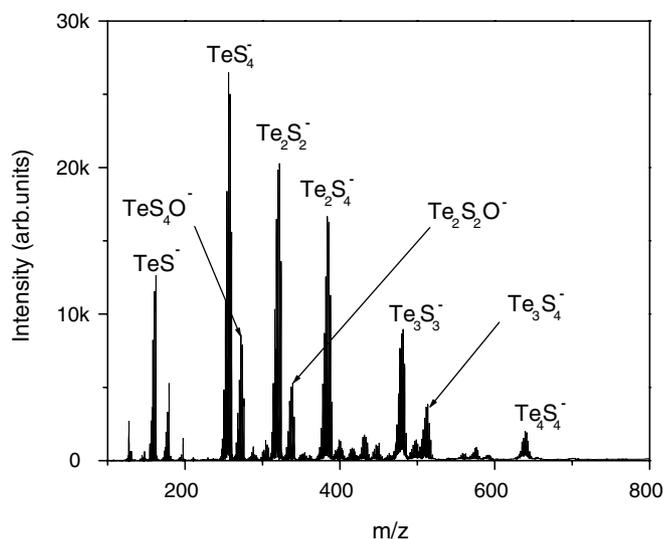


Fig. 2. LDI spectrum of tellurium sulfide in the negative ion mode.

but prominent species were only Te_nS_4^+ . Isotope pattern was clearly discernable in all the cluster peaks and a comparison of the theoretical and observed patterns was used to assign the peaks. These unique peaks were also seen in the negative ion mode, but along with several other cluster peaks. A few oxygen containing ions were observed, we attribute them to the impurities in the sample; these were not shown up in the positive ion mode, however. Instead, peaks with more or less sulphur compared to Te_nS_4^+ , such as Te_2S_2^+ and Te_3S_3^+ were observed.

The uniqueness of these cluster peaks was investigated subsequently by applying timed ion selection. This mode enables us to study each individual ion separately, without interference from other cluster products. We find that other ions do not yield them. We conclude that these clusters are formed directly in the gas phase during desorption ionization.

The formation of these clusters from a mixture of elemental Te and S was analysed. This experiment was carried out by mixing equimolar quantities of elemental Te and S, grinding the mixture in a ball mill, dispersing in acetone and spotting on the MALDI sample plate. This experiment gave a spectrum (Fig. 3) in which Te_nS_4^+ clusters are seen along with other clusters. The spectra exhibited intensity variation depending on the region of the sample analysed. This was found to be due to the inhomogeneity of the sample arising from a physical mixture.

The stability of Te_nS_4^+ clusters has been studied by post source decay (PSD). The analysis reveals that these clusters are stable and are not fragmented even at high laser intensities. In Fig. 4 we show PSD data of all the clusters.

Computational studies were carried out to understand the geometries and energies of Te–S clusters. The density functional method has gained widespread recognition due to its ability to achieve a considerable degree of success in the computation of molecular properties on medium to large size molecules. DFT has emerged as a computational

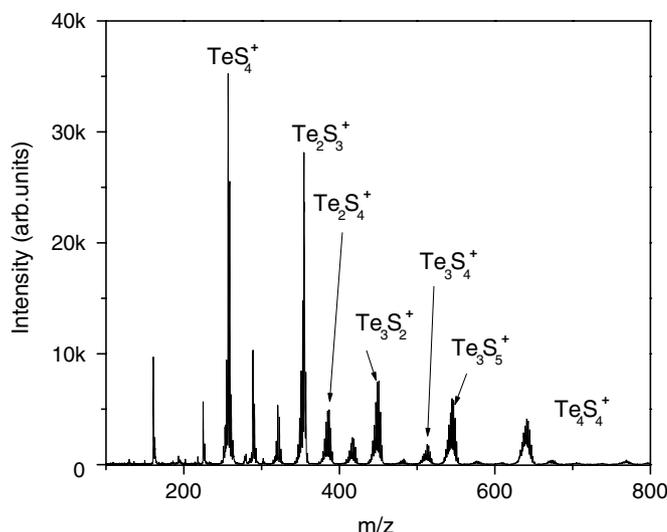


Fig. 3. LDI spectrum of Te and S mixture in positive ion mode showing Te_nS_4^+ clusters.

approach of comparable accuracy to the traditional correlated quantum mechanical methods. Among various proposed functionals, the combination of Becke's three-parameter hybrid exchange functional [18] with the Lee, Yang and Parr correlation functional, [19] B3LYP [20] is widely used and generally yields good results in the study of various chemical problems.

3.1. TeS_4

The experimental structure of TeS_4 moiety in the compound, $(\text{BzIPh}_3\text{P})_2[\text{Te}(\text{dtsq})_2]$ was reported by Drutkowski et al. [13]. They found that the Te centre is surrounded by four sulphur atoms in a planar arrangement. These four sulphur atoms are attached to the Te centre with bond

lengths of 2.67, 2.67, 2.75 and 2.75 Å, respectively. The S–Te–S bond angles are 89.45°, 87.16°, 86.77° and 96.62°. The deviation from the perfect planar compound with 90° bond angle and equal bond lengths is attributed to the neighboring ligands which are attached to each sulphur atom.

We find that the structure is highly symmetrical. The Te–S bond length in TeS_4 is 2.4 Å and the S–Te–S bond angle is 90°. Our results are somewhat different from the X-ray structure, because the TeS_4 unit has surrounding ligands and other molecules around it contributing to strain. Considerable distortion is seen when the cluster is ionized.

3.2. Te_2S_4

To predict this structure, we considered the structure of Te_2Se_4 as the starting point. Crystal structure of Te_2Se_4 was reported by Gillespie et al. [14]. In their work, they have synthesized the compounds, $\text{Te}_2\text{Se}_4(\text{SbF}_6)_2$ and $\text{Te}_2\text{Se}_4(\text{AsF}_6)_2$.

Our calculated structure of Te_2S_4 is similar to the experimental structure of Te_2Se_4 . The bond lengths (Å) calculated are: Te(1)–Te(2) 2.76, Te(1)–S(1) 2.40, Te(1)–S(4) 2.39, Te(2)–S(2) 2.39, S(2)–S(3) and S(3)–S(4) 2.01. The bond angles (°) are: Te(1)–S(1)–Te(2) 69.6, Te(2)–S(2)–S(3) 107.1 and S(2)–S(3)–S(4) 112.4. The mean bond length is 2.3 Å, close to the average of the Te–Te (2.54 Å) and S–S (2.05 Å) single bond lengths. This S–S bond length is taken as the length found in elemental sulphur, S_8 .

3.3. Te_3S_4

No prior experimental data exist on this cluster. In the calculated structure, the bond lengths (Å) are: Te(1)–Te(2) 2.82, Te(1)–S(1) 2.55, Te(1)–S(2) 2.54, S(2)–S(3)

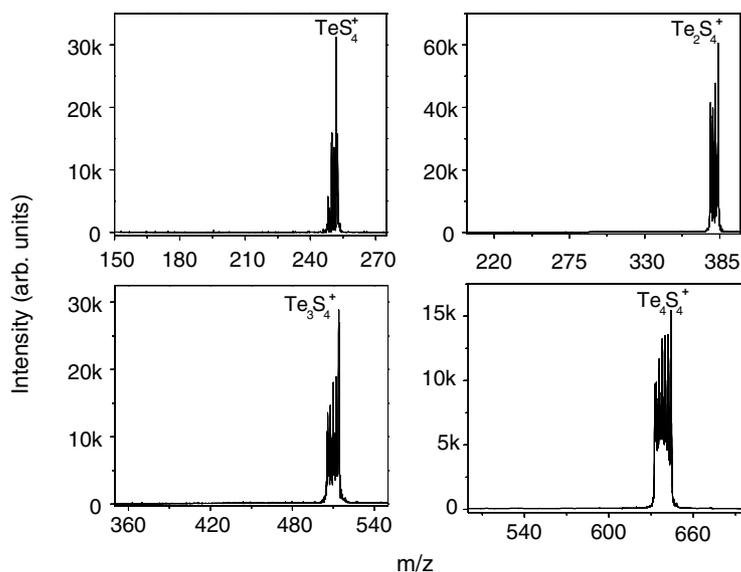


Fig. 4. PSD data of all clusters showing no fragmentation. No peaks are observed in still lower mass region also.

1.96, S(2)–S(4) and S(3)–S(4) 2.36, Te(3)–S(2) and Te(3)–S(3) 2.59. The bond angles (Å) are: Te(1)–S(1)–Te(2) 67.2, Te(1)–Te(2)–S(3) 79.7, S(2)–Te(1)–Te(2) 80.6, S(2)–Te(3)–S(3) 44.5, S(2)–S(4)–S(3) 49.0, Te(2)–S(3)–Te(3) 116.9 and S(1)–Te(2)–S(3) 109.8.

3.4. Te_4S_4

The structure of Te_4S_4 moiety was reported by Faggiani et al. [15]. This cluster exists in the compound, $Te_4S_4(AsF_6)_2 \cdot SO_2$. They have mentioned this structure to be a cage similar to S_4N_4 . The four sulphurs in this compound are almost coplanar. This plane of sulphur atoms cuts half the tetrahedron formed by the four tellurium atoms. The Te–Te distances of 2.716 and 2.710 Å are, within standard deviations, slightly shorter than twice the accepted radius of Te (2.74 Å) and are almost equal to the length of Te–Te single bond. Little work has been done on this kind of structures computationally. Paul et al. [21] reported the theoretical study on $Te_4S_4^{2+}$. They have considered the same structure of Te_4S_4 moiety, reported by Faggiani et al. [15]. The structure is similar to cuneane (pentacyclo octane, C_8H_8) but with three skeletal bonds cleaved. This cluster is isostructural with As_4S_4 , which has only two bonds broken relative to cuneane. Extended Huckel calculations on $Te_4S_4^{2+}$ have shown

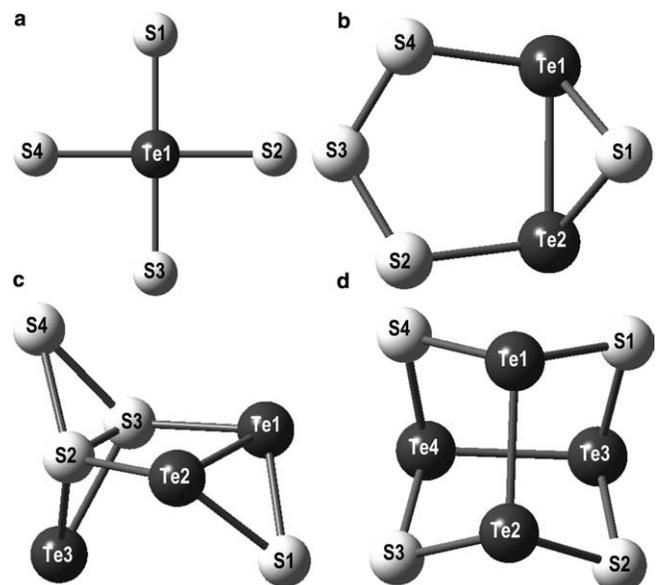


Fig. 5. Structures of tellurium sulfide clusters: (a) TeS_4^+ ; (b) $Te_2S_4^+$; (c) $Te_3S_4^+$ and (d) $Te_4S_4^+$ which are seen in the mass spectra. Tellurium atoms are shown as larger dark color balls and sulphur atoms are shown as smaller light color balls.

it to have a half occupied doubly degenerate highest occupied molecular orbitals. Accordingly, it has to undergo Jahn–Teller distortion. The geometries of $Te_4S_4^{2+}$ in the

Table 1
Summary of computational results

Formula	Energy in hartree			Structures ● Tellurium ● Sulphur
	B3LYP/3-21G	B3LYP/3-21G (Te) 6-31G (S)	B3LYP/LanL2DZ	
TeS_4	–8170.62247 –8170.26127	–8177.85713 –8177.49592	–48.26914 –47.90656	
Te_2S_4	–14756.52774 –14756.26404	–14763.26431 –14763.00223	–56.34104 –56.07010	
Te_3S_4	–21342.31273 –21342.04683	–21348.53832 –21348.27316	–64.28928 –64.01770	
Te_4S_4	–27928.22744 –27927.99716	–27933.94310 –27933.70186	–72.39880 –72.15100	

Tellurium atoms are shown as dark balls and sulphur atoms are shown as light balls. Values in bold face are for the positive ions in the doublet state.

triplet and singlet states have been optimized. The ion is found to have D_{2d} symmetry. The calculated Te–Te bond length is longer (3.03 Å) than the experimental (2.71 Å) value. This is because two electrons have entered an antibonding orbital which is localized predominantly on the tellurium atom. In conclusion, the addition of an electron pair into LUMO of $Te_4S_4^{4+}$ causes a lengthening of the Te–Te bond.

Our calculated structure of Te_4S_4 shows the bond lengths (Å) to be: Te–Te, 2.80 and Te–S, 2.39. The bond angles ($^\circ$) are S–Te–S, 98.7 and Te–S–Te, 97.4. This structure is highly symmetrical and all the Te and S atoms are placed in similar positions.

A summary of the results of the calculations is presented in Table 1. We have calculated the energies of these molecules both in neutral ground state and singly charged doublet excited state. The energy difference between the ground state molecule and singly charged species varied from 0.15 to 0.36 Hartree. No significant structural differences are observed in the ionic state. The structures of the ions are shown in Fig. 5, which may be compared with the structure of the neutrals discussed above.

4. Conclusion

We have shown the preferential existence of positively charged clusters of composition Te_nS_4 produced by laser desorption ionization of bulk TeS. These clusters and a number of others are formed in the negative ion mode. The $Te_nS_4^+$ clusters can also be produced from elemental mixtures of Te and S. Computations suggest that some of the structures are similar to those observed in experiments. $Te_3S_4^+$ and $Te_4S_4^+$ clusters have been observed for the first time in the gas phase. Computations suggest that there is no significant distortion upon ionization.

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