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Laser ablation generation of arsenic and arsenic sulfide clusters

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Abstract

Arsenic clusters As_n ($n = 2-7$) were generated from elemental arsenic using laser ablation on a commercial matrix assisted laser desorption ionization – time of flight (MALDI-TOF) mass spectrometric instrument. Singly charged As_n^+ clusters were observed only in the positive linear and/or reflectron mode. Negatively charged As_n^- species were not detected. The confirmation of cluster stoichiometries was done using isotopic pattern modelling. In spite of the high purity of arsenic (99.997%) several arsenic oxides and sulfides were observed during the laser ablation of the pure element. The formation of high clusters of arsenic ($n = 20, 60$) suggested from quantum chemistry calculations was not proved under the experimental conditions used. Additionally, commercially available As_2S_2 , As_2S_3 , As_2S_5 sulfides and/or arsenic-sulfur mixtures were studied as precursors for the generation of new As_nS_m clusters. Various arsenic sulfide ions (both negative and positive) were generated and identified: AsS , AsS_3 , As_2S , As_2S_2 , As_2S_3 , As_2S_5 , As_3S , As_3S_2 , As_3S_3 , As_3S_4 , As_3S_5 , As_3S_6 , As_3S_7 , As_4S_3 , As_4S_4 , while nine species (AsS_2 , AsS_4 , AsS_5 , AsS_6 , AsS_7 , AsS_8 , As_2S_4 , As_2S_6 , As_2S_7) were described for the first time.

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1. Introduction

Arsenic and its compounds have been of interest for a long time as a pigment as well as being one of the elements studied extensively by alchemists. Today, the application for arsenic is as a modifier of the mechanical properties of lead and copper alloys and as an additive to eliminate unwanted coloration of glass. The technological use of arsenic as passive layers in the semiconductor industry is well known. Arsenic and arsenic compounds are toxic and mobile in the environment

[1,2], their concentrations in the environment are controlled by strict guidelines [3] and ions of arsenic attack the –SH groups present in enzymes and alter their functions [4].

There are many applications of arsenic and arsenic compounds in electronics including the application of arsenic sulfides as optical fibers [5,6]. For example, pulsed laser ablation provides a promising method for thin film deposition applications. Mass spectrometry with a sufficiently high resolution, enabling the observation of isotopic patterns of peaks, can be a powerful tool for the identification of the morphology of the deposited thin layers.

Arsenic forms clusters and there are a great number of theoretical studies on the structure of arsenic clusters performed with the help of quantum chemistry methods, the most used approach in the theoretical studies is now the density functional theory (DFT) [7] and the ab initio

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method of self-consistent field (SCF) [8]. Thus, the theoretically calculated cluster species reported as being As_2 [9,10], As_3 [11] and As_4 [10,12,13] and also their formation has been proved experimentally.

Subsequently, Bowen et al. [14] determined the electron affinities of several As_n^- ($n = 1\text{--}5$) clusters using negative ion photoelectron spectroscopy. The confirmation of the evidence of several other metals' negatively charged cluster species, other than arsenic, was achieved using the pulsed UV laser ablation technique [15].

Lately, electron level theoretical calculations based on DFT and the prediction of infrared and Raman spectra of fullerene-like arsenic cages have been reported [16]. The work of Baruah et al. [16] concluded that clusters of As_n [$n = 4, 8, 20, 28, 32, 36, 60$] would be unstable and would dissociate into As_4 units except for a suggested As_{20} cluster.

Recently, in our laboratory, we have successfully applied commercial MALDI-TOF mass spectrometric instrumentation (MALDI-TOF-MS) for the generation of tellurium, selenium, phosphorus, or sulfur clusters and many new compounds [17–20]. In this work, the possibilities of laser desorption/ionization (LDI) and/or laser ablation as a promising approach towards the generation of As_n and As_nS_m clusters are studied.

2. Experimental

2.1. Chemicals and reagents

Elemental gray arsenic of 99.997% purity was purchased from Sigma Aldrich (Steinheim, Germany). Elemental sulfur of 99.98% purity was obtained from Aldrich Chemical Co., Milwaukee, USA. The arsenic sulfides As_2S_2 , As_2S_3 and As_2S_5 of 99.99% purity were purchased from Aldrich Chemical Co., Milwaukee, USA, as well. For the calibration of the mass spectrometer 2,5-dihydroxybenzoic acid (gentisic acid, DHBA) of analytical grade purity purchased from Sigma (Steinheim, Germany) was used. The experiments on the generation of As_n clusters with matrix assisted laser desorption/ionization were done using as matrices *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (AnorgPro) from Fluka (Buchs, Switzerland), 2-(4'-hydroxybenzoyl)-benzoic acid (HABA) from Sigma Aldrich (Steinheim, Germany) and α -cyano-4-hydroxycinnamic acid from Sigma Aldrich (Steinheim, Germany). C_{60} fullerene was purchased from Merck (Darmstadt, Germany). All the above mentioned chemicals were used as received without further purification.

2.2. Apparatus

Mass spectrometric measurements were performed on the commercial AXIMA CFR mass spectrometer

from Kratos Analytical (Manchester, United Kingdom) equipped with a nitrogen laser emitting on the wavelength of 337 nm. For the calibration of the mass spectrometer in the linear positive and reflectron positive mode, molecular ions $[\text{M} + \text{H}]^+$ of DHBA were used. In the case of the linear negative and reflectron negative mode, the calibration of the mass spectra was achieved using molecular ions $[\text{M} - \text{H}]^-$ of DHBA as well. Laser desorption/ionization mass spectra acquired for this work were obtained from at least 400 laser pulses per spectrum and the recorded spectra of all the laser shots were summed.

All the recorded spectra of post-source decay (PSD) measurement were obtained by setting the mass range windows 15 Da at least.

2.3. Sample preparation

Arsenic as well as arsenic sulfides and elemental sulfur are not soluble in any MALDI sample plate 'friendly' solvent. Because of that, the studied samples were placed directly on a spot of the MALDI sample plate and thoroughly milled in a mortar with a glass stick and mixed if necessary. In the case of matrix assisted generation of cluster species, the quick and dirty standard preparation technique was used. Thus, a suspension of arsenic powder in toluene at a concentration of 1 mg ml^{-1} was prepared. The matrices solutions were prepared by dissolving each matrix in toluene and then acidifying by adding 0.1 ml of 0.1% TFA to obtain a concentration of 20 mg ml^{-1} in a vial. A volume of 0.5 μl of both arsenic suspension and matrix were deposited onto a sample plate and air-dried at room temperature.

3. Results and discussion

3.1. The use of MALDI matrices

The investigation on the possibility of using matrices for the generation of homopolyatomic As_n cluster species was considered here. Several different matrices were examined including DHBA, HABA, AnorgPro matrix and C_{60} in order to examine the possibility of the MALDI approach for the cluster(s) production. Such an approach is rare, although recently its application has been described for gold cluster generation [21]. Also, we have tried the generation of cluster species from specially fabricated graphite crucibles as described thoroughly in a previous work [20].

However, it was found that for all the studied matrices, including the AnorgPro matrix especially recommended for inorganic samples by the producer, we were not able to produce arsenic clusters. Moreover, the presence of fragments of matrices in the mass spectra made their evaluation quite difficult and the signals of arsenic species

were suppressed. We have also observed this phenomenon at high laser energies when graphite crucibles were used where, in addition, carbon clusters became co-ablated and were detected in the mass spectra.

3.1.1. Generation of positively charged homopolyatomic As_n^+ clusters via the LDI approach

Because As_n clusters were not generated using MALDI matrices, we have turned to the laser desorption ionisation (LDI) approach.

An example of a mass spectrum of elemental arsenic obtained in the linear positive mode is shown in Fig. 1(a). In the mass spectra the formation of positively charged As_n^+ ($n = 2–7$) clusters has been observed only after applying sufficiently high laser energy, of at least 3 mW, to the solid sample of elemental arsenic. The values of m/z corresponding to As_3^+ , As_4^+ , As_5^+ , and As_7^+ clusters clearly indicated their formation (cf. Fig. 1(a),

peaks at m/z values equal to 224.94, 299.94, 374.73 and 524.48 Da). In the mass spectra the signal corresponding to As_2^+ has also been observed as a peak of relatively low signal intensity (cf. Fig. 1(a), peak at m/z value 150.42 Da), while the signal for the As_6^+ cluster was not observed.

The PSD spectra of detected clusters did not show any signs of decomposition, even at the highest possible laser power (6 mW). In the mass spectra measured in the positive mode, peaks corresponding to AsS^+ , As_2^+ and $As_2O_2^+$ are observed (cf. Fig. 1(b), m/z values at 107.26, 150.42 and 182.36 Da), while another peak of relatively weak intensity (cf. Fig. 1(b), m/z value at 153.14 Da) was assigned to $As_2H_3^+$, according to isotopic pattern modelling. Even if non-dissociative chemisorption of large amounts of H_2 on metal cluster anions has been recently reported [22], we rather suggest that in this case the species was “a chemical compound derived from arsan (AsH_3) or other As-hydrides”. We are suggesting that possibly, even in the highly pure arsenic product used in this work, a low but detectable amount of arsan was present and could be detected.

In addition to the peaks of As_n^+ clusters, there were others which were identified using isotopic pattern modelling as arsenic oxides As_nO_m and/or arsenic sulfides As_nS_m , even though elemental gray arsenic of high purity (99.997%) was used. In the case of arsenic sulfides, it can be suggested that the major source of contamination, according to the producer's Certificate of Guarantee, is sulfur, with a content of up to 0.003%. This corresponds to a sulfur molar content of 0.3 mmol kg^{-1} in the pure arsenic used in this work. In reality, such a concentration is very high, as usually in MALDI-TOF-MS a sample concentration of 10^{-5} to $10^{-6} \text{ mol l}^{-1}$ is commonly used (by the way, the limit of detection in MALDI is often 10^{-15} mol or even less). Consequently, taking into consideration the previous comments, we have detected and identified the following species: AsS^+ and As_3S^+ . Concerning arsenic oxides, it is

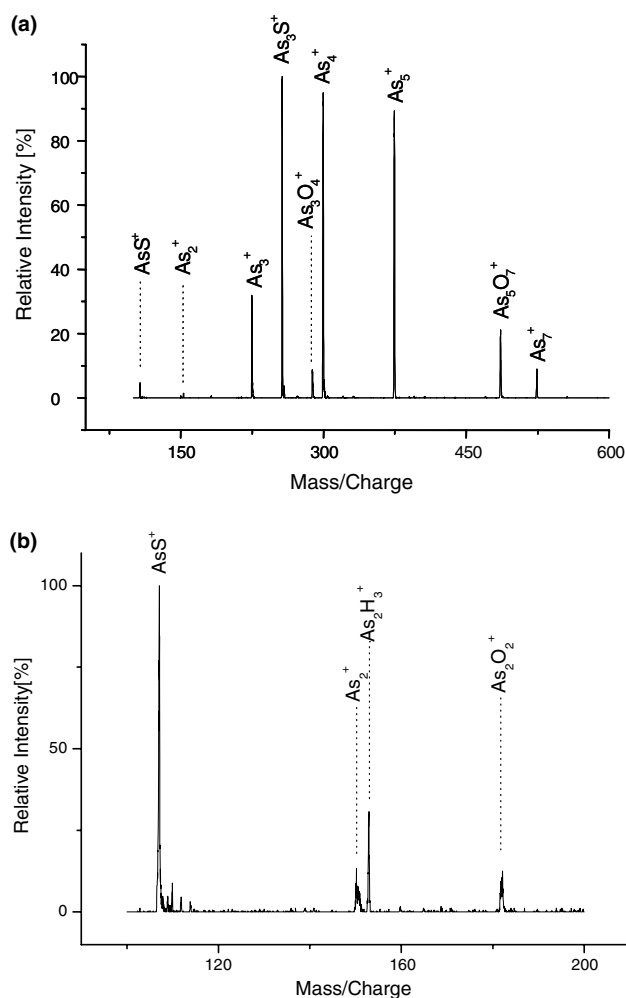


Fig. 1. The positive linear mode mass spectra concerning laser ablation of elemental arsenic. (a) An example of spectra displaying As_n^+ clusters and several other peaks reflecting the evidence of trace impurities contained in highly pure elemental arsenic (purity 99.997%). (b) Detailed view of the range 100–200 m/z showing the presence of AsS^+ , As_2^+ and As-hydride $As_2H_3^+$ derived from di-arsan (As_2H_4).

Table 1

Review of As_n species generated via laser ablation of metallic arsenic and identified from mass spectra

Cluster	Theoretical m/z	Observed m/z	References
As^+	74.92159	75.01	[27]
As_2^+	149.84318	150.42	[9]
As_3^+	224.76477	224.94	[11]
As_4^+	299.68636	299.93	[16]
As_5^+	374.60795	374.73	this work
As_6^+	449.52954	449.64	this work
As_7^+	524.45113	524.48	this work
As^-	74.92159	not observed	[14]
As_2^-	149.84318	not observed	[14]
As_3^-	224.76477	not observed	[14]
As_4^-	299.68636	not observed	[14]
As_5^-	374.60795	not observed	[14]
As_6^-	449.52954	not observed	not described
As_7^-	524.45113	not observed	not described

interesting to note that the presence of As_nO_m species such as As_3O_4 , and As_5O_7 (cf. Fig. 1(b), peaks at m/z values equal to 288.43, and 486.17 Da) were observed in the mass spectra obtained in the positive linear and reflectron modes as well as in both negative modes, in accordance with the literature [23].

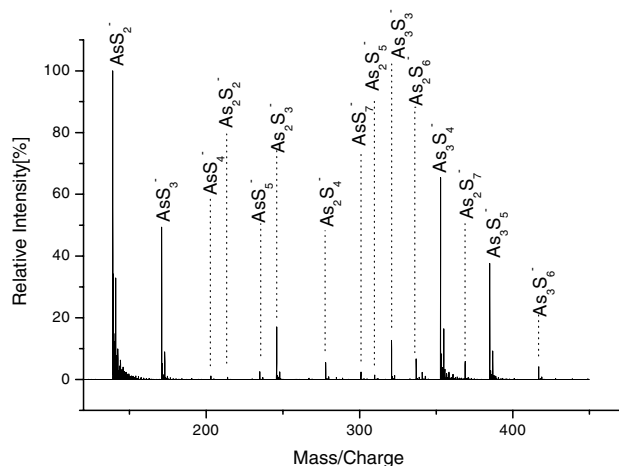


Fig. 2. An example of arsenic sulfide mass spectra recorded in the reflectron negative mode from laser ablation of As_2S_5 powder.

Not only As_2^+ , As_3^+ , As_4^+ , As_5^+ and As_7^+ , species of positively charged sulfide clusters, such as AsS^+ and As_3S^+ , but also positively charged species such as As_3O_4^+ , and As_5O_7^+ were observed as well. In addition, the As_2H_3^+ species derived from di-arsan was detected under the experimental conditions.

3.1.2. Generation of negatively charged As_n^- clusters

The formation of negatively charged As_n^- clusters was suggested theoretically by Zhao et al. [22] and species As^- , As_2^- , As_3^- , As_4^- , As_5^- have already been proved by photoelectron spectroscopy [14]. Therefore, in this chapter we examine the possibility to generate As_n^- clusters by the LDI approach.

The formation of negatively charged As_n^- ($n = 2-7$) clusters has not been observed even when applying a maximal laser power of at least 6 mW to the solid sample of the elemental arsenic. Also, the mass spectra measured in the linear negative and in the reflectron negative mode were represented only by a low number of signals corresponding to As_nS_m^- (S_3^- , AsS^- , AsS_2^-) and/or As_nO_m^- (AsO^- , As_3O_5^- , As_5O_7^-) species. The stoichiometries were confirmed according to isotopic pattern modelling.

Table 2

Review of As_nS_m species generated via laser ablation of fine As_2S_2 powder and identified from mass spectra of both negative and positive modes

	m	n			
		0	1	2	3
As_nS_m	0				
	1	$\text{S}^+ \text{S}^-$	$\text{AsS}^+ \text{AsS}^-^a$	As_2S^{+a}	
	2	$\text{S}_2^+ \text{S}_2^-^a$	$\text{AsS}_2^+ \text{AsS}_2^-$	$\text{AsS}_2^+ \text{AsS}_2^-^a$	
	3	$\text{S}_3^+ \text{S}_3^-$	$\text{AsS}_3^+ \text{AsS}_3^-^a$	$\text{As}_2\text{S}_3^+ \text{As}_2\text{S}_3^-^a$	$^{b,c}\text{As}_3\text{S}_4^+ \text{As}_3\text{S}_4^-$
	4	$\text{S}_4^+ \text{S}_4^-^a$	AsS_4^-	As_2S_4^-	$^{b,c}\text{As}_3\text{S}_4^+ \text{As}_3\text{S}_4^-$
	5		AsS_5^-		As_3S_5^-
	6				
	7				

^a As_nS_m species were found under [24] as neutral molecules.

^b [25].

^c [26].

Table 3

Review of As_nS_m species generated via laser ablation of fine As_2S_2 powder and identified from mass spectra of both negative and positive modes

	m	n			
		0	1	2	3
As_nS_m	0				
	1	$\text{S}^+ \text{S}^-$	$\text{AsS}^+ \text{AsS}^-^a$	As_2S^{+a}	$^c\text{As}_3\text{S}^+$
	2	$\text{S}_2^+ \text{S}_2^-^a$	$\text{AsS}_2^+ \text{AsS}_2^-$	$\text{AsS}_2^+ \text{AsS}_2^-^a$	$^{b,c}\text{As}_3\text{S}_2^+$
	3	$\text{S}_3^+ \text{S}_3^-$	$\text{AsS}_3^+ \text{AsS}_3^-^a$	$\text{As}_2\text{S}_3^+ \text{As}_2\text{S}_3^-^a$	$^{b,c}\text{As}_3\text{S}_4^+ \text{As}_3\text{S}_4^-$
	4	$\text{S}_4^+ \text{S}_4^-^a$	AsS_4^-	As_2S_4^-	$^{b,c}\text{As}_3\text{S}_4^+ \text{As}_3\text{S}_4^-$
	5		AsS_5^-		As_3S_5^-
	6				As_3S_6^-
	7				

^a As_nS_m species were found under [24] as neutral molecules.

^b [25].

^c [26].

Table 4

Review of As_nS_m species generated via laser ablation of fine As_2S_5 powder and identified from mass spectra recorded in the linear and reflectron positive, as well as both negative modes

As_nS_m	m	n			
		0	1	2	3
As_nS_m	0				
	1	$S^+ S^-$	$AsS^+ AsS^{-a}$	As_2S^{+a}	
	2	$S_2^+ S_2^{-a}$	$AsS_2^+ AsS_2^-$	$As_2S_2^+ As_2S_2^{-a}$	$^{b,c}As_3S_2^+ As_3S_2^-$
	3	$S_3^+ S_3^-$	$AsS_3^+ AsS_3^{-a}$	$As_2S_3^+ As_2S_3^{-a}$	$^{b,c}As_3S_3^+ As_3S_3^-$
	4	$S_4^+ S_4^{-a}$	AsS_4^-	$As_2S_4^-$	$^{b,c}As_3S_4^+ As_3S_4^-$
	5		AsS_5^-	$As_2S_5^{-a}$	$As_3S_5^-$
	6		AsS_6^-	$As_2S_6^-$	$As_3S_6^-$
	7		AsS_7^-	$As_2S_7^-$	$As_3S_7^-$

^a As_nS_m species were found under [24] as neutral molecules.

^b [25].

^c [26].

It is well known that the ionization potential (IP) (first IP of sulfur 10.4 eV and of arsenic 9.8 eV) and electron affinity (EA) (first EA of sulfur 200 kJ mol⁻¹ and of

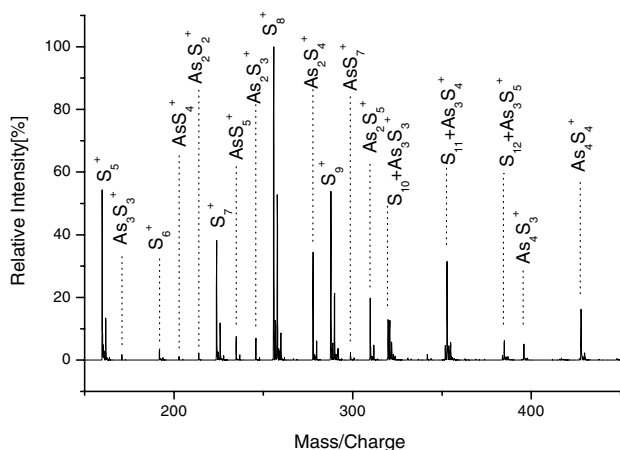


Fig. 3. An example of linear positive mode mass spectra obtained from an As_2S_2 and S_8 mixture used as a precursor for mixed As_nS_m species generation.

Table 5

Review of As_nS_m species generated via laser ablation of fine $As_2S_2 + S_8$ powder and identified from mass spectra of both negative and positive modes

As_nS_m	m	n			
		0	1	2	3
As_nS_m	0				
	1	$S^+ S^-$	$AsS^+ AsS^{-a}$		
	2	$S_2^+ S_2^{-a}$	$AsS_2^+ AsS_2^-$	$As_2S_2^+ As_2S_2^{-a}$	$^{b,c}As_3S_2^+ As_3S_2^-$
	3	$S_3^+ S_3^-$	$AsS_3^+ AsS_3^{-a}$	$As_2S_3^+ As_2S_3^{-a}$	$^{b,c}As_3S_3^+ As_3S_3^-$
	4	$S_4^+ S_4^{-a}$	$AsS_4^+ AsS_4^-$	$As_2S_4^+ As_2S_4^{-a}$	$^{b,c}As_3S_4^+ As_3S_4^-$
	5	$S_5^+ S_5^-$	$AsS_5^+ AsS_5^-$	$As_2S_5^+ As_2S_5^{-a}$	$^{b,c}As_3S_5^+ As_3S_5^-$
	6	$S_6^+ S_6^{-a}$	$AsS_6^+ AsS_6^-$	$As_2S_6^+ As_2S_6^-$	$^{b,c}As_3S_6^+ As_3S_6^-$
	7	$S_7^+ S_7^{-a}$	$AsS_7^+ AsS_7^-$	$As_2S_7^-$	$^{b,c}As_3S_7^+ As_3S_7^-$
	8	$S_8^+ S_8^{-a}$	AsS_8^-		
	9	$S_9^+ S_9^{-a}$			
	10	$S_{10}^+ S_{10}^{-a}$			
	11	$S_{11}^+ S_{11}^{-a}$			
	12	$S_{12}^+ S_{12}^{-a}$			

^a As_nS_m species were found under [24] as neutral molecules.

^b [25].

^c [26].

arsenic 78 kJ mol⁻¹) are important physico-chemical properties of atoms. This suggests that atoms with high positive values of ionization potential and high positive values of electron affinity would form, in the negative mode, more stable negatively charged species. Therefore, we conclude that the substantially different relative abundance of As_n and/or As_nS_m species in positive and negative modes under the LDI condition is due to preferred formation of As_nS_m species over singly charged As_n^- species as expected.

The complete summary of both negatively and positively charged arsenic cluster species described and/or identified is given in Table 1.

3.2. Arsenic-sulfur clusters

In the second part of this work we have studied the formation of arsenic sulfide clusters from various precursors. The following possibilities were examined: (i) laser ablation generation from As_2S_2 , As_2S_3 and As_2S_5 sulfides, (ii) generation of sulfides from As–S mixtures.

3.2.1. Laser ablation of As_2S_2 , As_2S_3 and As_2S_5 sulfides

The generation of As_nS_m species was achieved from thoroughly milled precursors placed directly on the MALDI plate as described elsewhere [17]. The experimental conditions of equal distribution of analysed molecules throughout the spot on the sample plate was strictly abided with the purpose of avoiding the co-ablation of the sample plate surface and formation of unexpected mixed cluster species. The arsenic-sulfur composite clusters were observed both in linear positive, linear negative as well as in the corresponding reflectron modes. Fig. 2 shows an example of a mass spectrum concerning As_nS_m species generated from the arsenic sulfide precursor. The stoichiometries were confirmed using isotopic pattern modelling. The summary of all identi-

fied compounds generated from the As_2S_2 , As_2S_3 and As_2S_5 sulfides, used as precursors, is given in Tables 2–4, respectively.

Species (both negative and positive) such as AsS_2 , AsS_4 , AsS_5 , AsS_6 , AsS_7 , As_2S_4 , As_2S_6 have been described for the first time and the richest generation of new heteroatomic arsenic-sulfur clusters was observed in the case of As_2S_5 sulfide.

3.2.2. Generation of As_nS_m species from a mixture of the elements

In the previous chapter, we have suggested that the increasing sulfur content in the studied arsenic sulfide precursors leads to a rich laser ablation synthesis of new members of the composite cluster species family.

Table 6

Review of As_nS_m species generated via laser ablation of fine $As_2S_3 + S_8$ powder and identified from mass spectra of both negative and positive modes

As_nS_m	m	n				
		0	1	2	3	4
	0					
	1	$S^+ S^-$	$AsS^+ AsS^-^a$			
	2	$S_2^+ S_2^-^a$	$AsS_2^+ AsS_2^-$	$As_2S_2^+ As_2S_2^-^a$	$^{b,c}As_3S_2^+ As_3S_2^-$	
	3	$S_3^+ S_3^-$	$AsS_3^+ AsS_3^-^a$	$As_2S_3^+ As_2S_3^-^a$	$^{b,c}As_3S_3^+ As_3S_3^-$	
	4	$S_4^+ S_4^-^a$	$AsS_4^+ AsS_4^-$	$As_2S_4^+ As_2S_4^-$	$^{b,c}As_3S_4^+ As_3S_4^-$	$^bAs_4S_4^+ As_4S_4^-$
	5	$S_5^+ S_5^-$	$AsS_5^+ AsS_5^-$	$As_2S_5^+ As_2S_5^-^a$	$^bAs_3S_5^+ As_3S_5^-$	
	6	$S_6^+ S_6^-^a$	$AsS_6^+ AsS_6^-$	$As_2S_6^-$	$^bAs_3S_6^+ As_3S_6^-$	
	7	$S_7^+ S_7^-^a$	$AsS_7^+ AsS_7^-$		$^bAs_3S_7^+ As_3S_7^-$	
	8	$S_8^+ S_8^-^a$	AsS_8^-			
	9	$S_9^+ S_9^-^a$				
	10	$S_{10}^+ S_{10}^-^a$				
	11	$S_{11}^+ S_{11}^-^a$				
	12	$S_{12}^+ S_{12}^-^a$				

^a As_nS_m species were found under [24] as neutral molecules.

^b [25].

^c [26].

Table 7

Review of As_nS_m species generated via laser ablation of fine $As_2S_5 + S_8$ powder and identified from mass spectra recorded in the linear and reflectron positive, as well as both negative modes

As_nS_m	m	n				
		0	1	2	3	4
	0					
	1	$S^+ S^-$	$AsS^+ AsS^-^a$	$As_2S^+^a$	$^cAs_3S^+$	
	2	$S_2^+ S_2^-^a$	$AsS_2^+ AsS_2^-$	$As_2S_2^+ As_2S_2^-^a$	$^{b,c}As_3S_2^+ As_3S_2^-$	
	3	$S_3^+ S_3^-$	$AsS_3^+ AsS_3^-^a$	$As_2S_3^+ As_2S_3^-^a$	$^{b,c}As_3S_3^+ As_3S_3^-$	
	4	$S_4^+ S_4^-^a$	$AsS_4^+ AsS_4^-$	$As_2S_4^+ As_2S_4^-$	$^{b,c}As_3S_4^+ As_3S_4^-$	
	5	$S_5^+ S_5^-$	$AsS_5^+ AsS_5^-$	$As_2S_5^+ As_2S_5^-^a$	$^bAs_3S_5^+ As_3S_5^-$	
	6	$S_6^+ S_6^-^a$	$AsS_6^+ AsS_6^-$	$As_2S_6^-$	$^bAs_3S_6^+ As_3S_6^-$	
	7	$S_7^+ S_7^-^a$	$AsS_7^+ AsS_7^-$	$As_2S_7^-$	$As_3S_7^-$	
	8	$S_8^+ S_8^-^a$				
	9	$S_9^+ S_9^-^a$				
	10	$S_{10}^+ S_{10}^-^a$				
	11	$S_{11}^+ S_{11}^-^a$				
	12	$S_{12}^+ S_{12}^-^a$				

^a As_nS_m species were found under [24] as neutral molecules.

^b [25].

^c [26].

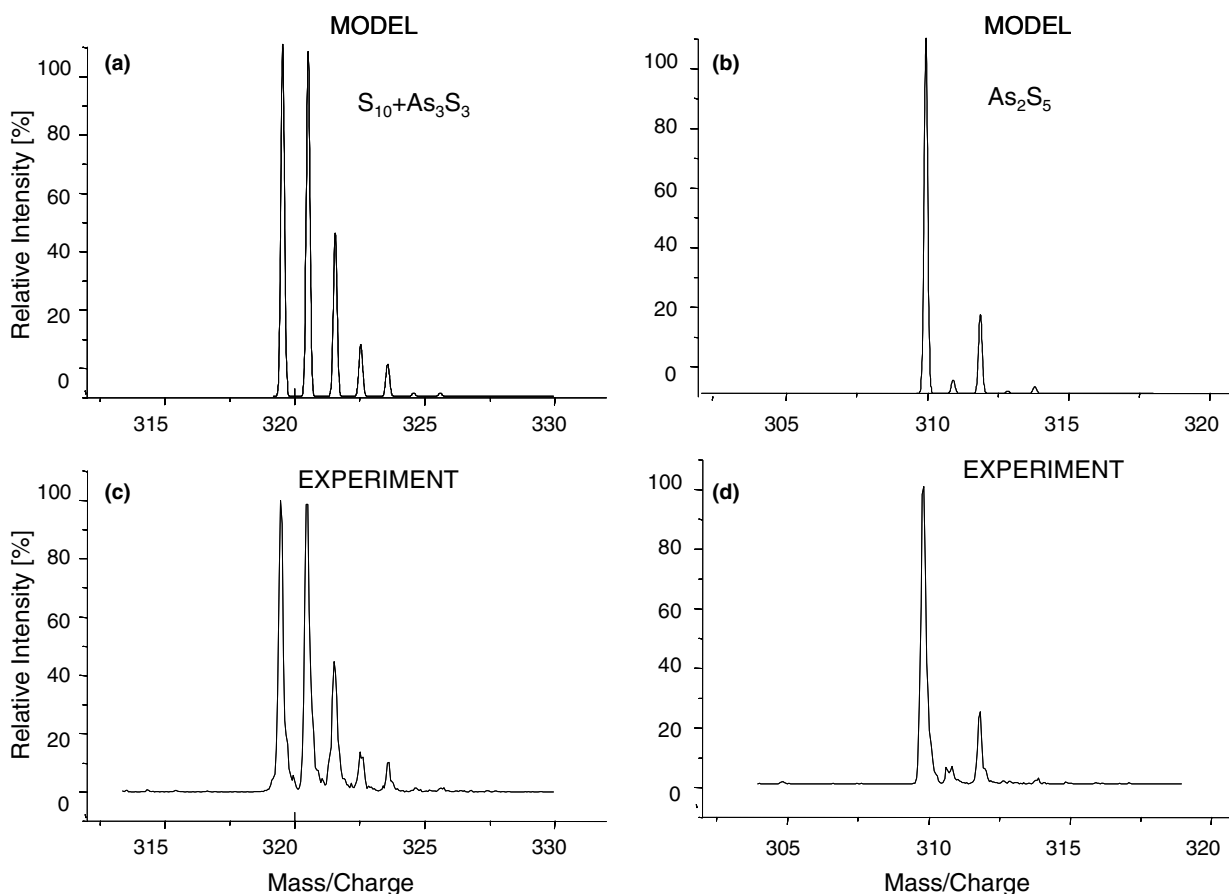


Fig. 4. Comparison of theoretical mass spectra reflecting the isotopic pattern of $S_{10} + As_3S_3$ and As_2S_5 species (a, b) with experimental spectra (c, d).

Therefore, the effect of sulfur as a possible MALDI matrix for the generation of As_nS_m species was considered and the possibility of different arsenic sulfide cluster generation from mixtures with sulfur was studied.

An example of the measured mass spectra is given in Fig. 3 and the overview of all newly identified stoichiometries generated from the mixture of elemental sulfur and the As_2S_2 , As_2S_3 and As_2S_5 sulfides is given in Tables 5–7. All stoichiometries were confirmed according to isotopic pattern modelling and an example of the isotopic pattern confirmation is given in Fig. 4.

The effect of sulfur as a MALDI matrix in the synthesis of mixed arsenic-sulfur clusters was confirmed and, in addition to previous experiments, clusters such as As_4S_3 and As_4S_4 were detected. The richest arsenic-sulfur cluster generation was observed from the mixture of As_2S_2 arsenic sulfide with elemental sulfur. On the other hand, a high excess of sulfur leads to the generation of various sulfur species only.

4. Conclusions

The generation of As_n^+ ($n = 2-7$) clusters, except As_6^+ , has been successfully achieved in the positive

mode. The As_6^+ cluster was observed in a few cases only, with an intensity equal to 5 mV, and we confirm here that it is formed in a low abundance and this cluster is most probably unstable. No As_n^- clusters were detected in the negative mode. Clusters with intensity lower or equal than three-times the level of threshold (≈ 1.2 mV) were considered as non-detected. The stability of arsenic clusters was confirmed in the post-source decay. However, the existence of arsenic fullerene-like cages As_n ($n = 20, 28, 32, 36, 60$) was not proved. In addition, laser ablation synthesis also leads to the formation of several arsenic oxide ions (AsO , As_3O_4 , As_3O_5 , As_5O_7) and a positively charged $As_2H_3^+$ arsenic hydride.

New single negatively and positively charged species were generated and identified: AsS_2 , AsS_4 , AsS_5 , AsS_6 , AsS_7 , AsS_8 , As_2S_4 , As_2S_6 , As_2S_7 . All stoichiometries were confirmed using isotopic pattern modelling.

Many new cluster species previously not described in the literature and/or suggested from quantum chemistry calculations were generated via laser ablation synthesis and identified. In pure arsenic, As_nS_m cluster species were detected in the positive mode (AsS and As_3S) and in the negative mode (S_3 , AsS , AsS_2). We have also shown that LDI and/or laser ablation mass spectrometry

is a suitable method for the rapid identification of low sulfur impurities in metallic arsenic. Thus, this approach can be used for the detection of super-low impurities found in arsenic for industrial purposes.

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