

Mass spectrometric identification of singly-charged anionic and cationic sulfur, selenium, tellurium and phosphorus species produced by laser ablation

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Abstract

Laser desorption/ionisation mass spectrometry of the elements sulfur, selenium, tellurium and phosphorus has shown a range of polynuclear ions in both positive and negative ion modes. Three-dimensional topographical surfaces are used to display changes in the speciation of sulfur ions with increasing laser power under laser desorption/ionisation conditions, using a technique described as energy-dependent laser desorption/ionisation mass spectrometry; the positive and negative ion spectra of sulfur are both dominated by singly-charged ions, with S_5^+ and S_3^- showing particular intensity. Similar results are also reported for the other title elements. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the most interesting features of the main group non-metallic elements is the wide variety of allotropic forms which have been identified. The classic case of the modifications of solid sulfur has been carefully reviewed by Meyer, [1] and the heavier congeners show similar, but apparently less complex, behaviour. Corbridge [2] has similarly described the allotropic modifications of phosphorus. The composition of the relevant gas phases, and the relationships of the species identified with the solid elements, has also been the subject of much study; we return to this below. Not surprisingly, the elements of Group 16 give rise to a wide variety of positive and negative ions. Mass spectrometry has been a most useful tool in studying the gas phase chemistry of these elements, and in recent years the combination of laser ablation and time-of-flight mass spectrometry has added to the available information.

We now report an extensive study of the positive and negative ions produced from solid sulfur, selenium and tellurium, from S/Se and Se/Te mixtures, and from phosphorus. In particular, we describe a novel treatment of the time-of-flight mass spectrometric (TOFMS) data which presents the differing relative intensities of these ions as a function of laser power, and this in turn suggests possible pathways by which these species may arise. As well as identifying the energy domains in which particular ions dominate, these results emphasise the potential danger in drawing conclusions about the predominance of certain ions, or decomposition pathways, on the basis of spectra recorded at a single laser energy. Finally, we have identified new polyatomic ions which might prove to be interesting ligands in inorganic and/or organometallic chemistry.

2. Results and discussion

2.1. Sulfur

The properties and inter-relationships of the many allotropic forms of solid state chemistry of elemental sulfur have been discussed in detail by Meyer, who has

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also discussed the liquid state chemistry and the composition of the equilibrium vapour phase. The experimental information on the vapour phase species in equilibrium with molten sulfur initially depended on the combination of mass spectrometry and Knudsen effusion [3], and such methods have identified S_n^+ ions with $n = 2$ –8. More recently, spark source mass spectrometry has been used to confirm the formation of these cations [4], while laser ablation/He jet methods with S_8 vapour have also shown the existence of S_n^+ clusters with $n = 8, 16, 24, 32, 40$ (and intermediate values) formed from the parent S_8 solid [5]. The production of neutral and anionic clusters by pulsed arc excitation in a helium atmosphere, coupled with photoionisation measurements, demonstrated the formation of negative S_n^- ions ($n = 2$ –7) under these conditions [6]. This work also included theoretical studies of both neutral and anionic species, but here, as elsewhere, the calculations do not always identify unique structures [7]. In the solid state, the doubly charged polysulfides S_n^{2-} far outnumber the singly-charged anions, of which only S_3^- and S_2^- are well characterised [8], and several cationic derivatives have been prepared and structurally characterised; these are all of the type S_n^{2+} ($n = 4, 8, 19$) [9].

In contrast, the present work identifies a wide range of singly-charged S_n^+ and S_n^- ions produced by the laser ablation of the solid element. Fig. 1 shows a single negative-ion LDI-TOF mass spectrum of sulfur recorded at low laser power, maximising intensity of the highest mass species. Spectra of this type can obviously be obtained at different laser powers, with each spectrum providing a picture of the fragmentation process at that energy (see Table 1). Since the presentation of all the data sets acquired in this fashion is impractical, we have devised a method of illustrating the fragmentation processes observed in LDI-MS spectra through a three-dimensional (3D) format; this involves collecting mass spectra across a range of laser powers and combining

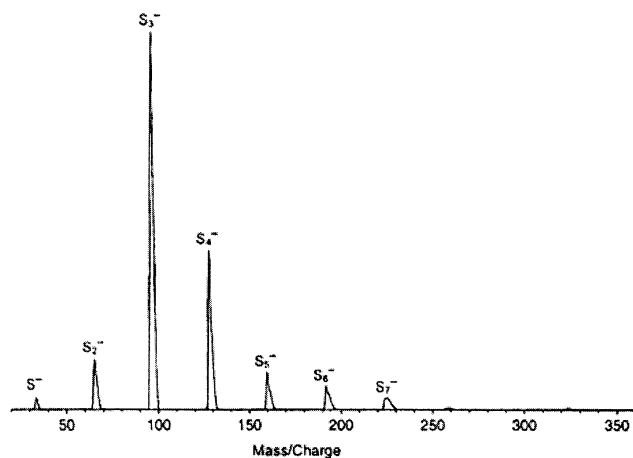


Fig. 1. The negative-ion laser desorption/ionisation mass spectrum of elemental sulfur at a low laser power setting.

the data into one topographical surface, in which mass-to-charge ratio and laser power form the x and y axes, and intensity is represented vertically. To achieve this, we adapted a function on the KRATOS KOMPACT™ software, which is designed to find the ‘sweet spot’ at which co-crystallisation of sample and matrix has occurred most efficiently on a MALDI slide. For convenience, the y -axis is labelled as laser power in arbitrary units (see further discussion) rather than profile number. The topographical surface thus generated allows simultaneous observation of the whole range of ions produced over all laser energies, and the technique leads to rapid identification of the most appropriate laser power required to obtain, for example, spectra at threshold, or to maximise high-mass species, or to present a single spectrum at maximum intensity. Furthermore, those ions which display special stability appear as large ‘islands’ whose size is determined both by the maximum intensity of the ion (height) and by their persistence across a wide range of laser powers (length).

This method of presenting mass spectrometric data has certain similarities to our recently presented technique of energy-dependent electrospray ionisation mass spectrometry (EDESI-MS) [10], in which collision energy is plotted against m/z to generate a 2D map of the fragmentation pattern of the target compound. While we do not expect that moderating the laser power can generate changes in the spectrum as profound as those which are brought about in EDESI-MS by changing the collision energy, it is convenient to adopt an analogous acronym to describe the LDI technique. We will therefore use ‘energy-dependent laser desorption/ionisation mass spectrometry’ (EDLDI-MS) as a shorthand in describing the 3D topographical surfaces presented in this paper. The example shown in Fig. 2 is the spectrum of elemental sulfur collected in the negative ion mode, and the corresponding positive-ion EDLDI-MS is shown in Fig. 3. We must emphasise that while increasing the laser power clearly does increase the incident energy at the sample surface, no quantitative measurement of this energy can be derived from the instrument readings. Despite this caveat, there can be no doubt that Fig. 2, and its companion spectra, do illustrate in a unique fashion the changes in spectral composition with increasing fluence energy. Equally important, we have found that essentially identical spectra could be generated on another mass spectrometer; the only requirement is, obviously, that the appropriate data-handling programmes be available.

In the negative-ion spectrum, (Fig. 2), the peaks can be assigned to the species S_n^- ($n = 1$ –8). The heavier clusters ($n = 4$ –8) appear at a relatively low laser power, and quickly disappear as the energy is increased. At the highest laser power, S^- dominates the spectrum, implying the complete dissociation of the higher species.

Table 1
MS data of sulfur ionic species

Laser power	(a) Sulfur positive ions												
	S ⁺	S ₂ ⁺	S ₃ ⁺	S ₄ ⁺	S ₅ ⁺	S ₆ ⁺	S ₇ ⁺	S ₈ ⁺	S ₉ ⁺	S ₁₀ ⁺	S ₁₁ ⁺	S ₁₄ ⁺	S ₁₅ ⁺
150 ^a	27	16											
125		100	8	6	11	2	3	4	1				
100					74	6	37	100	36	5	5	33	2
Laser power	(b) Sulfur negative ions												
	S ⁻	S ₂ ⁻	S ₃ ⁻	S ₄ ⁻	S ₅ ⁻	S ₆ ⁻	S ₇ ⁻	S ₈ ⁻	S ₁₀ ⁻				
150	100												
125	100	97	88	8	2								
100	0	3	100	61	17	12	5	2	2				

^a Spectrum dominated by K⁺.

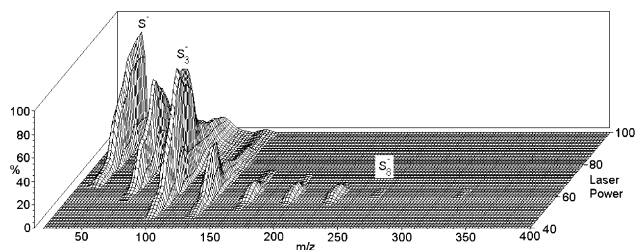


Fig. 2. The three-dimensional EDLDI-MS profile generated from 80 negative-ion mass spectra of elemental sulfur at laser power settings of 40–100.

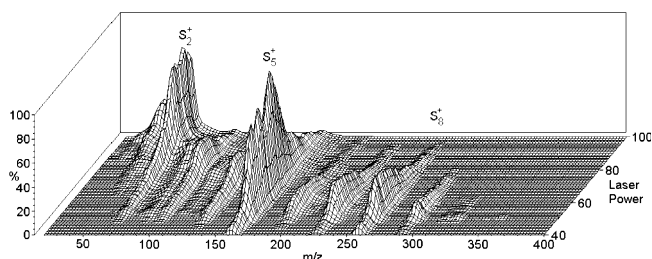


Fig. 3. The three-dimensional EDLDI-MS profile generated from 80 positive-ion mass spectra of elemental sulfur at laser power settings of 40–100.

The intermediate energies are characterised by the abundance of S₃⁻, and the preponderance of this island of stability is in keeping with the known behaviour of this ion in non-aqueous solution, and its wide occurrence in solid phases [3]. These spectra are clearly different from those reported earlier [3–7], and it is not easy to compare the two types; the plume produced by the impact of a high energy laser beam on a solid surface contains species which are not in equilibrium with the parent solid, and whose relative composition is not that of the equilibrium vapour.

The positive-ion spectrum (Fig. 3) shows a greater range of sulfur species than in the case of the anions, extending from S⁺ to S₁₁⁺, with an interestingly high intensity at S₁₄⁺. Again, the larger clusters exist over a small range of low laser powers, and the S⁺ ion dominates the spectrum at very high laser power. The

most abundant ion at intermediate laser powers is S₅⁺; in contrast to the situation for S₃⁻, there is no evidence of stable derivatives of this cation in the solid state.

The dominance of monatomic ions at the highest laser power clearly shows the almost complete decomposition of polyatomic species under these conditions. It is also possible to treat the data to compare, for example, the effect of laser energy on the formation of S₅⁺ and S₃⁻, by extracting the intensity profile for each as a function of laser power (Fig. 4). The close match suggests that the pathway



is important; the formation of S₃⁻ by other routes presumably accounts in part for the lack of congruence.

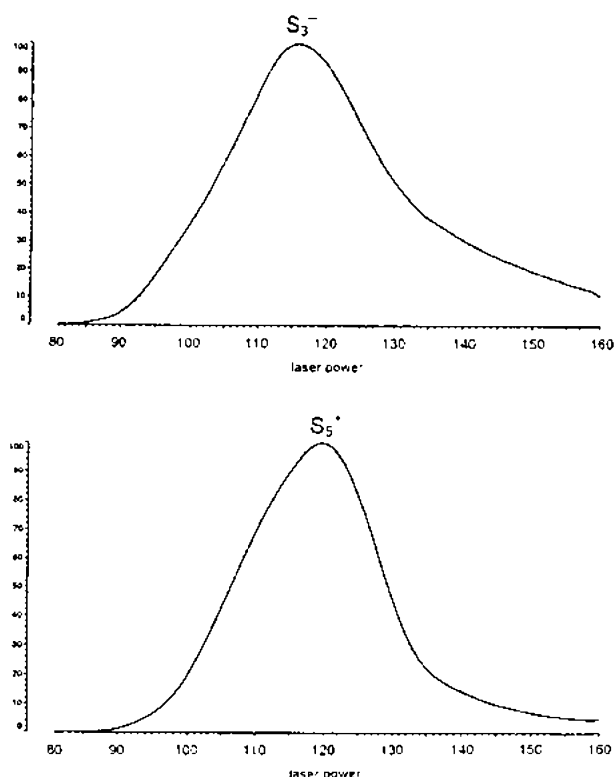


Fig. 4. Laser power setting (40–100) vs. intensity for: (top) S₃⁻ and (bottom) S₅⁺.

It would be premature to speculate on the nature of the presumed S_8^* excited state, or on the decomposition processes. An alternative route requires production of S from S_8 , followed by recombination and cooling to give the ions observed.

2.2. Selenium

There are interesting differences between the results for selenium and sulfur, and these may be due in part to the necessity of using higher laser power to produce detectable ion beams of selenium. A second, and possibly more important factor, is that while sulfur was the monoclinic solid containing *cyclo*- S_8 , the selenium source was the grey (metallic) allotrope, which has also been the source of ions in the previous mass spectrometric studies [11]. The structure of this solid consists of infinite helical unbranched chains, with $r(\text{Se}-\text{Se}) = 2.373(5) \text{ \AA}$ and $\text{Se}-\text{Se}-\text{Se} = 103.1(2)^\circ$ [12]. The speciation of selenium vapour has been discussed by Steudel and Strauss [13].

The dominant positive ions detected in the EDLDI mass spectrum of selenium (Fig. 5) were Se^+ , Se_2^+ and Se_5^+ ; the minor components included Se_3^+ and Se_4^+ , with a low intensity peak from Se_6^+ . No higher species were detected, and this observation, together with the minor significance of Se_6^+ and the importance of Se_2^+ , constitute the major differences from sulfur. In electron-impact mass spectrometry of vapour produced in a Knudsen cell at 210 °C, the dominant ion was Se_6^+ , with significant quantities of Se_n^+ with $n = 2-5$ and 7, but in this case the source was said to be hexagonal selenium, although the actual allotropic form(s) present at 210 °C were not specified (see also the comment above for sulfur vapour species). At high laser powers, the larger species Se_n^+ ($n = 3-6$) disappear in favour of Se^+ and Se_2^+ (Table 2). These results contrast with the positive-ion spectrum produced by a sequence of laser ablation, positive ion acceleration and photoionisation, in which the maximum intensities in the Se_n^+ manifold ($n = 2-8$) were at $n = 2, 5$ and 7 [14]. The data in Table 2 establish that the composition of the plume produced by

Table 2
MS data of selenium ionic species

Laser power	(a) Selenium positive ions					
	Se^+	Se_2^+	Se_3^+	Se_4^+	Se_5^+	Se_6^+
150	100	10	8			
125	6	100	4	2	4	
100		12	100	10	90	3
Laser power	(b) Selenium negative ions					
	Se^-	Se_2^-	Se_3^-	Se_4^-	Se_5^-	
150	100	11				
125	61	100	19	4		
100		19	100	49	5	

laser ablation depends critically on the experimental conditions, so that the difference between the two sets of results is not surprising. In the negative-ion mode at low laser powers, the dominant ion is Se_3^- , with small contributions from $\text{Se}_4^- > \text{Se}_2^- > \text{Se}_5^-$. As the laser power is increased there is a general decrease in the higher nuclearity species until the spectrum is almost completely dominated by Se^- , with a small contribution from Se_2^- .

In general, the pattern of behaviour is similar to that seen with sulfur anions, and the relative stabilities of Se_n^- and S_n^- species are presumably similar. As with sulfur, the decomposition of Se_x fragments formed by laser ablation of the solid seems the most likely route to these anions, since this is in keeping with the preponderance of Se^- and Se_2^- at high laser power. The Se_3^- anion may well be as important in the chemistry of selenium as is S_3^- for sulfur. As in the case of sulfur, we find no evidence of positive or negative doubly charged ions, although such species are of course important features of the solid state and solution chemistry of selenium.

2.3. Tellurium

Tellurium was melted on to a MALDI sample slide in much the same way as sulfur and selenium, but the higher melting point of Te metal (450 °C) meant that the process took some time. Appreciably, higher laser

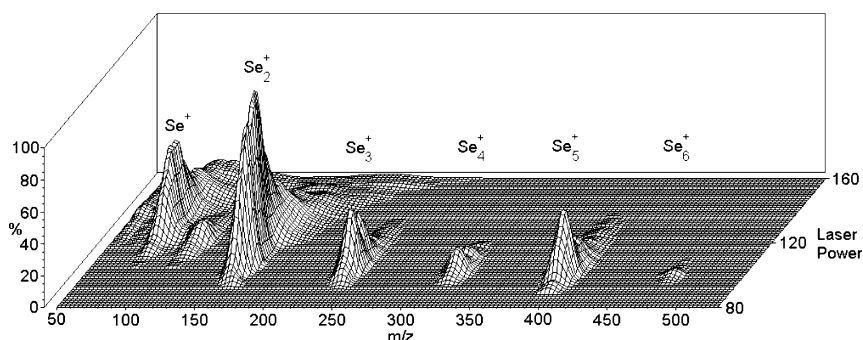


Fig. 5. The three-dimensional EDLDI-MS profile generated from 80 positive-ion mass spectra of elemental selenium at laser power settings of 80–160.

Table 3
MS data of tellurium ionic species

Laser power	(a) Tellurium positive ions				
	Te ⁺	Te ₂ ⁺	Te ₃ ⁺	Te ₄ ⁺	Te ₅ ⁺
150	93	94	26	12	7
125		100	24	10	
100					
	(b) Tellurium negative ions				
	Te ⁻	Te ₂ ⁻	Te ₃ ⁻	Te ₄ ⁻	
150 ^a	36	38	8	3	
125	14	100	43	10	
100					

^a Spectrum dominated by selenium.

powers were needed to ablate this sample than in the case of selenium or (especially) sulfur, and this may explain why only limited clustering was observed.

The negative-ion EDLDI spectrum of tellurium metal showed no peaks of significance at low laser powers (< 90), but the species Te⁻, Te₂⁻, Te₃⁻ and Te₄⁻ appear at higher laser powers, dominated by Te₂⁻ which reaches its maximum intensity at a laser power of approximately 120. Peaks attributable to Se_n⁻ (n = 1–4) species are also apparent in the EDLDI spectrum, and it seems likely that selenium is a low-level impurity in the tellurium sample, that it is present in the spectrum in disproportionate abundance because of its higher volatility. Interestingly, selenium species are not observed to any appreciable degree in the positive-ion spectrum (Table 3(a)), which contains peaks attributable to Te⁺, Te₂⁺, Te₃⁺ and Te₄⁺. Again, the dimer is found to have the highest abundance, but this species has the greatest intensity in the EDLDI spectrum (Fig. 6) at a laser power of 150, significantly higher than that observed for the Te₂⁻ anion (vide supra).

2.4. Mixtures of S/Se and Se/Te

In addition to the work on the Group 16 elements themselves, spectra were recorded in both positive and negative ion modes for solid mixtures of Group 16 elements. The method of sample preparation involved

simply melting approximately equimolar quantities of each element and applying the mixture to the sample slide. It was not possible to prepare S/Te samples in this way, for the trivial reason that at the melting point of Te (450 °C), sulfur is rapidly lost to evaporation (boiling point, 445 °C).

The positive-ion spectrum of the S/Se system is interesting in that only selenium-containing cations are detected over the whole energy range studied (Table 4(a)). The only homonuclear ions are Se⁺ and Se₂⁺, observed only at the highest laser energies, and Se₅⁺ and traces of Se₆⁺. The heteronuclear species are members of the groups [S_nSe_{5-n}]⁺ and [S_nSe_{6-n}]⁺, with low intensities assigned to Se₂Se₅⁺, SSe₆⁺ and S₄Se₄⁺. The five-membered entities show the highest abundance at SSe₄⁺. None of these ions correspond to known cationic solid-state species.

In contrast, the negative-ion EDLDI spectrum at low energies includes S₂⁻, Se₂⁻, S_nSe_{3-n}⁻, and S_nSe_{4-n}⁻ ions, while at high energies S⁻, S₂⁻ and S₃⁻ are the only significant ions observed (Table 4(b)). The persistence of the triatomic ions presumably relates to the corresponding stability of the S₃⁻ ion in the chemistry of this element, and it may be that salts of these heteroatomic ions will be more accessible than has proven to be in the case for S₃⁻.

The positive-ion spectrum from Se/Te sources does not extend beyond m/z = 500, and within this range we detected only M⁺, M₂⁺, SeTe⁺, the group Se_nTe_{3-n}⁺, and the lower members of Se_nTe_{5-n}⁺, with this last species in only very low intensities (Table 5(a)). The negative ions detected include Se⁻, Te⁻, each of the triatomic ions and a small intensity assigned to Se₃Te⁻; nothing was detected above m/z = 400 (Table 5(b)). As in the S/Se case, these positive and negative ions do not appear to correspond to known stable analogues in the solid state.

2.5. Phosphorus

As for the Group 16 elements, we have recorded positive- and negative-ion spectra produced by the laser

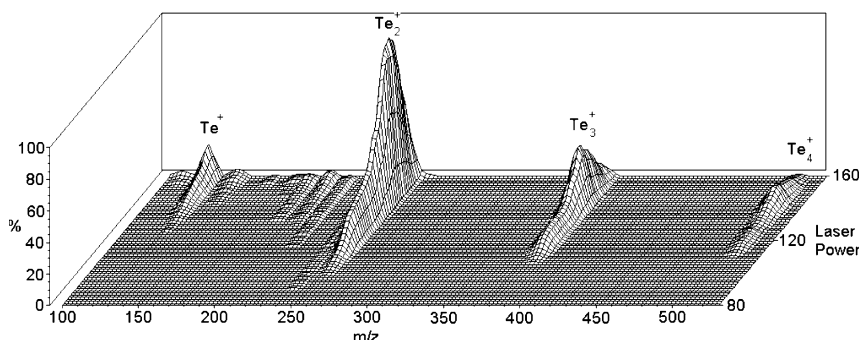


Fig. 6. The three-dimensional EDLDI-MS profile generated from 80 positive-ion mass spectra of elemental tellurium at laser power settings of 80–160.

Table 4
MS data of sulfur/selenium ionic species

Laser power	(a) Sulfur/selenium positive ions												
	SSe ⁺	Se ₂ ⁺	S ₄ Se ⁺	S ₃ Se ₂ ⁺	S ₂ Se ₃ ⁺	SSe ₄ ⁺	Se ₅ ⁺	S ₄ Se ₄ ⁺	S ₂ Se ₅ ⁺	Se ₆ ⁺	S ₃ Se ₅ ⁺	SSe ₆ ⁺	
150 ^a	3												
125	100	15											
100	22		10	36	54	100	66	7	13	6	16	15	
Laser power	(b) Sulfur/selenium negative ions												
	S ⁻	S ₂ ⁻	Se ⁻	S ₃ ⁻	SSe ⁻	S ₄ ⁻	S ₂ Se ⁻	S ₃ Se ⁻	SSe ₂ ⁻	S ₂ Se ₂ ⁻	Se ₃ ⁻	SSe ₃ ⁻	Se ₄ ⁻
150	100	19		4									
125	11	22	7	100	4	6	5						
100				100		4	66	7	26	4	6	3	1

^a Spectrum dominated by Na⁺, K⁺, Cu⁺.

Table 5
MS data of selenium/tellurium ionic species

Laser power	(a) Selenium/tellurium positive ions									
	Se ⁺	Te ⁺	Se ₂ ⁺	SeTe ⁺	Se ₃ ⁺	Te ₂ ⁺	Se ₂ Te ⁺			
150 ^a	6	4	2							
125 ^a	16	8	6	3	2					
100	14	56	100	30	10	2	4			
Laser power	(b) Selenium/tellurium negative ions									
	Se ⁻	Te ⁻	Se ₂ ⁻	SeTe ⁻	Se ₃ ⁻	Te ₂ ⁻	Se ₂ Te ⁻	SeTe ₂ ⁻	Te ₃ ⁻	SeTe ₃ ⁻
150	65									
125	54	20	100	34	10	4	8	10	2	8
100	2		2				6	100		54

^a Spectrum dominated by Na⁺, K⁺, Cu⁺.

ablation of solid phosphorus over a range of laser energies, with the results summarised in Table 6(a) and (b). Within the limits of the experimental technique, it appears that higher energies are required in order to produce either type of ion than is the case for sulfur. The positive-ion spectrum shows that the ions formed at the lowest laser energies are P₅⁺, P₇⁺ and P₁₁⁺, and P₇⁺ is the most abundant ion over a wide range of energies. This is in keeping with the early calculations of Baird [15]. A number of workers have also reported the formation of a wide range of P_{*n*}⁺ species by laser ablation, with values of *n* up to 91 being identified mass spectrometrically, and theoretical treatments have been applied in attempts to understand the results [16]. Our spectra add little to the published information on P_{*n*}⁺ ions with *n* > 5, but do show that at high laser energies the ions P₂⁺, P₃⁺ and P₄⁺ contribute increasingly to the ion current. Baird has shown that P₃⁺ has a pseudo-aromatic trigonal planar structure while P₂⁺ and P₄⁺ are related to two reasonably stable neutral phosphorus molecules [15], so that the presence of these ions is in keeping with the predicted stabilities.

Surprisingly, there does not appear to have been any study of the corresponding negative spectrum arising from the laser ablation of phosphorus. As Fig. 7 illustrates, the P₅⁻ anion requires the lowest excitation energy, and is the most abundant ion throughout the energy range investigated. This anion has been the

subject of considerable theoretical interest [17] in view of its aromatic character and its relationship to the cyclopentadienyl anion. The spectroscopic properties of solutions of P₅⁻, and its reactivity, have also been reported [18]. At higher laser energies, a range of anions up to P₂₅⁻ is observed, mostly of low abundance; peaks are seen for P₆⁻, P₁₃⁻ and P₁₇⁻ over small regions of laser energy. The structures of such ions present interesting challenges, as does the absence of even-numbered P_{*n*}⁻ ions for *n* > 10. Equally interesting is the presence of P⁻, P₂⁻ and P₃⁻ at high laser energies. The electron affinity [19] of atomic phosphorus is 71.7 kJ mol⁻¹, so that the formation of P⁻ from atomic phosphorus present in the plume from the decomposition of polyatomic species is readily understood. The ion P₂⁻ can be derived from P₂, similarly produced, and the bond order of 2.5 (cf. Baird) should give this ion considerable stability, and P₃⁻ can be formulated as the analogue of the azide anion.

3. Conclusions

The new experimental approach described in this paper allows the ready investigation of the energy dependence of positive and negative ions formed in the laser ablation of solid samples of the title elements, and by extension to other substances. In addition to the

Table 6
MS data of phosphorus ionic species

Laser Power	(a) Phosphorus positive ions												
	P ₂ ⁺	P ₃ ⁺	P ₄ ⁺	P ₅ ⁺	P ₇ ⁺	P ₈ ⁺	P ₉ ⁺	P ₁₁ ⁺	P ₁₃ ⁺	P ₁₅ ⁺			
75 ^a	2	3	2	1	3								
60 ^a	14	8	8	4	10								
45		12	30	33	100	6	8	19	4	3			
Laser Power	(b) Phosphorus negative ions												
	P ₂ ⁻	P ₃ ⁻	P ₄ ⁻	P ₅ ⁻	P ₆ ⁻	P ₇ ⁻	P ₈ ⁻	P ₉ ⁻	P ₁₀ ⁻	P ₁₁ ⁻	P ₁₃ ⁻	P ₁₅ ⁻	P ₁₇ ⁻
75	100	25	3	42		4	2	3			4	1	2
60	64	12	2	100	1	11	3	4	1	1	6	3	2
45 ^b	6	6	1	100	2	37	16	19	7	6	22	8	12

^a Spectrum dominated by Na⁺ and K⁺.

^b Other species seen at laser power of 45: P₁₉⁻ (1%), P₂₃⁻ (3%), P₃₃⁻ (2%), P₄₁⁻ (1%).

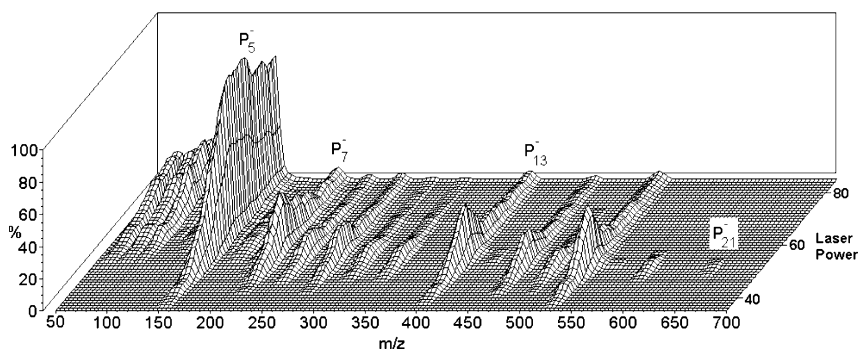


Fig. 7. The three-dimensional EDLDI-MS profile generated from 80 negative-ion mass spectra of elemental phosphorus at laser power settings of 40–80.

intrinsic interest of the results, some synthetic applications are immediately suggested. First, a number of examples of organometallic molecules with P_n ligands have been reported [20] and possible routes to these, and other novel substances, could be based on the formation of P_n⁺ and/or P_n⁻ ions in the gas phase by laser ablation or related methods. Similar comments apply to the possible synthesis of derivatives of the ions of the Group 16 elements. Secondly, the stabilisation of P₅⁻ suggests that a search for solution or solid-state derivatives of the P_n⁻ ions, and the analogous cations, might be fruitful.

4. Experimental

LDI mass spectra were collected using a Kratos Kompact MALDI 4 in both positive and negative-ion mode. The instrument is equipped with a nitrogen laser, $\lambda = 337$ nm, pulse length of 3 ns on a target ~ 100 μ m in diameter. The laser power is moderated by a wheel of varying opacity in steps from 0 (no transmission) to 180 (full transmission). Five laser shots were collected at each increment in laser power, and averaged into one profile; the sum of 80 profiles was used to generate the chromatogram display, which was smoothed. EDLDI spectra were recorded in linear mode to maximise signal-

to-noise. Five laser shots were collected at each increment in laser power and averaged into one profile; a total of 80 profiles were used to generate the display, which was smoothed.

Elemental sulfur (flowers of sulfur) was melted, cooled and dissolved in carbon disulphide; the resulting solution was spotted onto the slide and the solvent allowed to evaporate. Qualitatively identical results were obtained by smearing flowers of sulfur directly on to the slide, but the former method gave a more even coverage and hence smoother EDLDI spectra. Selenium and tellurium were melted and allowed to solidify directly on the slide. The same procedure was used for the S/Se and Se/Te mixtures, in which equimolar mixtures of the elements were melted together. Red phosphorus was mixed with CH₂Cl₂ and this suspension added to the slide; evaporation of the solvent left a thin coating of phosphorus on the slide.

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