Gas-phase Silver Chalcogenide Ions Investigated by Laser-ablation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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When laser-ablated and monitored by FTICR mass spectrometry, silver sulphide, selenide and telluride, and elemental mixtures of silver with selenium or tellurium, yield large silver chalcogenide cluster anions, including the series $[Ag_{2n-1}E_n]^-$ (E = S, Se, Te) with $n \leqslant 14$.

The importance and variety of metal chalcogenide clusters characterized in the condensed phase[1] has led us to investigate the formation and properties of metal chalcogenide clusters in the gas phase.[2,3] Very few studies of metal chalcogenide species in the gas phase have been undertaken.[4–6].

A Nd-YAG laser (1064 nm) was used at various powers (150–1600 MW cm^{-2}) and focused onto discs of pressed solid samples of Ag_2E (E = S, Se, Te), as well as element mixtures of Ag + Se, and Ag + Te, in various ratios. A variety of silver chalcogenide anions was detected by Fourier transform ion cyclotron resonance mass spectrometry.

Representative mass spectra for three samples are shown in Fig. 1, and the ion compositions are listed in Table 1. The principal results apparent in this data are: (*i*) For Ag_2Se, and various mixtures of Ag and Se, the compositions of the ions observed are largely independent of the chemical composition of the ablated sample, although there are some intensity differences: the same independence of sample is observed with Ag_2Te, and Ag plus Te mixtures; (*ii*) For each sample the spectrum contains distinctively different lower-mass and higher-mass regions; (*iii*) In the lower mass region for Ag_2S there is a full distribution of $[Ag_xS_y]^-$ ions up to $x = 9$, while

Table 1 Negative ions formed by laser-ablation of Ag_2S, Ag_2Se, Ag + Se, Ag_2Te and Ag + Te, observed by FTICR mass spectrometry. The most intense ions (S_3^-, Se^- and Te^-) and ions with more than 21 Ag atoms, are not listed.

	(Intensity) m/z				
Ion	Ag_2S	Ag_2Se	Ag + Se^a	Ag_2Te	Ag + Te^b
$[AgE]^-$	(100) 139	(57) 187	(100)	(30) 237	(69)
$[AgE_2]^-$	(77) 171	(14) 267	(16)		
$[AgE_3]^-$	(38) 203	(12) 347	(10)	(12) 493	(—)
$[AgE_4]^-$	(48) 235			(33) 621	(52)
$[Ag_2E_2]^-$	(58) 280	(19) 374	(19)	(25) 474	(—)
$[Ag_2E_3]^-$	(100) 312	(27) 454	(19)		
$[Ag_2E_4]^-$	(38) 344				
$[Ag_3E]^-$	(38) 355				
$[Ag_3E_2]^-$	(67) 387	(26) 483	(19)	(13) 581	(100)
$[Ag_3E_3]^-$	(44) 421	(29) 563	(8)		
$[Ag_3E_4]^-$	(39) 453	(—) 633	(25)		
$[Ag_4E_2]^-$	(18) 496	(—) 596^c	(6)		
$[Ag_4E_3]^-$	(100) 528	(—) 670^c	(6)		
$[Ag_4E_4]^-$	(63) 560				
$[Ag_5E_2]^-$	(24) 603				
$[Ag_5E_3]^-$	(80) 636				
$[Ag_5E_4]^-$	(98) 668			(11) 1062	(—)
$[Ag_5E_5]^-$	(30) 700				
$[Ag_6E_4]^-$	(34) 775				
$[Ag_6E_5]^-$	(82) 807				
$[Ag_6E_6]^-$	(42) 839				
$[Ag_7E_3]^-$	(27) 850				
$[Ag_7E_4]^-$	(61) 916	(—) 1081^c	(8)	(21) 1268	(26)
$[Ag_7E_5]^-$	(40) 948			(15) 1393	(—)
$[Ag_8E_5]^-$	(30) 1023			(—) 1503	(21)
$[Ag_9E_5]^-$	(100) 1132	(36) 1366	(24)	(90) 1611	(79)
$[Ag_9E_6]^-$	(28) 1164	(—) 1442^c	(7)		
$[Ag_{10}E_5]^-$				(26) 1712	(30)
$[Ag_{10}E_8]^-$		(—) 1714^c	(12)		
$[Ag_{11}E_6]^-$	(62) 1380	(50) 1660	(29)	(100) 1953	(68)
$[Ag_{13}E_7]^-$	(42) 1628	(76) 1955	(31)	(84) 2297	(66)
$[Ag_{13}E_8]^-$	(15) 1660				
$[Ag_{15}E_8]^-$	(47) 1875	(100) 2249	(33)	(80) 2641	(54)
$[Ag_{17}E_9]^-$	(44) 2123	(73) 2544	(34)	(33) 2983^c	(39)
$[Ag_{19}E_{10}]^-$	(57) 2371	(43) 2840	(26)	(21) 3329^c	(—)
$[Ag_{21}E_{11}]^-$	(46) 2619	(30) 3134^c	(10)		

[a] 3 : 1 (w/w) mixture of Ag and Se, [b] 3 : 1 (w/w) mixture of Ag and Te. [c] Low intensity ions: composition not confirmed by high resolution narrow band spectroscopy.

there are relatively few $[Ag_xSe_y]^-$ and $[Ag_xTe_y]^-$ ions with $x < 9$; (*iv*) In the lower mass region for Ag_2S, all $[Ag_xS_y]^-$ ions with $x \leqslant 6$ and $x - 2 \leqslant y \leqslant x$ are present. Within the set for each value of x, the ion with $y = x - 1$ is the most intense; (*v*) In the higher mass region there are well-developed series of intense ions with the general composition $[Ag_{2n-1}E_n]^-$, for E = S ($4 \leqslant n \leqslant 14$), Se, and Te; (*vi*) As each of the $[Ag_{2n-1}E_n]^-$ series of ions progresses (by addition of Ag_2E), the relative abundances increase before diminishing; (*vii*) Apart from the $[Ag_{2n-1}E_n]^-$ series, there are few other ions with more than nine Ag atoms, although the beginning of another series is apparent at high mass for Ag_2S.

Result (*i*) suggests that the ions are formed in gas-phase reactions in the plasma plume, during or immediately after the short pulse (8 ns) of high energy from the laser. This is observed also for nickel chalcogenides[3] and tantalum carbides.[7]

The range of compositions of the $[Ag_xS_y]^-$ ions with $x \leqslant 9$ is similar to that observed for the $[Ni_xS_y]^-$ ions on laser ablation of Ni_3S_2.[3] However, the series of ions $[Ag_{2n-1}E_n]^-$ are distinctive for the silver chalcogenides, although similar series $[Cu_{2n-1}E_n]^-$ occur on laser ablation of copper chalcogenides.[2] Comparable uncharged fragments, such as $[Ag_{2n}E_n]^0$, may be formed in the laser ablation but not detected, but comparable cations, such as $[Ag_{2n+1}E_n]^+$, have not been observed in the positive ion spectra. There is no structural precedent for clusters with the composition $[Ag_{2n-1}E_n]$ in condensed phases, but the high relative stabilities of these ions provides a guide to potential silver chalcogenide cluster types as yet unknown. The copper selenide clusters $Cu_{29}Se_{15}(PPr^i_3)_{12}$, $Cu_{30}Se_{15}(PPr^i_3)_{12}$ and $Cu_{36}Se_{18}(PBu^t_3)_{12}$ recently

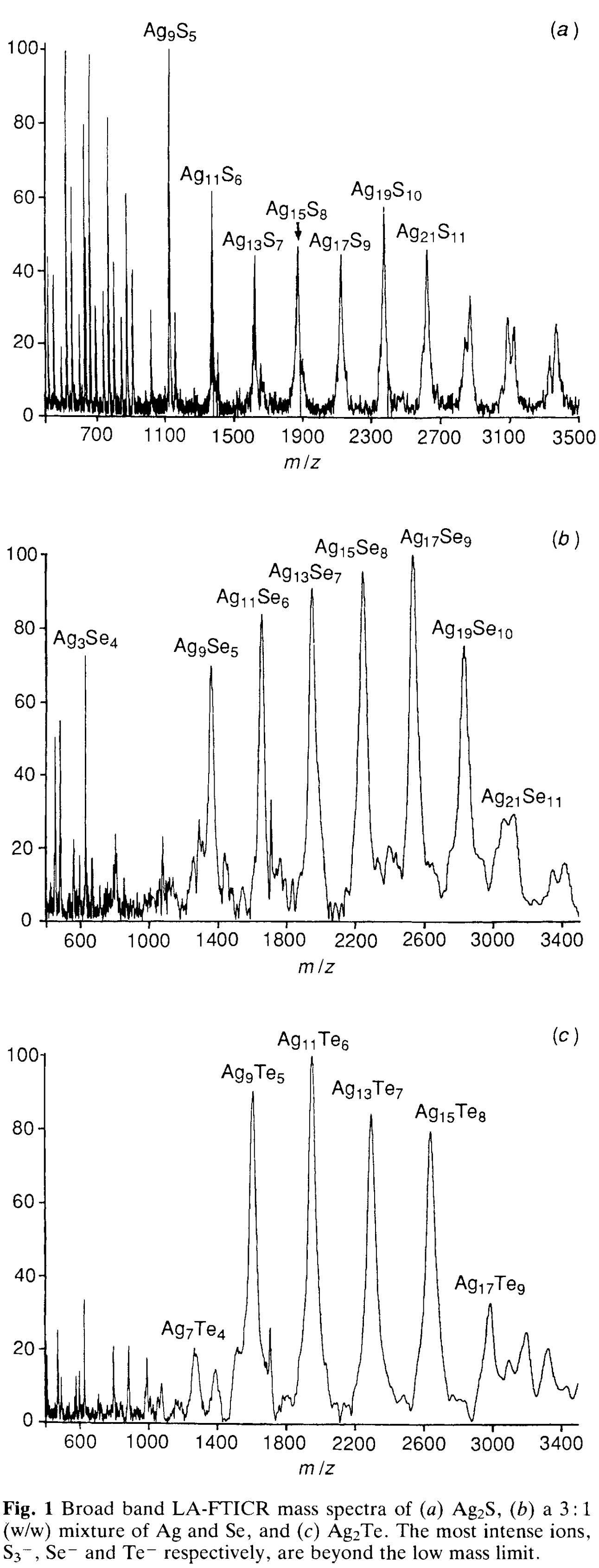

Fig. 1 Broad band LA-FTICR mass spectra of (*a*) Ag_2S, (*b*) a 3 : 1 (w/w) mixture of Ag and Se, and (*c*) Ag_2Te. The most intense ions, S_3^-, Se^- and Te^- respectively, are beyond the low mass limit.

reported[8] have similar metal chalcogenide ratios to the ions we have observed here, and to the ions $[Cu_xE_y]^-$.[2] We are currently probing the reactivities of these ions by collisional activation and ion molecule reactions: for example, charge transfer occurs with NO_2.

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