

# Prediction and observation of ring and chain isomers in $S_n^-$ ions

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Received 27 January 1995

## Abstract

Experimental and theoretical studies have been performed on singly charged anions of sulphur clusters  $S_n^-$  up to  $n = 9$ . Density functional calculations with simulated annealing predict the existence of two general classes of structure comprising rings and chains, respectively, with markedly different vertical detachment energies (VDE) for transitions to states of the neutral clusters. VDE and vibration frequencies obtained from photoelectron detachment measurements using a pulsed arc cluster ion source (PACIS) agree well with the calculated values and provide unambiguous spectroscopic evidence for the existence of two types of isomers in both  $S_6^-$  and  $S_7^-$ .

## 1. Introduction

Charged and neutral clusters of sulphur ( $S_n$ ,  $S_n^\pm$ ) are among the best studied of any element. Many crystalline forms of sulphur comprise ring molecules ( $n = 6, 7, 8, 10\text{--}13, 18, 20$ ) [1], the cations  $S_n^+$  were detected up to  $n = 56$  some years ago [2], and the anions  $S_n^-$  have been the subjects of many studies. Theoretical studies include those on neutral clusters up to  $n = 13$  by Hohl et al. [3] – using a combination of density functional (DF) calculations with molecular dynamics (MD) – and Raghavachari et al. [4] – using Hartree–Fock calculations with fourth-order Møller–Plesset corrections.

We extend here the previous MD/DF calculations on neutral sulphur clusters [3] to sulphur anions up to  $S_9^-$ , with particular focus on the energy difference between charged and neutral systems. We also describe photoelectron detachment measurements of the same ions, generated using the pulsed arc cluster ion source (PACIS) [5]. The features in the spectra correspond to transitions from the ground state of the ions to states of the neutral cluster and provide

information about both. Vibrational fine structure is resolved for  $n = 2, 3, 4$  and 6. We show that the comparison between theory and experiment for the vertical detachment energies (VDE) and vibration frequencies allows us to identify both ring and chain isomers for  $S_6^-$  and  $S_7^-$ . Full details of the method of calculation and the experiment will be given elsewhere [6].

## 2. Calculations

### 2.1. Method

The basic method was applied previously to neutral sulphur clusters [3]. The calculations are performed in a face-centred cubic unit cell with lattice constant 30 au, but with no other symmetry restrictions. The orbital basis set of Ref. [3] has been extended to an energy cutoff of 7 au ( $\approx 3200$  plane waves at  $k = 0$ ), with the density expanded in  $\approx 9000$  plane waves. Extensive tests were made to

ensure the reliability of the calculated energy differences [6].

We focus on the geometrical structures of the anions and on the energy differences – for these structures – between the most stable isomers and the states of the neutral cluster. The vertical detachment energy (VDE) is the smallest such difference. The calculation of the total energy for a charged system with periodic boundary conditions (PBC) is complicated by the divergence of the Coulomb energy per cell of a periodic array of charges. We first carry out cluster calculations using PBC, but with an additional uniform charge to neutralize the system. This density is used to calculate the Coulomb potentials for periodic arrays in which the densities are separated by successively larger distances. In the limit of infinite separation, the background density vanishes everywhere and the Coulomb potential converges to that of an isolated cluster, subject to zero boundary conditions at infinity [6].

## 2.2. Structures

In the structural plots, ‘bonds’ are shown only for interatomic distances less than 5.3 au, the minimum

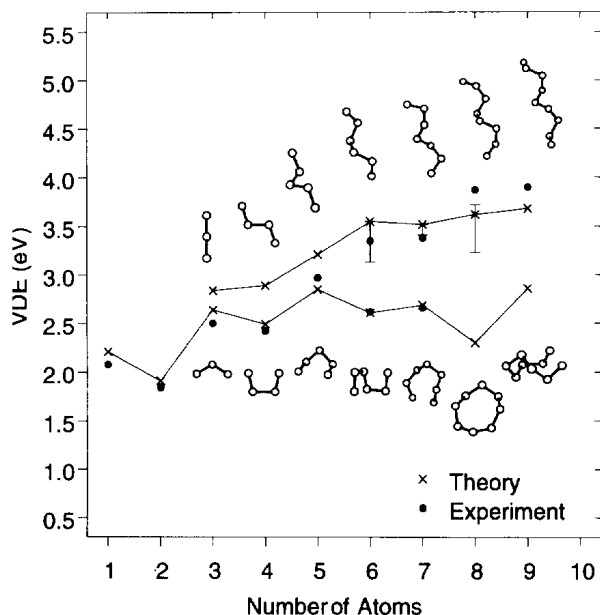


Fig. 1. Structures and vertical detachment energies of sulphur anions  $S_n^-$ ,  $n=1-9$ . Circles: experiment; crosses: calculations, including values for helical chains. The bars show the range for other chain structures.

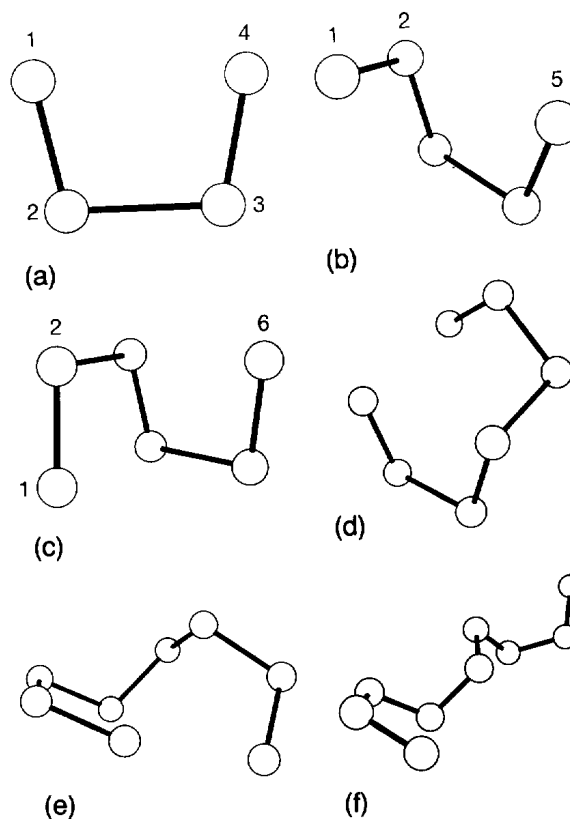


Fig. 2. Structures of sulphur anions  $S_n^-$ : (a)  $n=4$ ; (b–f) structures with terminal near-planar units for  $n=5-9$ .

in the pair correlation function of liquid sulphur between the first peak for covalently bonded pairs and the second peak for non-bonded pairs [7]. Both ‘ring’ and ‘chain’ structures are found in the anions, and Fig. 1 shows the most stable isomers of the former and representative isomers of the latter. The most stable structures are generally opened or puckered rings of the neutral clusters, where at least one bond is strained or broken by the presence of the additional electron. The ground states of  $S_5^-$ ,  $S_7^-$ ,  $S_8^-$  and  $S_9^-$  belong to this family.

There are many open chainlike structures, and the all-trans helical structures are shown in Fig. 1. Of particular interest are chains with a planar tetramer at one or both ends, because such structures had not been found in the neutral chains. The planar motif with approximately  $C_{2v}$  symmetry was encountered in  $S_4^-$  (Fig. 2a) and appears in sections of the larger anions (Figs. 2b–2f). Structures consisting entirely of this pattern exist only for even values of

$n(S_4^-, S_6^-, S_8^-)$ , in which case they are among the most stable isomers. This motif represents a compromise between a relatively open structure that can accommodate an additional charge and a closed structure with one large internuclear separation. The hybrids of all-trans chains with the  $C_{2v}$  cis-planar unit of  $S_4^-$  (Fig. 2) are on average  $\approx 0.1$  eV more stable than their all-trans counterparts.

### 2.3. Vertical detachment energies

In order to calculate the VDE (ionization energies of the anions) we use the scheme of von Barth [8] to relate the multiplet energies of the clusters to the energies of single determinantal states. In Fig. 1 we plot the VDE values for cage- and ring-like structures found for the anions. For  $n > 5$  there are many chain structures, and the ranges of VDE values are shown by bars for  $n = 6-8$ . The VDE of the two classes of structures are strikingly different. While the broken ring structures show almost constant or even decreasing VDE with increasing cluster size, the values for the chains increase initially and then saturate near  $S_6^-$ . The outermost electron is more tightly bound in the chains. The relatively small gap between the eigenvalues of the uppermost two occupied orbitals in the chain isomers is consistent with a high VDE, since the sum of the eigenvalues is one contribution to the total energy. The gap decreases continuously with increasing cluster size from 0.83 eV in the  $C_{2h}$  chain isomer of  $S_4^-$  to 0.06 eV in the  $C_2$  helical chain isomer of  $S_9^-$ . An analysis of the densities shows that the additional electron occupies an antibonding orbital localized mainly on the terminal bonds of the chain. The potential energy is then lower in longer chains with larger distances between the ends. This picture is consistent with the saturation of the VDE found in longer chains.

The charged broken rings and planar structures are more compact, and both the energy eigenvalue of the highest occupied orbital and its separation from the next occupied orbital remain large as the cluster size increases. Apart from  $S_1^-$ ,  $S_2^-$  and the  $D_{3h}$  and  $D_{2h}$  rings of  $S_3^-$  and  $S_4^-$ , the largest eigenvalue gap (2.23 eV) and the lowest VDE was found in the first genuine ring in  $S_8^-$ .  $S_2^-$  has a very low VDE, since the additional electron occupies an orbital with a pronounced antibonding character.

Table 1

Comparison of calculated vibration frequencies ( $\omega_e$ ,  $\text{cm}^{-1}$ ) with experimental values for  $S_2^-$  (in ultramarine green solution) and  $S_3^-$  (in sulphur solutions in dimethylformamide and hexamethylphosphoramide) [11]

Molecule	Symmetry	Method	Frequency $\omega_e$
$S_2^-$	$D_{2h}, {}^2\Pi_g$	exp	589.4 ( $\sigma_g$ )
		calc	577
$S_3^-$	$C_{2v}, {}^2B_1$	exp	235.5 ( $a_1$ ), 535 ( $a_1$ ), 571 ( $b_1$ )
		calc	216 ( $a_1$ ), 529 ( $a_1$ ), 557 ( $b_1$ )

### 2.4. Vibration frequencies

We have used an eigenmode detection scheme [9] to calculate the vibration frequencies of the neutral clusters closest to the geometry of the most stable isomer of the anion. The calculations require non-thermally equilibrated MD trajectories for the system in question. We remove an electron from the anion and allow the systems to evolve in MD runs (at 300–500 K) to find the closest minimum on the energy surface of the neutral cluster. The cluster atoms are then displaced by small amounts, and the trajectories followed for 2000 to 5000 time steps at 300 K. Vibration frequencies for the anions  $S_2^-$  and  $S_3^-$  are compared with experimental values in Table 1, and the results for selected neutral clusters are given in Table 2, with experimental frequencies and earlier calculated values. The overall agreement with earlier work is very satisfactory.

## 3. Experimental

The sulphur clusters are generated in a pulsed arc cluster ion source (PACIS), the main features of which have been described elsewhere [5]. In the PACIS, a pulse of He gas is flushed through the gap between the electrodes during ignition. The lower electrode is shaped like a crucible and contains a reservoir of S. The He/S plasma cools in an extender and forms clusters, which grow further on cooling in a supersonic jet. Adjustments of the source that can influence the structure of the clusters include the He stagnation pressure and the voltage and duration of the arc. However, the most important parameter is the time spent by the clusters in the extender.

Table 2

Experimental and calculated vibration frequencies  $\omega_e$  ( $\text{cm}^{-1}$ ) of selected isomers of neutral  $S_n$ ,  $n = 2, 3, 4, 6$ . meas refers to the present electron photodetachment measurements, calc to the present calculations

Molecule	Symmetry	Method	Frequency $\omega_e$
$S_2$	$D_{\infty h}, {}^3\Sigma_g^-$	expt <sup>a</sup>	725.65 ( $\sigma_g$ )
		meas	725 $\pm$ 12
		calc	691 ( $\sigma_g$ )
		CI <sup>b</sup>	778 ( $\sigma_g$ )
$S_3$	$C_{2v}, {}^1A_1$	meas	570 $\pm$ 24
expt <sup>c</sup>		256 ( $a_1$ ), 575 ( $a_1$ ), 656 ( $b_2$ )	
calc		247 ( $a_1$ ), 583 ( $a_1$ ), 660 ( $b_2$ )	
DF <sup>d</sup>		257 ( $a_1$ ), 602 ( $a_1$ ), 690 ( $b_2$ )	
$S_3$	$D_{3h}$	MP2 <sup>e</sup>	263 ( $a_1$ ), 577 ( $a_1$ ), 758 ( $b_2$ )
		calc	478 ( $e'$ ), 625 ( $a_1'$ )
		DF <sup>d</sup>	478 ( $e'$ ), 619 ( $a_1'$ )
$S_4$	$C_{2v}, {}^1A_1$	meas	256 $\pm$ 16, 630 $\pm$ 24
calc		111 ( $a_1$ ), 238 ( $a_2$ ), 334 ( $b_2$ ), 336 ( $a_1$ ), 652 ( $b_2$ ), 689 ( $a_1$ )	
$S_4$	$D_{2h}, {}^1A_g$	calc	67 ( $b_{3u}$ ), 249 ( $a_u$ ), 322 ( $a_g$ ), 335 ( $b_{1g}$ ), 668 ( $b_{2u}$ ), 697 ( $a_g$ )
$S_4$	$C_{2h}, {}^1A_g$	calc	98 ( $a_u$ ), 107 ( $b_u$ ), 216 ( $a_g$ ), 462 ( $a_g$ ), 638 ( $b_u$ ), 648 ( $a_g$ )
$S_6$ (II)	$D_{3h}$	meas	570 $\pm$ 32
$S_6$ helix		calc	619
$S_6$		calc	108 ( $e''$ ), 161 ( $a_2''$ ), 207 ( $e'$ ), 249 ( $a_1''$ ), 271 ( $a_1'$ ), 301 ( $e''$ ), 672 ( $e'$ ), 710 ( $a_1'$ )
$S_6$	$D_{3d}$	expt <sup>f</sup>	180 ( $e_u$ ), 203 ( $e_g$ ), 265 ( $a_{1g}$ ), 312 ( $a_{2u}$ ), 390 ( $a_{1u}$ ), 451 ( $e_u$ ), 462 ( $e_g$ ), 477 ( $a_{1g}$ )
		calc	160 ( $e_u$ ), 187 ( $e_g$ ), 255 ( $a_{1g}$ ), 303 ( $a_{2u}$ ), 347 ( $a_{1u}$ ), 458 ( $e_u$ ), 474 ( $e_g$ ), 476 ( $a_{1g}$ )

<sup>a</sup> Ref. [12]. <sup>b</sup> Ref. [13], CISD (TZ2P + f). <sup>c</sup> Ref. [14].

<sup>d</sup> Ref. [15], TZ2P + f, LSD.

<sup>e</sup> Ref. [16], quoted by Ref. [15], MP2, 6-31G\*. <sup>f</sup> Ref. [17].

The beam of anions is separated, according to their velocities, into a sequence of cluster bunches with a defined mass. A selected bunch is irradiated by a laser pulse of a given photon energy (3.49 or 4.66 eV), and the electrons detached are guided by magnetic fields towards an electron detector. The kinetic energy of the electrons is related to the times-of-flight, and the binding energy is the difference between the photon energy and the kinetic energy. The energy resolution of the electron spectrometer, which depends on the kinetic energy of the electrons and the velocity of the anions, is limited

here to 40–70 meV by charging arising from reactions between sulphur and the surfaces of the optic elements.

### 3.1. Mass spectra

In Fig. 3 we compare mass spectra of  $S_n^-$  clusters obtained at two different adjustments of the PACIS. Adjustment a favours small clusters with  $n = 2-7$ . The intensity is low for the monomer, highest for the dimer, and then decreases slightly up to  $n = 6$ . The intensity of  $S_7^-$  is again higher and then there is a sharp drop for the larger clusters. With the exception of the trimer, clusters with  $n < 6$  have a very low intensity in spectrum b. The progression starts at  $S_6^-$  and reaches a maximum at  $S_{10}^-$ . Only  $S_3^-$ ,  $S_6^-$  and  $S_7^-$  have relatively high intensities in both spectra.

It is possible to generate mass spectra with an intensity distribution averaged between the two spectra shown, for the monomer alone, or for very large

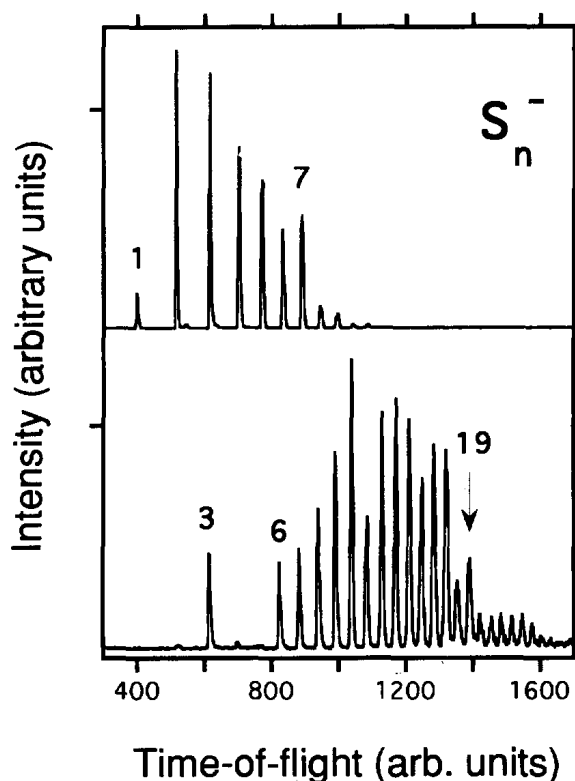


Fig. 3. Mass spectra of  $S_n^-$  clusters generated by the PACIS. (a) Slow cooling of the sulphur plasma; (b) more rapid cooling, but higher S vapour pressure.

clusters. The spectra displayed in Fig. 3 are of special interest, because the photoelectron spectra for  $S_6^-$  and  $S_7^-$  are quite different, suggesting that different isomers have been generated. Spectrum a probably results from a relatively slow ‘annealing’ of the clusters, and spectrum b from more rapid cooling.

### 3.2. Photoelectron spectra

The VDE are determined from the photoelectron spectra of the  $S_n^-$  clusters as the binding energy (BE) of the maximum of the peak corresponding to the transition from the anion ground state into the ground state of  $S_n$ . Vibrational fine structure is resolved for  $S_n^-$  with  $n = 2, 3, 4, 6$ , and the vibration frequencies (‘meas’ in Table 2) are assigned to modes of states of the neutral cluster. For  $S_4^-$  a second progression corresponds to a transition into an excited state of  $S_4$ . The corresponding binding energies are given in Table 3.

Photoelectron spectra (Figs. 4a, 4b) have been recorded for  $S_6^-$  using the source adjustments a and b shown in the mass spectra of Fig. 3. We also found adjustments that produce a superposition of these spectra. We assign the dominant features (A, B, C) observed to photoemission from two different isomers of  $S_6^-$ , denoted (I) and (II), respectively. The only vibrational fine structure observed, feature A in the spectrum of  $S_6^-$  (II), corresponds to a frequency of  $570 \pm 32 \text{ cm}^{-1}$  (Table 2). Two different spectra (Figs. 4c, 4d) have also been recorded for  $S_7^-$ ,

corresponding to two different isomers  $S_7^-$  (I) and  $S_7^-$  (II). No vibrational fine structure has been resolved in the heptamer isomers.

## 4. Comparison of theory and experiment

### 4.1. Vertical detachment energies

Fig. 1 shows a comparison of the calculated VDE – for the most stable closed and open isomers – with values extracted from the photoelectron spectra. Values are shown for both spectra of  $S_6^-$  and  $S_7^-$ . More details are given in Table 3, which covers a range of states of the neutral clusters and provide information about the ordering of their energies, at least for the ground state geometries of the anions. The overall agreement is remarkably good.

In the case of ions with  $n > 5$ , there are numerous chain structures, and we show both the range of VDE values and the result for the helical chain. For the clusters up to  $S_5^-$  the experimental VDE agree with the values for the most stable closed structures to within 0.15 eV, and the two measured values for  $S_6^-$  and  $S_7^-$  are very close to the calculated VDE of the most stable closed and open forms. The experimental values for  $S_6^-$  and  $S_9^-$  are in the same range as those for the chainlike structures. For the cases where a definite assignment of the transition could be made, the largest discrepancy was in the  $C_{2v}$  (ground) state of  $S_3^-$ , where the calculated and mea-

Table 3

Binding energies (at the maxima A–D) of transitions in the photoelectron spectra of  $S_n^-$  (eV). Experimental numbers are given in the left column with uncertainties in parentheses, calculated values in the right column. frag denotes features assigned to photoemission from  $S_1^-$  ions generated by photofragmentation

$n$	A		B		C			D		E		
2	1.84	(0.05)	1.91	2.3	(0.1)	2.45	2.73	(0.1)	2.98	4.4	(0.15)	
3	frag			2.50	(0.05)	2.64	3.7	(0.1)	3.73/3.77	3.9	(0.1)	3.95
4	frag			2.42	(0.05)	2.49	2.7	(0.1)		2.96	(0.05)	3.19 3.87 (0.1) 3.96
5	frag			2.97	(0.03)	2.85/3.28	3.9	(0.1)	3.81/3.92			
6(I)	2.62	(0.1)	2.61	3.3	(0.15)	3.17	4.1	(0.1)	3.80			
6(II)	3.35	(0.05)	3.55									
7(I)	2.66	(0.05)	2.69	3.47	(0.07)	3.88	4.14	(0.07)	4.15	4.4	(0.1)	4.51
7(II)	3.38	(0.05)	3.52	3.6	(0.2)	3.62						
8	3.87	(0.07)	3.62/3.89	4.3	(0.07)	4.12						
9	3.9	(0.1)	3.68/3.94	4.3	(0.1)	4.24						
10	3.9	(0.15)		4.35	(0.1)							
11	3.75	(0.2)		4.1	(0.15)							

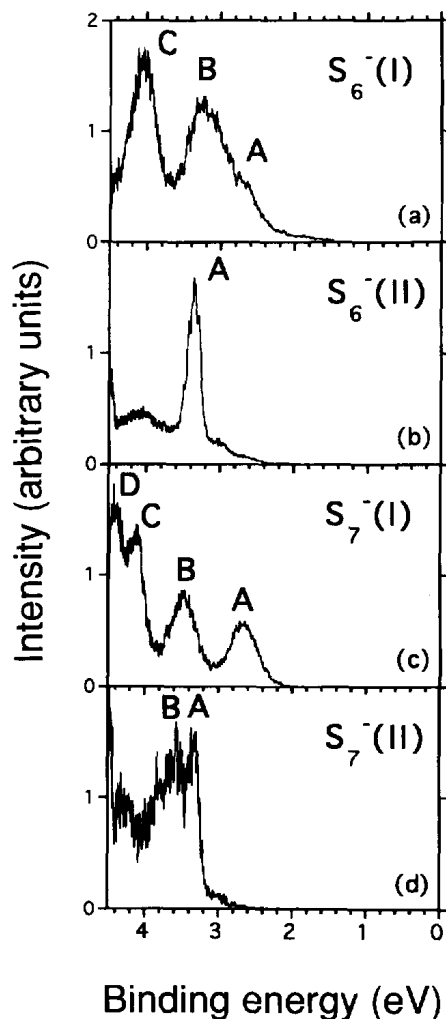


Fig. 4. Photoelectron spectra of  $S_6^-$  and  $S_7^-$  for photon energy  $h\nu = 4.66$  eV. Spectra are shown for each cluster for two source adjustments corresponding to the mass spectra shown in Fig. 3. Adjustment a:  $S_6^-$  (I) and  $S_7^-$  (I); adjustment b:  $S_6^-$  (II) and  $S_7^-$  (II).

measured VDE were 2.64 and  $2.50 \pm 0.05$  eV, respectively.

In addition to transitions to the most stable states of the neutral clusters (Fig. 1), valuable information can be obtained by measuring transitions into excited states of  $S_n^-$ . Some of the measured peak positions in the photoelectron spectra are compared with calculated excitation energies in Table 3. The first three peaks in the dimer (1.84, 2.45, 2.73 eV) are in satisfactory agreement with the calculated excitation energies to the  $^3\Sigma_g^-$ ,  $^1\Delta_g$ , and  $^1\Sigma_g^-$  states of  $S_2$

(1.91, 2.45, 2.98 eV). Information about the structures of the clusters can also be obtained. In  $S_3^-$ , for example, the measured excitation energies (2.50, 3.7, 3.9 eV) are consistent with transitions for the open structure to the  $^1A_1$ ,  $^3A_2/{}^3B_1$  and  $^3B_2$  states of the neutral cluster (2.64, 3.73/3.77, 3.95 eV), but not with excitations for the ring structure (1.34, 2.93, 2.94 eV for the  $^1A_1$ ,  $^3A_2$ ,  $^3B_1$  states, respectively). The measured binding energies in  $S_4^-$  (Table 3) are consistent with the calculated multiplet structures of the closed  $C_{2v}$  and  $D_{2h}$  geometries, but not with those for the open  $C_{2h}$  form (2.89, 3.36, 4.07 eV for  $^1A_g$ ,  $^3B_u$ ,  $^1B_u$ , respectively).

#### 4.2. Vibration frequencies

The calculated vibration frequencies in two- and three-atom clusters (Tables 1 and 2) are in generally good agreement with previous data. For  $S_4$ , the measured frequencies are closer to the calculated values for the  $C_{2v}$  and  $D_{2h}$  isomers than those of the  $C_{2h}$  form, which is consistent with the relative stabilities calculated. The only frequency measured for the  $S_6$  structure ( $570 \pm 32$   $\text{cm}^{-1}$ ) is significantly higher than both the calculated and Raman frequencies of the  $D_{3d}$  isomer and falls in a pronounced gap of the spectrum for the  $D_{3h}$  isomer. Since the vibrational structure was only observed in spectrum  $S_6^-$  (II), where the anions are chainlike, this is evidence that the neutral cluster does not have time to relax to one of the more stable isomers during the measurement. It is also consistent with the observation [10] that *all* unbranched sulphur rings regardless of the size have no fundamental frequencies above  $530$   $\text{cm}^{-1}$ . We have studied the vibrations of  $S_6$  with the helical ( $C_2$ ) geometry found for the  $S_6^-$  anion, and the existence of a totally symmetric (a) vibration with frequency  $619$   $\text{cm}^{-1}$  supports this picture.

#### 5. Discussion and concluding remarks

We have performed a theoretical and experimental study of negatively charged and neutral sulphur clusters, focusing on trends in the geometries and energy differences. The comparison between theory and experiment (Fig. 1) indicates that clusters generated by the source are ringlike up to  $S_5^-$  and chain-

like for  $S_8^-$  and  $S_9^-$ .  $S_6^-$  and  $S_7^-$  can occur in both forms, with source adjustments a and b favouring rings (low VDE) and chains (higher VDE), respectively. The photoelectron spectra (Figs. 4a–4d) then provide direct spectroscopic evidence for the existence of different cluster isomers in the gas phase. The calculated and measured vibration frequencies are consistent with this picture.

The transition from closed to open structures as  $n$  increases through 6–7 is of particular interest, since our calculations predict that closed (ringlike) isomers are the most stable for *all* cluster sizes. In fact, the smallest clusters have few isomers, the relaxation of the structure requires less time, and only the most stable ringlike structures are observed. Energetic stability is, however, not the only criterion for the occurrence of particular structures in a cluster beam. Rings are observed for  $S_6^-$  and  $S_7^-$  when conditions allow a slower cooling of the plasma and more time for structural rearrangement. Structure formation is necessarily more complex in closed structures than in chains, where growth can occur by the addition of terminal atoms. Ring formation from  $S_n^-$  chains is hampered by the negative charge localized on the terminal atoms, in contrast to neutral clusters, where simulated annealing calculations indicate that all chain structures relax to a closed form if the additional electron is removed.

The numerical preference for chain isomers in the larger clusters can be appreciated by examining the pattern of the signs of the dihedral angles (“motif”) in different structures. Closed structures require distinct patterns (such as  $+ - + - + - + -$  in the most stable isomer of  $S_8^-$ ), while open structures can have many combinations of  $+$ ,  $-$ , and  $0$ , since the beginning and the end of the chain are not constrained to coincide. The higher configurational freedom of chains means that they are favored if the time available for cluster formation is too short to allow annealing. The observation of chainlike isomers is consistent with the higher electron affinities found in these structures [6], since such clusters are more likely to survive growth, fragmentation and

charge transfer processes. Clusters with lower EA are not excluded, as we have seen in  $S_6^-$  and  $S_7^-$ , and suitable annealing of the cluster beam could lead to ringlike structures.

### Acknowledgement

We thank many colleagues, particularly P. Ballone, for discussions and suggestions, and the German Supercomputer Center (HLRZ) for a grant of CPU time on the Cray YMP8/864 in the Forschungszentrum Jülich.

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