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

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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 ($n = 6, 7, 8, 10-13, 18, 20$) [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 (≈ 3200 plane waves at $k = 0$), with the density expanded in ≈ 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 motif 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 ≈ 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_6^- . 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 (ω_e , 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 ω_e
S_2^-	$D_{\infty h}$, $^2\Pi_g$	exp	589.4 (σ_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 ω_e (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 ω_e
S_2	$D_{\infty h}, {}^3\Sigma_g^-$	expt ^a	725.65 (σ_g)
		meas	725 $\pm$ 12
		calc	691 (σ_g)
		CI ^b	778 (σ_g)
S_3	$C_{2v}, {}^1A_1$	meas	570 $\pm$ 24
S_3		expt ^c	256 (a_1), 575 (a_1), 656 (b_2)
		calc	247 (a_1), 583 (a_1), 660 (b_2)
		DF ^d	257 (a_1), 602 (a_1), 690 (b_2)
		MP2 ^e	263 (a_1), 577 (a_1), 758 (b_2)
S_3	D_{3h}	calc	478 (e'), 625 (a'_1)
		DF ^d	478 (e'), 619 (a'_1)
S_4	$C_{2v}, {}^1A_1$	meas	256 $\pm$ 16, 630 $\pm$ 24
S_4		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 ^f	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})

^a Ref. [12]. ^b Ref. [13], CISD (TZ2P + f). ^c Ref. [14].

^d Ref. [15], TZ2P + f, LSD.

^e Ref. [16], quoted by Ref. [15], MP2, 6-31G*. ^f 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.

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).

sured VDE were 2.64 and 2.50 ± 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 ± 32 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 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 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.

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