5100 J. Phys. Chem. A **1998,** *102,* 5100−5105

Sulfur Cluster Dianions

V. Berghof, T. Sommerfeld, and L. S. Cederbaum*

Theroretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

Received: January 22, 1998; In Final Form: April 1, 1998

Free dianionic sulfur clusters have been studied by standard ab initio methods. Chainlike S_n^{2-} isomers have been found to exhibit nonlinear twisted geometries, and the onset of electronic stability in this series is predicted to occur at $n = 7$. S_8^{2-} is the smallest system *clearly* stable with respect to electron autodetachment and is predicted to be sufficiently long-lived to allow the observation in a mass spectrometer. Branched isomers have been found to be electronically more stable than the corresponding chainlike isomers but are expected to be more sensitive to fragmentation. The bonding mechanisms of the excess electrons in the different isomers are discussed, and the stable systems are compared to other small gas-phase dianions. Our results broaden the overall picture of isolated dianionic species.

1. Introduction

In comparison to neutral particles, the properties of dianions and higher negatively charged species depend drastically on their environment. Practically all small textbook dianions that are well-known in condensed phases, e.g., CO_3^{2-} or SO_4^{2-}, are unstable with respect to electron autodetachment in the gas phase.[1,2] On the other hand, many dianions that have been observed or predicted to exist as isolated species, e.g., KF_3^{2-} [3] or C_7^{2-},[4,5] are unknown in solution or solid-state chemistry. These surprising differences can be traced back to the strong Coulomb repulsion of the two excess charges confined to a small molecular region. In condensed phases a dianion can be stabilized by a crystal field or solution effects, whereas in the gas phase no environmental stabilization is present. The key ingredient that determines the structural properties and the very existence of a given *free* dianionic species is *not* a low total energy but its stability to electron autodetachment. Thus, the diversity between isolated and embedded/solvated dianions goes back to different stability criteria.

A class of dianions that may be present in condensed as well as in the gas phase are sulfur cluster dianions. In polysulfide solutions there exist chainlike S_n^{2-} dianions with practically arbitrary chain lengths *n*. These sulfur cluster dianions will obviously be stable in the gas phase if the chain gets long enough. In this paper we will examine the electronic and geometric structures of free sulfur cluster dianions and investigate the onset of stability with increasing chain length *n*. In addition, the question of other structure types that form small stable dianions will be considered. The paper is organized as follows. In section 2 we describe the standard quantum chemical methods employed in our investigation. In section 3 the crucial points in the theoretical investigation of free dianions are briefly reviewed, and our results for different sulfur cluster dianions are discussed. Section 4 constitutes a summary.

2. Computational Details

The data at the independent particle level were obtained using the standard self-consistent field (SCF) restricted Hartree−Fock (RHF) and restricted open-shell Hartree−Fock (ROHF) techniques. Our double-ζ (DZ) basis set consisted of Cartesian Gaussian-type functions comprising Dunning's[6] contraction of Huzinaga's[7] primitive set. In addition, the standard DZ basis was augmented with one d-type ($\alpha = 0.542$) polarization and one s-type ($\alpha = 0.04$) and p-type ($a = 0.037$) diffuse functions (DZPD). The influence of more extended basis sets of triple-ζ quality as well as DZ basis sets containing more polarization and diffuse functions have been investigated but found to have only minor effects on the relevant properties[8] In this paper we present only results obtained using the DZPD basis set and note that the electron detachment energies tend to be more positive, i.e., the dianion to be more stable, if larger basis sets are employed.

The geometry optimizations at the SCF level of theory were performed straightforwardly, and at all obtained structures the harmonic vibrational frequencies have been computed but are not reported here in detail. The ab initio packages used stem from the GAMESS,[9] GAUSSIAN94,[10] and MOLCAS[11] systems of programs.

The decisive quantity in the investigation of dianions is the electron detachment energy (EDE). Vertical EDEs can be obtained directly at the level of Koopmans' theorem (KT)[12] or using the outer-valence Green's function (OVGF) approach.[13] The latter technique has been discussed in detail elsewhere,[14] and we only briefly note that it allows the direct calculation of ionization spectra and includes electron correlation and relaxation effects. At the SCF and single plus double excitation configuration interaction (SDCI) levels of theory, the electron detachment energies have been obtained "indirectly", i.e., by computing the difference between the total energies of the monoanion and its corresponding dianion referred to as ΔSCF and ΔSDCI. In the SDCI and OVGF calculations only the valence electrons have been correlated; i.e., the sulfur 1s, 2s, and 2p electrons have been frozen.

3. Dianionic Sulfur Clusters

Before we describe our search for stable S_n^{2-} dianions, let us briefly consider the study of doubly negative charged systems from a general point of view. It has been established that a

---

* To whom correspondence should be addressed.

S1089-5639(98)00837-8 CCC: $15.00

stable gas-phase dianion has to possess two basic properties;[15] first, it has to be stable with respect to electron autoejection and, second, with respect to fragmentation of the nuclear framework. We note that for example the prominent inorganic dianions CO_3^{2-} [16,17] and SO_4^{2-} [16,18] are as isolated species unstable with respect to electron autoejection. However, from an experimental point of view a dianion just has to show a sufficiently long lifetime on the experimental time scale. Thus, depending on the relevant time scale dianionic systems that are only metastable with respect to certain fragmentation channels may nevertheless be detected.

Systems that are metastable with respect to vertical electron loss are in general short-lived ($\tau = 10^{-12}-10^{-15}$ s) and can only be observed as resonances in electron scattering cross sections. In this paper we concentrate on long-lived species, where long-lived implies a lifetime of at least 10^{-5} s, such that the dianion can be detected in a mass spectrometer. The minimum requirement for a long lifetime in the latter sense is a positive vertical EDE which has been termed *local* stability in ref 19. Local stability implies the existence of a local minimum on the dianionic potential energy surface (PES) where stability with respect to vertical electron autoejection is given. Of course, this requirement is only necessary but not sufficient for a long lifetime. In the next step one needs to consider electronic stability for a range of molecular geometries probed in the zero-point vibrational motion and the barrier heights to unimolecular dissociation. The former property can often be estimated based on the EDE computed with respect to the geometrically closest minimum on the monoanionic PES (referred to as *adiabatic EDE*) and the latter based on the dissociation energy.

The first step in the search for stable dianions is to find an appropriate structure. It has been established for several classes of dianions that the geometrical configuration adopted by a dianion can differ markedly from the ground-state structures of the corresponding monoanions and neutrals.[1,20] Nevertheless, the structures of known monoanions and neutrals can provide valuable hints, and in the following we briefly summarize what is known about the geometries of neutral and monoanionic sulfur clusters. Small neutral and monoanionic sulfur clusters have been studied by several authors.[21−24] For S_3-S_5 there exist several isomers that are almost isoenergetic, and the ground states seem to correspond to ringlike structures. In the monoanionic species the additional electron occupies an orbital that has an antibonding character with respect to at least one bond of the neutral ringlike system, and consequently the structures become more open or even a bond break may occur. These trends have been substantiated for larger systems;[23] the ground-state structures of $S_6^- - S_9^-$ correspond to "rings" where one bond is lengthened or broken.

Extrapolation of the structural trends of neutral and monoanionic sulfur clusters leads to chainlike dianions, since the addition of a second excess electron to a sulfur ring may be expected to break one of the bonds completely. This is in accordance with the structures of polysulfides in solution. Moreover, a chainlike S_n^{2-} dianion shows a well-defined Lewis structure, which from earlier studies on different classes of free dianions has been established as a criterion to find promising candidates for electronically stable dianions.[25,26] One may expect that geometrical configurations with "reasonable" Lewis structures exhibit closed-shell electronic ground states and "large" HOMO−LUMO gaps; i.e., all electrons, including the two excess electrons, occupy energetically favorable bonding MOs. Loosely speaking, in structures of this type the Coulomb repulsion of the excess charges may be expected to be contrasted with a rare gaslike stabilization. Another structure type that fulfills the criterion of a "reasonable" Lewis structure are branched geometrical configurations where the sulfur atom at the branching point shows a tetrahedral configuration. We come back to this type of geometry below.

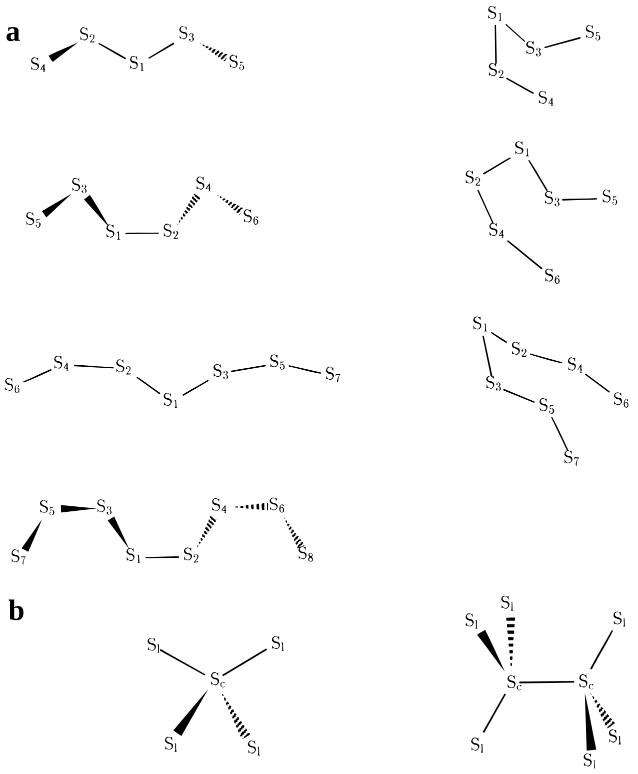

Figure 1. (a) Geometrical structures of the stretched chain (left) and folded chain (right) S_n^{2-} clusters. The bond lengths and angles of the stretched isomers are found in Table 1. (b) Geometrical structures of the branched S_5^{2-} and S_8^{2-} clusters. The corresponding geometrical parameters are mentioned in the text.

At this points we briefly note that in case of the smaller species we are discussing structures of electronically unstable dianions. However, these results allow us to classify the structural types of electronically favored dianions and provide consequently a good starting point in the investigation of larger systems. Moreover, the favored small clusters will become stable in a polar environment and may hence have their own significance.

Let us first investigate chainlike S_n^{2-} dianions. These isomers show—as expected—closed-shell electronic ground states. We have concentrated, on the one hand, on conformers where the distance between the two chain ends is maximal (*stretched chain conformers*) and, on the other hand, on conformers that resemble the structures of the corresponding monoanions described above. In the latter conformers the terminal sulfur atoms are more or less adjoined, and we refer to these structures as *folded chain conformers*. Both conformer types represent local minima on the associated S_n^{2-} PES; i.e., the computed harmonic frequencies show real values. The stretched chains are somewhat twisted and show C_2 symmetry, whereas the folded chain isomers adopt chairlike configurations (Figure 1a). Despite this structural differences, the two conformer types are extremely similar. The folded chain conformers are only slightly higher in total energy (≈0.2 eV), and independent of the conformer and the number of sulfur atoms, in all examined chain structures all sulfur−sulfur bonds show lengths of about 2.08 Å (with deviations of

TABLE 1: Geometrical Parameters for the Stretched Chain S_n^{2-} Conformers Depicted in Figure 1a (Left)[a]

	S_1-S_2	S_2-S_4	S_4-S_6	S_6-S_8	∠ (S_3, S_1, S_2)	∠ (S_1, S_3, S_5)	∠ (S_4, S_6, S_8)
S_5^{2-}	2.0891	2.0989			111.0	110.2	
S_6^{2-}	2.0865	2.0846	2.0909		109.4	110.2	
S_7^{2-}	2.0838	2.0825	2.0867		109.5	110.1	
S_8^{2-}	2.0784	2.0829	2.0810	2.0837	107.5	109.0	109.7

[a] The bond lengths are given in angstroms and the bond angles in degrees.

TABLE 2: Electron Detachment Energy of the Chainlike S_n^{2-} Isomers at Different Theoretical Levels (All Values Are Given in eV)

	ΔSCF			ΔSDCI	
	KT	vertical	adiabatic	vertical	OVGF
	Stretched Chain Isomers				
S_2^{2-}	−3.17	−4.14	−4.40		
S_3^{2-}	−2.26	−3.03	−3.32		−4.38
S_4^{2-}	−0.88	−2.02	−2.16	−1.62	−2.56
S_5^{2-}	−0.09	−0.59	−0.86	−0.82	−1.75
S_6^{2-}	0.44	−0.005	−0.14	−0.23	−0.51
S_7^{2-}	0.98	0.51	0.36	0.34	0.04
S_8^{2-}	1.32	0.81	0.70	0.70	0.39
	Folded Chain Isomers				
S_4^{2-}	−1.53	−2.10	−2.45	−2.28	
S_5^{2-}	−0.19	−0.70	−1.38	−0.93	
S_6^{2-}	0.30	−0.19	−0.78	−0.51	
S_7^{2-}	0.92	0.44	0.24	0.093	−0.0085

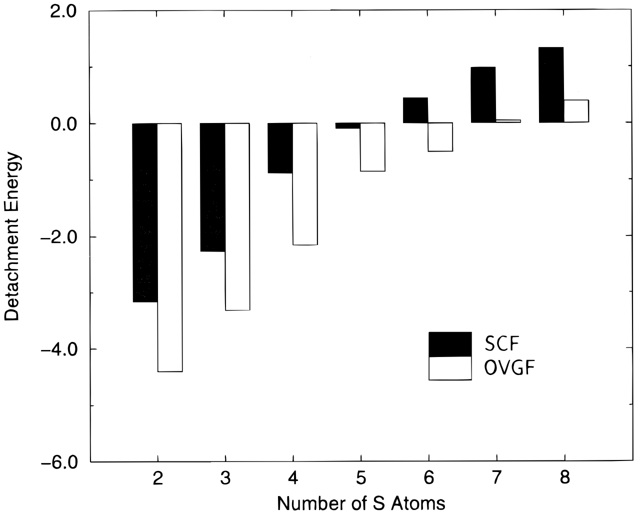

Figure 2. Dependency of the vertical electron detachment energy on the chain length of the sulfur cluster dianions. The detachment energy is given in eV.

less than 0.02 Å) and all bond angles have values close the tetrahedral angle (109 ± 2°) (see Table 1). Moreover, the distance between the two terminal atoms is only reduced by 10−20% in going from the stretched to the corresponding folded chain conformer.

Having established the structural characteristics of chainlike sulfur cluster dianions, we now turn to their electronic stability. The vertical EDE of the various conformers has been calculated at different levels of theory (Table 2). As expected, the smallest clusters ($n = 2$, 3) are very unstable with respect to electron loss, but if the chain is elongated, the electonic stability grows considerably (Figure 2). At the KT level of theory S_6^{2-} is the smallest system showing a positive EDE, but this trend is not substantiated at higher levels. The first cluster found to be electronically stable at all employed levels of theory is S_7^{2-}. The vertical EDE of the stretched chain conformer of S_7^{2-} is 0.98, 0.51, 0.36, and 0.04 eV at the KT, ΔSCF, ΔSDCI, and OVGF levels of theory, and these values are only slightly reduced for the folded chain conformer, stressing again the great similarity of the two chainlike conformers. It is however difficult to draw final conclusions on the exact value of the vertical EDE for the following reasons. In contrast to the experience with other dianionic systems, where the EDE based on KT lies at least 1 eV above the ΔSCF value and where the ΔSCF is usually close to the EDE calculated at correlated levels, for the dianionic sulfur clusters ($n > 5$) the difference between KT and ΔSCF is as small as 0.5 eV, and correlation effects have a marked influence on the EDE. We note however that the differences between the EDE values at different levels of theory decrease with the size of the clusters. Nevertheless, in this paper we restrict our conclusions to the clearly observed trend that S_7^{2-} marks the onset of electronic stability in the S_n^{2-} series and that S_8^{2-} is beyond doubt locally stable. To give more accurate values, a thorough study at highly correlated levels is needed.

Let us briefly analyze the trends in the EDE in the light of the charge distribution of the chainlike conformers. The results of our Mulliken and Löwdin population analysis are depicted in Figure 3. Both show that the two additional charges are essentially localized at the outermost sulfur atoms whereas the inner atoms carry only small amounts of negative charge. Consequently, the facts that the stretched chain conformers are electronically more stable than the folded chain clusters as well as that the latter, which are based on ringlike structures, are opened up to the extent described above can easily be explained by the Coulomb repulsion between the excess charges localized at the terminal atoms. In comparison to the linear chain carbon cluster dianions, where the excess charge is mainly localized at the terminal C_2 groups rather than at the terminal atoms, the dianionic sulfur clusters closely resemble the model dianion put forward in ref 4, which consists of an atomic chain with two electrons attached to the terminal atoms. Thus, the question of the electronic stability of a chainlike sulfur dianion comes down to a matter of distance.

We now turn to properties beyond the local stability of the chainlike sulfur cluster dianions. We have calculated the adiabatic electron affinity at the ΔSCF level. To this end the geometry of the S_n^- monoanions was optimized starting from the structure of the associated dianions. In this way we found geometrical configurations analogous to those described in refs 22 and 23. Most of our bond lengths differ from those described in the literature by less than 0.01 Å, and the differences in the bond angles are in the order of 0.5°. Hence, we do not report the geometrical parameters of the monoanions and just note that in the chainlike S_n^- monoanions the bond lengths and angles are similar to those of the dianions apart from the two terminal bond lengths which are shortened by about 0.1 Å. The adiabatic EDE of the two S_7^{2-} conformers is found to be less than 0.2 eV lower than the corresponding vertical value, and for S_8^{2-} the difference between vertical and adiabatical EDE is even reduced to 0.1 eV (Table 2). Thus, if a sulfur cluster dianion is clearly stable with respect to vertical electron autodetachment, is can be expected to be stable with respect to adiabatic electron loss as well.

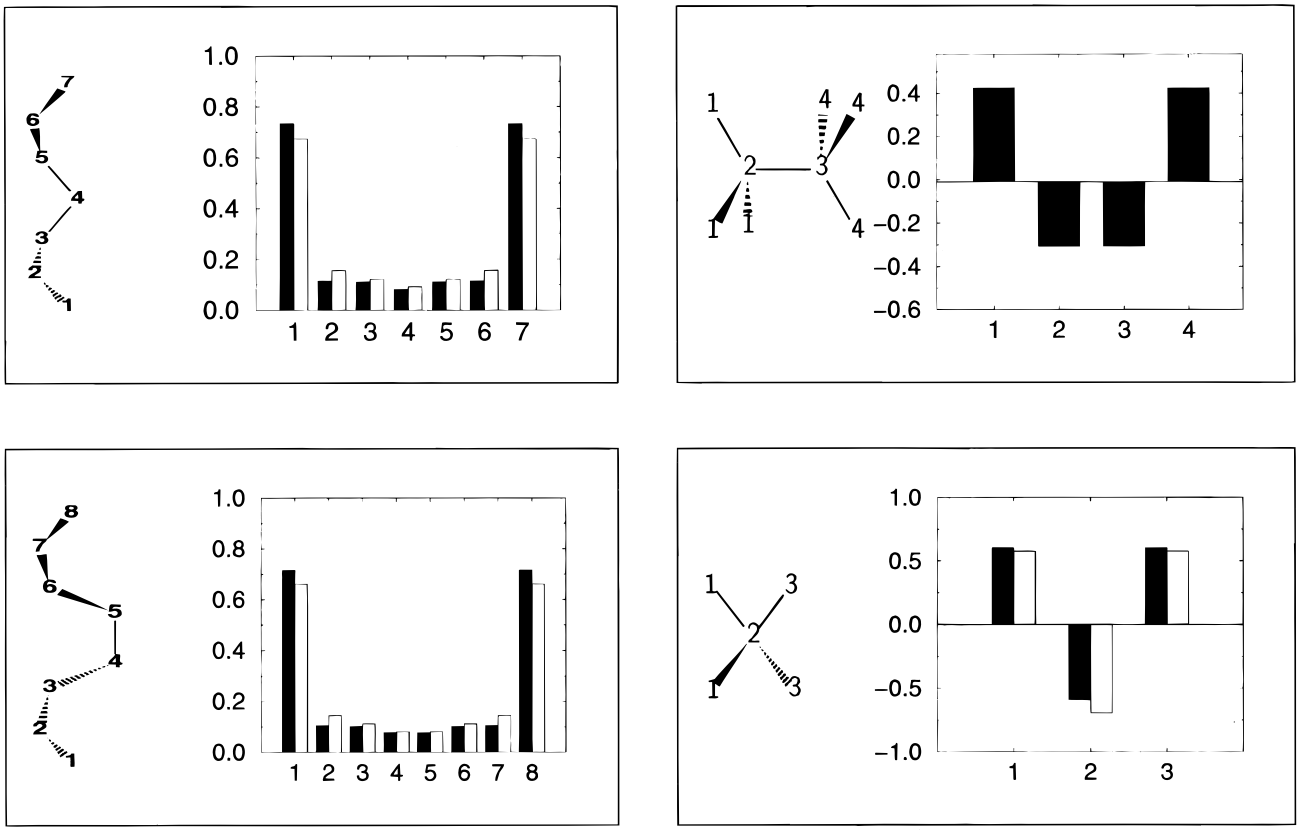

Figure 3. Mulliken (black bars) and Löwdin (white bars) population analysis data for the S_7^{2-} and S_8^{2-} stretched chain conformers as well as for the S_5^{2-} and S_8^{2-} branched isomers.

TABLE 3: Dissociation Energies for Different Fragmentation Channels of the Chainlike S_7^{2-} and S_8^{2-} Isomers[a]

$S_8^{2-} \rightarrow S^- + S_7^-$	0.74	$S_7^{2-} \rightarrow S^- + S_6^{2-}$	0.61
$S_8^{2-} \rightarrow S_2^- + S_6^-$	−0.17	$S_7^{2-} \rightarrow S_2^- + S_5^-$	−0.52
$S_8^{2-} \rightarrow S_3^- + S_5^-$	−0.69	$S_7^{2-} \rightarrow S_3^- + S_4^{2-}$	−1.44
$S_8^{2-} \rightarrow S_4^- + S_4^-$	−1.05		

[a] The data have been obtained at the ΔSCF level of theory and are given in eV. Note that all fragmentations are hindered by a Coulomb barrier (see text).

We have also computed fragmentation energies with respect to all possible monoanionic dissociation products and the results for S_7^{2-} and S_8^{2-} are listed in Table 3. Clearly the most favorable dissociation pathway corresponds to a "symmetric" bond breaking leading to fragments of equal or similar size. Both S_7^{2-} and S_8^{2-} are unstable with respect to these "symmetric" fragmentations by about 1.4 and 1.0 eV, respectively. We expect these dissociations to be, however, hindered by broad barriers, arising from the long-range Coulomb repulsion and the short-range attraction leading to a sulfur−sulfur bond between two S_n^- monoanions. To describe the associated homolytic bond breaking appropriately, one has to apply *at least* a two-configurational SCF procedure. Furthermore, many reoptimizations of the dissociating constituents are required to obtain the minimal energy dissociation pathway. This is a very demanding task for a many electron system as large as S_8^{2-}. To nevertheless estimate the barrier height, we have computed the barrier of the smaller dianion $S_2O_6^{2-}$. This system has been investigated experimentally as well as theoretically[27,28] (see also below), and the sulfur−sulfur bond of the $S_2O_6^{2-}$ dianion shows a dissociation energy of about −1.7 eV comparable to those of S_7^{2-} and S_8^{2-}. We have examined the minimal energy pathway corresponding to dissociation of $S_2O_6^{2-}$ into two open-shell SO_3^- monoanions using the DZPD basis and a two-configuration SCF wave function.[8] At this theoretical level the barrier is indeed very broad, and the computed height of 1.1 eV is clearly sufficient to support many vibrational states. We expect qualitatively similar results for S_7^{2-} and S_8^{2-} and consequently predict S_7^{2-} as well as S_8^{2-} to be metastable with respect to fragmentation. We conclude that S_7^{2-} is at the verge of electronic stability and predict S_8^{2-} to exibit a long lifetime from a mass spectrometrical point of view.

Having established the onset of stability in the series of chainlike sulfur cluster dianions, let us now consider other structures. The chainlike geometries had been investigated based on the structures of polysulfide dianions in solution and on the gas-phase geometries found for neutral and monoanionic sulfur clusters. A chain structure obviously allows the maximum distance between two excess charges, if these are localized at the terminal atoms of the chain. It has however been found for other dianionic species that structures exhibiting more than two electron accommodating subunits often possess a higher EDE than the associated chainlike arrangement,[5,20] even though the former species are more compact. In other words, in order to form a structure that is able to bind two excess electrons, there is a tradeoff between the number of and the distance between electron accommodating groups, i.e., groups showing a large local electron affinity.

Translated into sulfur clusters this implies a branched structure with more than two terminal atoms, since in our population analysis discussed above terminal sulfur atoms have been identified to accommodate nearly one excess charge. Furthermore, we could not find any small group of two or three sulfur atoms, comparable to the C_2[20] or SiO_2[25,26] group, that had a larger electron affinity than a single terminal sulfur atom. The most simple *branched sulfur clusters* are the analogous of the

TABLE 4: Relative and Vertical Electron Detachment Energies of Different S_5^{2-} and S_8^{2-} Isomers Are Compared (All Energies Are Given in eV)

isomer	rel energy	KT	ΔSCF	ΔSDCI	OVGF
		S_5^{2-} Isomers			
str chain	0.0	−0.09	−0.59	−0.82	−1.02
folded chain	0.19	−0.19	−0.70	−0.93	
tedrahedral	1.39	0.46	0.0025	−0.31	−0.59
		S_8^{2-} Isomers			
str chain	0.0	1.30	0.81	0.70	0.39
branched	3.88	1.42	0.88		0.44

well-known sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}) dianions. The sulfite and sulfate analog S_4^{2-} and S_5^{2-} dianions show a pyramidal (C_{3v}) and tetrahedral (T_d) geometrical structure, respectively, with bond lengths of 2.095 and 2.064 Å, and both possess closed-shell electronic ground states of $^1A_1$ symmetry. But whereas the branched S_4^{2-} isomer is only slightly more stable than the corresponding chainlike cluster (its EDE is still clearly negative at the KT level), the sulfate analog S_5^{2-} dianion is electronically far more stable than its corresponding chainlike isomer and shows a positive KT EDE of 0.46 eV (Table 4). The pronounced difference between these two branched S_n^{2-} systems can be traced back to the electronic structure of the two species. The HOMO of the sulfite analog S_4^{2-} dianion shows a considerable contribution from the lone-pair orbital at the central sulfur atom and has a positive orbital energy of about 0.5 eV. Obviously, the local electron affinity at the pyramidal coordinated sulfur atom is too small to bind the lone-pair electrons. In contrast, in the sulfate analog S_5^{2-} system the central sulfur atom exhibits a tetrahedral coordination and possesses consequently no lone pair. The HOMO of the tetrahedral S_5^{2-} cluster can be described as a combination of lone pairs localized at the terminal sulfur atoms and reflects thus the distribution of the excess electrons over these four atoms (Figure 3).

The enhanced electronic stability of the tetrahedral S_5^{2-} isomer can be rationalized by comparing it with related metal halide type dianions.[1,3,29] Dianions of the type MX_4^{2-}, where M is an alkaline earth metal and X is F or Cl, have been found to be stable with respect to electron autodetachment and to show very long lifetimes with respect to dissociation of one halide ion. The bonding in these species is essentially ionic, and their stability can be understood in the framework of the *ionic model*.[17] In the tetrahedral geometrical configuration the Coulomb repulsion of the four X^- anions is overcompensated by the Coulomb attraction to the central alkaline earth cation. Our population analysis data (Figure 3) show that similar favorable electrostatic effects are present in the tetrahedral S_5^{2-} cluster. In contrast to the chainlike configurations, in the branched structure there are enough electron accommodation groups such that the center can be positively charged, leading to an increased electronic stability.

However, despite its four electron accommodating terminal sulfur atoms and its positive KT EDE, the sulfate analog S_5^{2-} dianion is found to be electronically unstable at correlated levels of theory (Table 4). One way to construct a larger sulfur dianion based on the same ideas is the branched S_8^{2-} cluster depicted in Figure 1b. It consists of two central and six terminal atoms showing a structure analog to the dithionit dianion ($S_2O_6^{2-}$), which has been found to possess a long lifetime in the gas phase.[27,28] The branched S_8^{2-} isomer exhibits a closed-shell $^1A_{1g}$ electronic ground state, and the equilibrium structure corresponds to a staggered conformation (D_{3d} symmetry). In comparison with the typical sulfur−sulfur bond lengths of the chainlike isomers, the inner bond of the branched S_8^{2-} dianion is considerably longer (2.504 Å) whereas the terminal bonds are slightly shorter (1.997 Å). The $S_c-S_c-S_l$ angle is 104°. The favorable electrostatic effects observed for the tetrahedral S_5^{2-} cluster are also present in the branched S_8^{2-} cluster (Figure 3), but the EDEs of the branched and chainlike S_8^{2-} isomers are nevertheless much closer to each other than those of the two S_5^{2-} clusters (Table 4). Whereas the S_5^{2-} chain is about 0.5 eV less stable with respect to electron loss than its branched isomer, the corresponding difference is reduced to about 0.1 eV for the two S_8^{2-} isomers; i.e., the EDE of the branched S_8^{2-} isomer is only slightly more positive than that of its chainlike partner. Moreover, the branched S_8^{2-} cluster is 3.9 eV higher in total energy than the chainlike S_8^{2-} isomer (for S_5^{2-} this difference is only 1.4 eV), and consequently the D_{3d} S_8^{2-} dianion is expected to be far more sensitive with respect to fragmentation—especially with respect to breaking of the long central sulfur−sulfur bond. Thus, as long as further studies are not available, we expect the chainlike S_8^{2-} isomer to be the more promising candidate for a mass spectrometrical observation.

4. Summary and Conclusions

In this paper we have investigated the onset of stability in the S_n^{2-} series of dianions. Based on the known geometries of neutral and monoanionic sulfur clusters as well as on the structures of polysulfide dianions in solution, chainlike systems were examined. For all chainlike clusters the bond lengths and bond angles depend only weakly on the cluster size and position within the chain. The typical bond length is 2.08 ± 0.01 Å, and the typical bond angle is close to the tetrahedral angle (±2°). Consequently, all chainlike S_n^{2-} isomers resemble twisted chains, and there are several conformers that are very similar in geometry and total energy. Regarding electronic stability, the smallest clusters S_2^{2-} and S_3^{2-} are very unstable with respect to autodetachment, but the stability with respect to electron loss was found to increase considerably with the chain length. S_7^{2-} is at the threshold of electronic stability, and S_8^{2-} is beyond doubt locally stable.

A population analysis revealed that the two excess charges are essentially localized at the terminal atoms of the sulfur chains such that the inner atoms carry only small amounts of negative charge. Thus, the electronic stability of chainlike sulfur cluster dianions is virtually a question of distance. This is reflected by the fact that for a given chain length the stretched chain conformer exhibiting the largest distance between its terminal atoms is electronically most stable. However, the EDE of other conformers is only a few tenths of an electronvolt smaller, and the differences decrease with increasing chain length. We note that the only electron accommodating unit we have found for sulfur clusters is the terminal sulfur atom. In contrast to carbon, sulfur atoms seem to be unable to form subunits of substantial electron affinity.

Regarding properties beyond local stability, it has on the one hand been found that the adiabatic EDE of the chainlike S_n^{2-} clusters is only about 0.2 eV smaller than their corresponding vertical EDE. Thus, if a system is clearly stable with respect to vertical electron loss, one may as well expect adiabatic stability. On the other hand, S_7^{2-} and S_8^{2-} are unstable with respect to fragmentation into two monoanions of similar or equal size. Due to the broad Coulombic barrier hindering this dissociation, we nevertheless predict both species to be metastable with respect to fragmentation. Consequently, the chainlike S_8^{2-} cluster is predicted to be long-lived enough to allow its detection in a mass spectrometer.

In addition, branched S_5^{2-} and S_8^{2-} isomers have been investigated. In these clusters the central sulfur atoms are positively charged, and due to these favorable electrostatic effects the sulfate analogue tetrahedral S_5^{2-} cluster is electronically considerably more stable than the associated chainlike isomer but nevertheless unstable to electron autodetachment at correlated levels of theory. In going to S_8^{2-} the branched cluster is only 0.1 eV more stable with respect to electron loss than its chainlike isomer. Moreover, the branched isomers are higher in total energy and thus more sensitive to fragmentation.

Let us finally compare the sulfur cluster dianions to other small dianions predicted to exist in the gas phase. The most basic requirement to the stability of small gas-phase dianions are electron accommodating atoms or groups of atoms. Depending on the structural properties and variabilities of the system, there is then a tradeoff between compact forms possessing many electron affine substructures and chainlike forms showing only two electron accommodating groups but maximizing their distance. For metal halide dianions[1] only compact structures are possible where the excess electrons are distributed over several elector affine halogene atoms. In covalent bound systems such as organic diacids[30] or silicon–oxygen clusters[26] chainlike structures dominate, whereas for carbon clusters C_n^{2-} the form of the most—and often only—stable isomer depends on the number of carbon atoms n.[20] For sulfur clusters we meet the unique situation that both chainlike and compact branched isomers are able to bind two extra electrons. As discussed above, we predict the chainlike S_8^{2-} isomer to exhibit a lifetime that allows experimental detection, whereas we are presently unable to draw the same conclusion for the branched S_8^{2-} isomer since its barrier with respect to dissociation needs to be examined in detail. However, for larger sulfur clusters we expect both types of isomers to exist as isolated doubly neagtive charged species.

References and Notes

(1) Scheller, M. K.; Compton, R. N.; Cederbaum, L. S. *Science* **1995**, *270*, 1160.

(2) Kalcher, J.; Sax, A. F. *Chem. Rev.* **1994**, *94*, 2291.

(3) Scheller, M. K.; Cederbaum, L. S. *J. Chem. Phys.* **1993**, *99*, 441.

(4) Schauer, S. N.; Williams, P.; Compton, R. N. *Phys. Rev. Lett.* **1990**, *65*, 625.

(5) Sommerfeld, T.; Scheller, M. K.; Cederbaum, L. S. *Chem. Phys. Lett.* **1993**, *209*, 216.

(6) Dunning, T. H., Jr. J. *Chem. Phys.* **1970**, *53*, 2823.

(7) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(8) Berghof, V. Diploma Thesis, Universität Heidelberg, 1996.

(9) Schmidt, M. W.; Boatz, J. A.; Baldridge, K. K.; Koseki, S.; Gordon, M. S.; Elbert, S. T.; Lam, B. GAMESS: *QCPE Bull.* **1987**, *7*, 115.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision C.2.

(11) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-A.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P. O. Molcas Version 3, University of Lund, Sweden, 1994.

(12) Koopmans, T. *Physika* **1933**, *1*, 1.

(13) Cederbaum, L. S. *J. Phys. B* **1975**, *8*, 290.

(14) Von Niessen, W.; Schirmer, J.; Cederbaum, L. S. *Comput. Phys. Rep.* **1984**, *1*, 57.

(15) Weikert, H. G.; Cederbaum, L. S.; Tarantelli, F.; Boldyrev, A. I. Z. *Phys. D: At., Mol. Clusters* **1991**, *18*, 229.

(16) Janoschek, R. Z. *Anorg. Allg. Chem.* **1992**, *616*, 101.

(17) Scheller, M. K.; Cederbaum, L. S. *J. Phys. B* **1992**, *25*, 2257.

(18) Boldyrev, A. I.; Simons, J. *J. Chem. Phys.* **1994**, *98*, 2298.

(19) Gutowski, G. L.; Boldyrev, A. I.; Ortiz, J. V. J. Simons, *J. Am. Chem. Soc.* **1994**, *116*, 9262.

(20) Sommerfeld, T.; Scheller, M. K.; Cederbaum, L. S. *J. Phys. Chem.* **1994**, *98*, 8914.

(21) Von Niessen, W. *J. Chem. Phys.* **1991**, *95*, 8301.

(22) Zakrzewski, V. G.; Von Niessen, W. *Theor. Chim. Acta* **1994**, *88*.

(23) Ganteör, G.; Hunsicker, S.; Jones, R. *Chem. Phys. Lett.* **1995**, *236*, 43.

(24) Hohl, D.; Jones, R. *J. Chem. Phys.* **1988**, *89*, 6823.

(25) Sommerfeld, T.; Scheller, M. K.; Cederbaum, L. S. *J. Chem. Phys.* **1995**, *103*, 1057.

(26) Sommerfeld, T.; Scheller, M. K.; Cederbaum, L. S. *J. Chem. Phys.* **1996**, *104*, 1464.

(27) Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1994**, *116*, 10761.

(28) McKee, M. L. *J. Phys. Chem.* **1996**, *100*, 3473.

(29) Weikert, H. G.; Cederbaum, L. S. *J. Chem. Phys.* **1993**, *99*, 8877.

(30) Maas, W. P. M.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Processes* **1989**, *88*, 257.