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# Helium Droplets Doped with Sulfur and C_{60}

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ABSTRACT: Clusters of sulfur are grown by passing superfluid helium nanodroplets through a pickup cell filled with sulfur vapor. In some experiments the droplets are codoped with C_{60}. The doped droplets are collided with energetic electrons and the abundance distributions of positively and negatively charged cluster ions are recorded. We report, specifically, distributions of S_m^+, S_m^-, and $C_{60}S_m^-$ containing up to 41 sulfur atoms. We also observe complexes of sulfur cluster anions with helium; distributions are presented for $He_nS_m^-$ with $n \leq 31$ and $m \leq 3$. The similarity between anionic and cationic $C_{60}S_m^{\pm}$ spectra is in striking contrast to the large differences between spectra of S_m^+ and S_m^-.
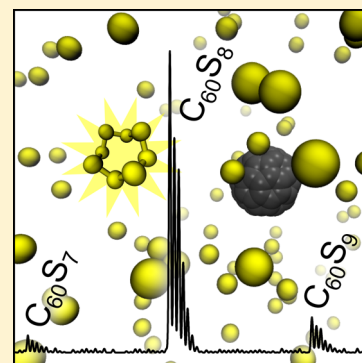
1. INTRODUCTION

Sulfur is a most unusual chemical element. It has the most complex phase diagram of all elements; about 30 allotropes have been experimentally characterized.[1,2] Most of them consist of unbranched cyclic molecules containing as many as 20 atoms. The crown-shaped S_8 molecule is energetically most favorable; it presents the dominant component in liquid sulfur over a wide range of temperatures.[3]

S_8 is also the main component in the equilibrium vapor phase at low temperatures,[4−9] while species as large as S_{10} have been identified.[8]

In spite of the tendency of sulfur to form large molecules, very few attempts to identify and characterize clusters larger than S_8 in the gas phase have been published. Martin reported mass spectra of sulfur clusters that were grown from sulfur vapor in a gas aggregation source.[10] The cation distribution showed a pattern that reflected the dominance of S_8 in the sulfur vapor. In another experiment Martin and co-workers coated C_{60} with sulfur molecules.[11] Two ion series were identified in the spectra, $C_{60}(S_8)_x^+$ and $C_{60}(S_8)_{x-1}S_6^+$ ($x = 1, 2,...$). Evidence was provided that 12 S_8 molecules completely cover a fullerene. The C_{60}−sulfur system has attracted considerable attention because of the existence of a monoclinic molecular binary compound $C_{60} \cdot 2S_8$.[12−14]

The only study of larger S_m^- cluster anions that we are aware of is a photoelectron study by Ganteför and co-workers for $m \leq 11$. They observed the presence of structural isomers, which could be identified as rings and chains by comparing measured values with calculated vertical detachment energies.[15]

In the present work we present size distributions of charged sulfur clusters, either pure or complexed with C_{60} or helium. The neutral precursors are prepared by doping superfluid helium nanodroplets in a pickup cell that contains sulfur vapor (and, in some experiments, C_{60} vapor). The doped droplets are then ionized with energetic electrons; the size distributions of

positively and negatively charged clusters are reported for complexes containing up to 41 sulfur atoms and, for the $He_nS_m^-$ system, as many as 31 helium atoms.

2. EXPERIMENTAL SECTION

Neutral helium nanodroplets were produced by expanding helium (Messer, purity 99.9999%) with a stagnation pressure of 23 bar through a 5 μm nozzle, cooled by a closed-cycle refrigerator (Sumitomo Heavy Industries LTD, model RDK-415D) to about 9.6 K, into vacuum. The average number of atoms per droplet formed in the expansion equals about 10^5;[16] these droplets are superfluid with a temperature of ∼0.37 K.[17] The resulting supersonic beam was skimmed by a 0.8 mm conical skimmer, located 12 mm downstream from the nozzle. The skimmed beam traversed a 20 cm-long pick-up region into which sulfur (Merck, 99%) was vaporized from a crucible at about 50 °C. The doped droplets passed through another pickup region into which a small amount of C_{60} (MER Corp., 99.9%) could be vaporized from a crucible kept at 320 °C. After the pick-up region the doped helium droplets passed a region in which they were ionized by collisions with electrons. The ion signal was optimized by tuning the electron energy. It was about 90 eV for positive ions, 9.5 eV for S_m^- and HeS_m^-, and 22 eV for $C_{60}S_m^-$.

The ions were accelerated to 40 eV into the extraction region of a commercial time-of-flight mass spectrometer equipped with a reflectron (Tofwerk AG, model HTOF); its mass resolution was $\Delta m/m = 1/3600$ (Δm = full-width at half-

maximum). The base pressure in the mass spectrometer was 10^{-5} Pa. The ions were extracted at 90° into the field-free region of the spectrometer by a pulsed extraction voltage. At the end of the field-free region they entered a two-stage reflectron, which reflected them toward a microchannel plate detector operated in single ion counting mode. Additional experimental details have been described elsewhere.[18,19]

3. DATA ANALYSIS AND RESULTS

A sample mass spectrum of ions formed by electron attachment to helium nanodroplets doped with sulfur is presented in Figure 1; the ion yield is plotted on a logarithmic scale. The most
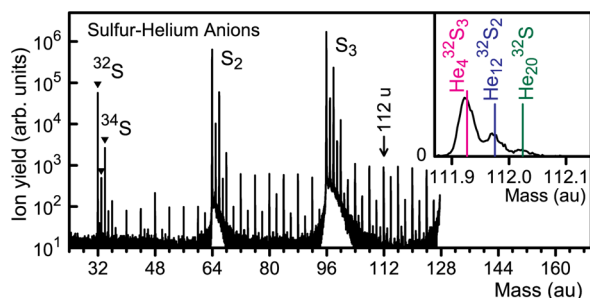

Figure 1. Mass spectrum of negatively charged sulfur−helium complexes showing the series $He_nS_m^-$ for $m = 1, 2, 3$. The inset zooms into the region at 112 au; it shows the presence of three distinct, nominally isobaric ions.

abundant ions are pure sulfur ions S^-, S_2^-, and S_3^-. Sulfur has four naturally occurring isotopes; their abundances are 94.9%, 0.8%, 4.3%, and 0.02% for ^{32}S, ^{33}S, ^{34}S, and ^{36}S, respectively. Thus, cluster ions as small as S_3^- contribute several lines to the spectrum that tend to overlap other ions of interest.

The region below $^{32}S^-$ signals the absence of He_n^- ions. Small helium cluster anions are unstable although He^- and He_2^- have been observed; they are metastable if electronically excited.[20,21]

Ions between the S_m^- ion peaks are due to $He_nS_m^-$, $m \geq 1$. The spectra quickly become congested beyond S_2^- because $He_n{}^{32}S_{m+1}^-$ and $He_{n+8}{}^{32}S_m^-$ are nominally isobaric. However, for small values of m the mass resolution is sufficient to distinguish between these ions. This is demonstrated in the inset of Figure 1, which shows that three different ions, $He_4{}^{32}S_3^-$, $He_{12}{}^{32}S_2^-$, and $He_{20}{}^{32}S^-$ contribute to the mass peak at 112 au.

The ion abundance of the various ions is extracted from the mass spectra by applying a matrix method, which takes into account the yield of all isotopologues (including, for example, the contribution of $He_{11}{}^{34}S_2^-$ to the ion peak at 112 au).[22] The approach reaches its limit in the mass regions of pure S_m^-. For example, we cannot reliably extract the abundance of $He_8{}^{32}S_2^-$ or $He_9{}^{32}S_2^-$ because they are swamped by $^{32}S_3^-$ and $^{34}S_2{}^{32}S^-$, respectively, which are orders of magnitude more abundant as evident from Figure 1.

The ion abundance of S_m^- extracted from the spectrum shown in Figure 1 is displayed in Figure 2b; the abundance of $He_nS_m^-$ versus n is displayed in Figure 3 for $m = 1, 2$, and 3 (panels a−c). Connecting lines are drawn across missing data points in the regions of pure S_m^-.

Mass spectra of S_m^+ cations were recorded without changing the experimental parameters of the cluster source and pickup
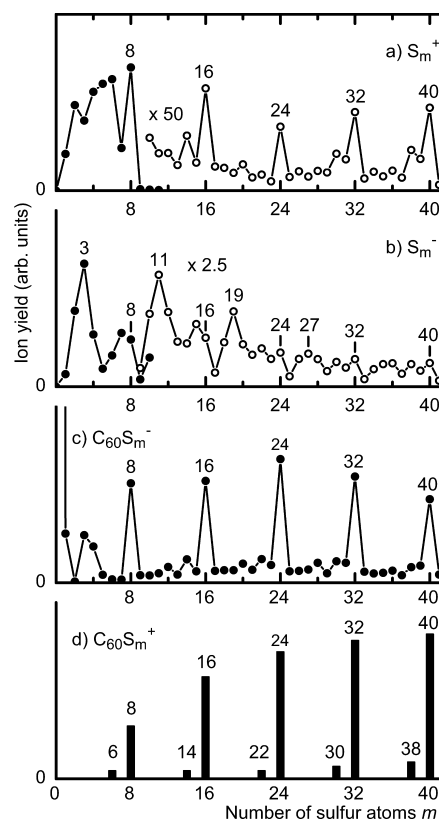

Figure 2. Ion abundance of sulfur cluster cations, anions, and $C_{60}S_m^-$ anions (panels a−c, respectively). Note the change in scale beyond the 8-mer in panels a and b. The histogram in panel d displays the abundance of $C_{60}S_m^+$ reported by Martin and co-workers;[11] see text for details.
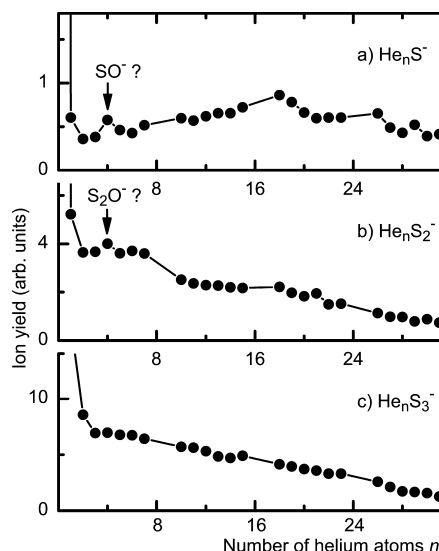

Figure 3. Abundance of anionic $He_nS_m^-$ versus n for $m = 1, 2, 3$. Data for ions that are contaminated by the strong S_m^- signal have been omitted.

cell; the ion abundance is displayed in Figure 2a. No cationic sulfur−helium complexes were observed.

In another series of experiments C_{60} was introduced into a second pickup cell. Electron attachment resulted in $C_{60}S_m^-$ anions; their abundance is displayed in Figure 2c. The corresponding cation spectra were not recorded but, for the

sake of comparison, panel 2d shows the abundance of $C_{60}S_m^+$ reported by Martin and co-workers using a gas aggregation source, which produces bare C_{60}–sulfur complexes.[11] One-photon ionization at 10.5 eV was employed to reduce fragmentation. Only two ion series of significant abundance were observed, $C_{60}(S_8)_x^+$ and $C_{60}(S_8)_{x-1}S_6^+$ (x = 1, 2,...).

4. DISCUSSION

A. Composition of Doped Helium Nanodroplets. The relative ion abundances presented in this work reflect a variety of factors, including the composition of vapor in the pickup cell, probability of capture of dopants in the helium droplets, ionization efficiencies, and fragmentation probabilities. We will discuss these before turning to an interpretation of measured ion abundances.

Molecules colliding with a superfluid helium nanodroplet will be captured with very high probability provided that their relative velocity exceeds the critical Landau velocity.[23] The condition is easily met in the present experiments; the root-mean-square speed of S_8 molecules in the lab reference system is about three times the critical Landau velocity.[24] Successive pickup of molecules will lead to growth of a single cluster at the center of the superfluid droplet.[17] Growth of the helium nanodroplet and subsequent capture of dopants is a statistical process; clusters covering a large range of sizes are typically formed in droplets. Their size distribution is featureless; anomalies in the distributions of cluster ions provide evidence for ionization-induced dissociation, which preferentially populates particularly stable species.[25]

In the present experiment the pickup cell is filled with sulfur vapor, and in some experiments, a second pickup cell is filled with C_{60} vapor. The composition of sulfur vapor has been investigated by a variety of techniques; work prior to 2005 has been reviewed by Steudel et al.[8] Information about the molecular composition comes, last but not least, from mass spectrometric data, but their interpretation is challenging because extensive fragmentation occurs once the electron energy exceeds the ionization energy of S_8 (9.3 ± 0.2 eV)[7] by more than a few eV.[7,26,27] Nevertheless it appears safe to say that around 500 to 600 °C saturated vapor consists mostly of S_6, S_7, and S_8 with some smaller contributions of S_2 through S_5.[4,6] Evidence has been reported for the existence of S_9 and S_{10} but their fractional abundance is minor.[8] The structure and stability of neutral sulfur clusters has been subject to many theoretical studies.[8] Beginning with S_4 the most stable isomers are ring-shaped but oftentimes chains are not much higher in energy. The most stable isomer of S_8 is crown-shaped.[30,31]

At low temperature S_8 is clearly the most abundant oligomer.[9,28] Data published by Berkowitz and Marquart suggest that, at temperatures relevant to the present study (50 °C), the mole fraction of $S_8/S_7/S_6$ equals about 100:30:7 in thermal equilibrium.[4]

However, Berkowitz and Chupka later found that a very large ($\geq 2 \times 10^5$) number of collisions of S_8 with the sulfur-covered walls of their Knudsen cell would be required before the equilibrium concentration of oligomers is established in the cell.[5] Vapor emitted from the surface of rhombic sulfur at low temperature (73 °C) directly into vacuum consists solely of S_8 even though S_8^+ constitutes only 35% of the ion current in a mass spectrum (measured at an electron energy of 75 eV).[5] The pickup cell used in our present work does not provide for a large number of molecule–wall collisions; thus, the sulfur vapor will consist nearly exclusively of S_8 molecules.

In some experiments, C_{60} was vaporized in a second pickup cell. A temperature of 320 °C was chosen in order to optimize the number of droplets that contain just one C_{60}.

B. Ionization of Doped Helium Nanodroplets. For positive ion formation the doped helium droplets are collided with electrons at an energy of about 90 eV, well above the ionization energy of helium (24.587 eV).[32] Ionization commences with formation of He^+, followed by resonant charge transfer between helium atoms and ends with charge transfer from He^+ to the dopant.[33] This latter step will release an energy equal to the difference between 24.587 eV and the ionization energy of the dopant. Fragmentation of the dopant cluster will be substantial. It is not efficiently quenched by ejection of helium from the nascent ions, and anomalies in the size distributions of cluster ions are likely to reflect anomalies in their stabilities.[34−37]

Anions resulting from electron attachment to doped helium droplets have been observed before.[36,38−41] Details of their formation have emerged from recent studies in which the energy dependences of anion yields, which reach a maximum at about 22 eV, was explored in detail.[20,21,42] An incident electron enters the helium droplet and excites a helium atom into the 1s2s $^3S_1$ state. Within a few picoseconds the inelastically scattered electron thermalizes and becomes self-trapped in a bubble state.[43] The highly polarizable He* and the electron bubble may move toward each other and combine to form metastable He*$^-$ in a quartet state.[44] The ion is heliophilic and highly mobile. If a dopant is present, the attraction between He*$^-$ and the polarized dopant will steer the former to the latter within an estimated time of 1 ns, which is much shorter than the lifetime of He*$^-$ in helium.[42,44] The journey ends with electron transfer, which releases some 25 eV, the sum of the excitation energy of He and the electron affinity of the dopant.

In small doped helium droplets a more direct path may open up, namely, motion of the electron bubble toward the dopant and subsequent electron transfer. In this case the excess energy would be much smaller, close to the electron affinity of the dopant. However, in the present study the droplets contain about 10^5 helium atoms and the indirect process, via formation of metastable He*$^-$, is the more likely one. However, at electron energies well below 20 eV helium cannot be excited and direct bubble formation is the only viable process.

C. Discussion of Ion Abundances. The distribution of S_m^+ cations is presented in Figure 2a. For $m \leq 8$ it is qualitatively similar to the NIST mass spectrum of sulfur vapor, which shows local maxima at m = 2 and 8 and local minima at m = 3 and 7.[32] Details, though, depend on the temperature of the sulfur vapor, electron energy, and the type of source (Knudsen cell versus free vaporization). Properties of S_m^+ including their stability and structure have been reviewed by Krossing.[45] The calculated stabilities of cations containing six or more sulfur atoms are quite sensitive to the level of theory used.[46]

The abundance distribution of clusters larger than S_8^+ shows a strong preference for ions containing multiples of 8 atoms. This reflects the fact that the neutral precursors consist of aggregates of S_8 embedded in helium; polymerization, although ubiquitous in elemental sulfur, will not occur in the cold environment of the helium droplet because ring opening and bond interchanges are impeded by energy barriers.[30,47] The strong preference for cations containing multiples of eight sulfur atoms suggests that intramolecular fragmentation is weak.

It is interesting to compare the ion abundance in Figure 2a with the one reported by Martin.[10] In that work sulfur was vaporized in a gas aggregation source filled with helium at a temperature of 77 K; the ensuing sulfur clusters were ionized by electron impact at 30 eV. Although the mass spectrum also showed a preference for multiples of S_8 units the contrast was much weaker; neighboring mass peaks corresponding to the loss of 1 to 7 atoms were almost as strong. This would imply either stronger ionization-induced fragmentation or a higher concentration of sulfur oligomers other than S_8 in the vapor. However, in a later publication by Martin's group[11] (which will be discussed below) it was concluded that the sulfur vapor consisted mostly of S_8 plus some S_6 at the 10% level. Unfortunately the temperatures of the sulfur sources were not specified in these reports.

The size distribution of sulfur cluster anions (Figure 2b) is very different. One consistent feature is a propensity for ions of the form $(S_8)_p S_3^-$, especially for $p = 0, 1, 2$. A strong preference for S_3^- has also been observed in negative laser desorption mass spectra of sulfur that were, however, limited to $m \leq 7$.[48,49] Another consistent feature in Figure 2b is a local minimum at $(S_8)_p S^-$ ($3 \leq p \leq 5$).

The patterns may result from a combination of two factors, strong fragmentation into anions of enhanced stability or electron detachment from ions with low electron affinity. Either way, the periodicity of the patterns (*modulo* 8) suggests octamers retain their identity in the larger anions.

To the best of our knowledge only one experimental study of sulfur cluster anions containing more than 8 atoms has been published.[50] Anions were formed in a pulsed arc cluster ion source. Negative ion mass spectra extended to S_{27}^-; photoelectron spectra were reported for $m \leq 11$. Local maxima in the mass spectra were observed at $m = 3$ and 19 in agreement with our data (Figure 2b) but a pronounced local minimum occurred at S_{11}^- where we observe a maximum, and there was no evidence of minima at $(S_8)_p S^-$. However, the mass spectra depended strongly on the conditions in the cluster source, and the photoelectron spectra revealed that those conditions affected the population of different structural isomers, in particular for S_6^- and S_7^-.

A DFT study of S_m^- for $m \leq 9$ showed that small anions produced in the experiment were in the most stable, closed configuration, while S_8^- and S_9^- were helical chains whose vertical detachment energies significantly exceed those of the closed structures.[15] S_6^- and S_7^- could be produced in either configuration. Furthermore, the calculated energies of S_m^- in their most stable configurations showed that S_2^- and S_3^- are relatively stable, while S_5^- and S_7^- are less stable than their neighbors. These predicted trends are not mirrored in the ion abundance (Figure 2b and ref 50) but minima in Figure 2b at $(S_8)_p S_5^-$ and $(S_8)_p S_7^-$ for $2 \leq p \leq 4$ seem to support these predictions.

Negative ion mass spectra of helium droplets codoped with sulfur and C_{60} results nearly exclusively in ions of the form $C_{60} S_m^-$ where m is an integer multiple of 8, see Figure 2c. Their abundances are a factor 5 to 10 larger than those of other $C_{60} S_m^-$ ions. The difference to the distribution of pure S_m^- (Figure 2b) is striking.

Unfortunately we did not obtain usable data for $C_{60} S_m^+$ cations. For a discussion of the role of the charge state we turn to the data in Figure 2d that were extracted from a mass spectrum reported by Tast et al., who condensed sulfur molecules on C_{60} in a gas aggregation source.[11] Positive ions

were formed by one-photon ionization at 10.5 eV thus reducing fragmentation. Only two ion series of significant abundance were observed, $C_{60}(S_8)_p^+$ and $C_{60}(S_8)_{p-1} S_6^+$. The latter was a factor 10 less abundant than the former for $p \leq 5$ (see Figure 2d), but the ratio gradually increased to 1 at $p \approx 30$. The authors attributed the $C_{60}(S_8)_{p-1} S_6^+$ ions to fragmentation-free ionization of neutral $C_{60}(S_8)_{p-1} S_6$, which forms if S_6 is a significant component in the vapor phase. The interpretation is consistent with the observed gradual increase of the relative $C_{60}(S_8)_{p-1} S_6^+$ yield with increasing p.

Our data of C_{60}–sulfur anions (Figure 2c) show an abundance ratio $C_{60}(S_8)_p^-$: $C_{60}(S_8)_{p-1} S_6^-$ of about 5:1 except for $p = 0$ where the ratio is 30:1. The experiment by Tast et al. differs in many ways from ours; it is impossible to draw firm conclusions. In particular, different temperatures of the sulfur source will result in different vapor compositions (the source temperature was not specified in ref 11. However, we would like to point out that for anions the $C_{60}(S_8)_{p-1} S_6^-$ series is not particularly strong compared to $C_{60}(S_8)_{p-1} S_x^-$ with x other than 6.

More generally, it is not obvious why mass spectra of cationic and anionic C_{60}–sulfur complexes should resemble each other. Suppression of intramolecular fragmentation in *positively* charged complexes of C_{60} and molecular clusters has been reported for many molecules including N_2, H_2O, NH_3, and CH_4 (see ref 35 for a review). It can be traced to the low ionization energy of C_{60} (7.6 eV); the adsorbate molecules remain essentially neutral.[51] However, the argument does not extend to negatively charged complexes of C_{60} and S_8 because the electron affinity of S_8 (3.59 eV)[15] exceeds that of C_{60} (2.68 eV).[32] The similarity of the anion and cation spectra (Figure 2c,d) suggests that, even though the negative excess charge will be concentrated on the adsorbed cluster of S_8 molecules, the presence of C_{60} does suppress intramolecular fragmentation. The interaction of sulfur with C_{60} has been investigated in several papers because of its high solubility in liquid sulfur and the existence of a $C_{60} \cdot 2 S_8$ monoclinic compound,[13,14,52] but we are not aware of any theoretical studies of anionic C_{60}–sulfur complexes.

We now turn to the distribution of $He_n S_m^-$ anions shown in Figure 3 for $m = 1, 2, 3$. Because of the weak binding energy, complexes of helium atoms attached to an ion are not routinely observed; their formation requires special source conditions. Most experimental studies in this arena have dealt with complexes where the charge was positive and localized at a metal atom (see ref 25 and references therein) or a noble gas atom (see ref 37 and references therein), but a few have explored larger charge carriers such as argon clusters containing as many as seven argon atoms[37] or C_{60}^+.[35] The data may reveal the presence and size of rigid solvation shells around the ion. For example, three distinct solvation shells have been identified for $He_n Ar^+$.[37,53] For larger charge carriers such as C_{60}^+ or C_{70}^+ anomalies often reflect the corrugation of the substrate.[35]

Studies of anions complexed with helium are particularly rare; they include halide ions[54−56] and a few metal ions.[55] Unfortunately, the abundance distributions of $He_n S_m^-$ in Figure 3 are largely featureless. Small local maxima at the positions of $He_4 S^-$ and $He_4 S_2^-$ are probably due to SO^- and $S_2 O^-$. It is possible that features occur for sizes that we had to exclude from Figure 3 because the weak $He_n S_m^-$ yield was swamped by the strong yield of pure S_m^- ions. There are some irregularities in the trace of $He_n S^-$ and a conspicuously large drop in the abundance between $He_7 S_2^-$ and $He_{10} S_2^-$, which suggests the

presence of anomalies, but they cannot be pinned down unless the resolution of the spectrometer can be substantially improved or, alternatively, experiments are carried out with isotopically enriched ^{34}S. A large number of high-level theoretical studies of ions solvated in helium have been performed (see, e.g., refs [53] and [57] and references therein), but none has been devoted to the sulfur−helium system.[58]

CONCLUSIONS

We have presented mass spectra of positively and negatively charged sulfur clusters, sulfur cluster anions complexed with C_{60}, and sulfur cluster anions complexed with helium. One remarkable feature is the close resemblance of the distribution of positively charged[11] and negatively charged $C_{60}S_m^{\pm}$ ions, which contrasts with the marked dissimilarity between S_m^+ and S_m^- distributions. It is not surprising that the presence of C_{60} would suppress ionization-induced fragmentation in cations because its ionization energy is about 1.7 eV below that of S_8; i.e., the sulfur complex will remain essentially neutral. However, this is not so for anions; the electron affinity of S_8 exceeds that of C_{60} by 0.9 eV. Theoretical work is needed to understand the nature of binding in negatively charged C_{60}−sulfur complexes.

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Notes

The authors declare no competing financial interest.

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