



Evolution of the structure and electronic properties of neutral and anion FeS_n^μ ($n = 1-7$, $\mu = 0, -1$) clusters: A comprehensive analysis



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ABSTRACT

The structural evolution, stabilities and electronic properties of neutral and anionic FeS_n^μ ($n = 1-7$, $\mu = 0, -1$) clusters have been investigated with the aid of previous photoelectron spectroscopy (PES) and density functional theory. For each sized iron–sulfur cluster, the low-lying isomers are generated using Saunders “kick” global optimization method. The theoretical vertical and adiabatic electron detachment energies (VDEs and ADEs) were compared with the experimental values to corroborate the ground state structures. The results indicate that the combination of photoelectron spectroscopy experiments and density functional theory calculation is powerful for obtaining the accurate electronic structures. By calculating the binding energies, fragmentation energies and second difference energies, we found FeS , FeS_4 , FeS_2^- and FeS_4^- clusters have the relative stronger stability. Furthermore, the two equal maxima of HOMO–LUMO gaps (2.81 eV) for the most stable configurations appear at FeS and FeS_2^- . Additionally, to probe into the electron transfer information and redistribution of electron density induced by bonding, the natural population analysis (NPA) and electron density difference are investigated and discussed.

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1. Introduction

Iron–sulfur clusters are ubiquitous in biology [1,2], yet they were only recognized approximately 50 years ago. Since then, the knowledge of iron–sulfur system keeps growing all the time with the increasing investigations. It is gradually found that the iron–sulfur clusters play critical roles in the active sites of wide-variety metalloproteins and metalloenzymes, which are involved in biological electron transfer processes (ferredoxins, high-potential iron proteins) [3–5], small molecule activation (nitrogenase hcycho-gense, carbonmonoxide dehydrogenase) [6–9], radical-based catalytic transformations (H-atom abstraction, S insertion in biotin synthase) [10], DNA repair [11], and signal transduction [12].

Therefore, iron–sulfur systems, ranging from bare Fe–S clusters to analogue complexes and proteins, are prevalent throughout bio-inorganic chemistry. A series of experimental investigations have been reported to probe into the electronic structure and chemical bonding of a broad range of iron–sulfur clusters. For example, according to the photoelectron spectroscopic (PES) experiment of FeS_n^- ($n = 1-6$) clusters, Zhai et al. proposed that the Fe atom is likely to maintain its favorite +3 oxidation state in all the FeS_n^- ($n > 1$) clusters with $(\text{S}_m^{2-})\text{Fe}^{3+}(\text{S}_{n-m}^{2-})$ type of structures [13]. The

electronic structure and reactivity of Fe_nS_m^- ($n = 1-8$, $m = 2-6$) clusters were first investigated by Nakajima et al. [14] using PES with different photon energies. The results show that their electronic affinities (EAs) greatly change at the composition of $n = m$ where the clusters are more stable. The same results are also shown in the results of cationic [15] and anionic [16] Fe_nS_m clusters which is produced by direct laser ablation. It is well known that Fe_nS_n ($n = 2, 4$ and 6) clusters are nitrogen fixation or other electron transfer centers in many metal–sulfur proteins. The compositions Fe_2S_2^- , Fe_3S_3^- , Fe_4S_4^- , and Fe_6S_6^- , which are the Fe–S centers in proteins, are also stable in the condition of supersonic jet expansion. In addition, the Fe_nS_m clusters produced in gas phase seemingly take the structure having alternate bonds (–S–Fe–S–Fe–) between Fe and S atoms, and have been observed as a reaction product of Fe_n and H_2S [17]. Furthermore, the collision-induced dissociation (CID) of anionic iron–sulfur clusters (Fe_nS_m^-) [18] has shown that FeS cluster ions have interesting mass distribution and unique structural characteristics. For anionic FeS_6^- and FeS_7^- clusters, loss of neutral S_2 fragments was observed as a major dissociation channel [18]. Indeed, these detailed experiments of the Fe–S complexes are useful for calibrating the computational investigations.

From a theoretical point of view, there are a number of calculations on the electronic structure of FeS and FeS^- [19–22]. The ground state of FeS is proved to be $^5\Delta$, in analogy with the ground state of FeO [23]. However, in a recent calculation, Hübner et al. [24] found a $^5\Sigma^+$ ground state for FeS , and the $^5\Delta$ state is predicted

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to be very closely spaced. The DFT calculations of $\text{FeS}_2^{+0/-2}$ cluster were carried out by Schröder et al. [25], and the results show that FeS_2^- has an open ground state structure with electronic state (${}^6\text{A}_1$), Fe–S bond 2.12 Å and $\angle\text{SFeS}$ angle of 166.7°. This is in well agreement with the most stable geometry of the anionic FeS_2^- cluster found by Zhai et al. [13]. Clima et al. [26] CASPT2 (complete active-space second-order perturbation theory) geometry optimization yield the almost same conformation for the anion FeS_2^- with a Fe–S bond of 2.087 Å and can formally be regarded as $\text{S}^{2-}\text{Fe}^{3+}\text{S}^{2-}$. The geometric optimizations and harmonic vibration frequencies for FeS_3 and FeS_3^- clusters were also performed by them [27], but the electronic state of neutral FeS_3 complex and the ground state of anion FeS_3^- are still far from clear. Besides, most of the calculations are devoted to Fe–S clusters in protein environments [28–31]. For the larger Fe–S clusters, as far as we know, there are few studies. Only the computational study on $\text{Fe}_2\text{S}_2^{+0/+2+}$ clusters [32] and freestanding $\text{Fe}_2\text{S}_2^{0/-/+}$, $\text{Fe}_3\text{S}_4^{0/-/+}$, $\text{Fe}_4\text{S}_4^{0/-/+}$ clusters [33] have been performed, and the preliminary study on FeS_n^- ($n = 1–6$) [13] was carried out. In multicenter clusters, the electrons of iron atoms exhibit a weak magnetic coupling. This not only leads to a manifold of nearly degenerate states, but also leads to considerable difficulties in the computational study of their electronic structure and bonding. As a result, their electronic structure and chemical bonding are still not well understood at present. In addition, for the iron–sulfur clusters, the d–d interactions of iron are quite weak, and the closed-shell solution is unstable to perturbations that allow electron spins to localize at the iron centers. Furthermore, theoretical ab initio methods are very elaborate and unfeasible for larger Fe–S systems. This is the consequence of the fact that the correct description of the iron–sulfur bond requires inclusion of extensive non-dynamical correlation. Thus, to gain insight into the elementary properties of iron–sulfur bonding and offer more information for studying complicated inorganic and biological systems, we report a detailed density functional theory study of FeS_n^μ ($n = 1–7$, $\mu = 0, -1$) clusters.

The main goals of present work are threefold. The first intention is to determine true various global minimum structures and corresponding electronic state of FeS_n^μ ($n = 1–7$, $\mu = 0, -1$) clusters; The second intention is to compare some results of our extensive computations with those determined by previous experimental and theoretical studies on neutral or anion Fe–S clusters; The third is to understand the influence of iron atom on pure sulfur structure and offer more detailed information for further investigations on complicated inorganic and biological systems in future.

2. Computational details

Unbiased searches were first performed for the global minimum structures of the potential energy surfaces on FeS_n^μ ($n = 1–7$, $\mu = 0, -1$) clusters, using the Saunders “kick” method [34–37]. This stochastic method, which is much simpler and faster to implement than manual procedures, generates structures randomly and facilitates the thorough exploration of unknown isomers. In order to avoid biasing the search, all the atoms are placed at the same point initially and then are kicked randomly within a box of chosen dimensions. This kick method can be operated at the B3PW91/3-21G level as many times as desired until all the known minima did not lead to any new ones. Afterwards, the top ranked 20 isomers were further re-optimized and refined at the B3PW91/6-311+G* level. We found the previous structures are still minima on the B3PW91/6-311+G* surface so it is not necessary to start all over. Since no symmetry constraints are imposed, the obtained geometries should correspond to minima. The minima at the B3PW91/6-311+G* level are further re-optimized and refined,

Table 1

Calculated values of bond length r (Å), frequency ω (cm^{-1}) and dissociation energy D (eV) for the S_2 , S_2^- , FeS and FeS^- molecules at different level.

Clusters		S_2	S_2^-	FeS	FeS^-
Multi		3	2	5	4
Methods	Para				
PW91	r	1.94	2.06	2.02	2.05
	ω	665	526	516	470
	D	4.61	4.13	4.22	3.61
B3LYP	r	1.93	2.05	2.01	2.09
	ω	638	536	528	449
	D	4.08	3.67	3.16	2.90
TPSS	r	1.93	2.06	2.02	2.06
	ω	671	528	518	469
	D	4.36	3.93	4.03	3.40
BP86	r	1.94	2.06	2.02	2.05
	ω	660	519	515	468
	D	4.57	4.06	4.15	3.52
PBE	r	1.94	2.06	2.02	2.06
	ω	667	528	515	468
	D	4.61	4.11	4.20	3.60
B3PW91	r	1.91	2.04	2.02	2.09
	ω	706	561	525	461
	D	4.19	3.80	3.69	3.18
MP3	r	1.91	2.04	2.00	2.06
	ω	708	559	484	472
	D	1.70	1.84	0.53	1.16
MP4	r	1.93	2.05	1.95	2.01
	ω	664	530	599	570
	D	1.67	1.83	0.23	1.25
EXPERIMENT	r	1.89^a		2.04^b	2.18^c
	ω	726^a	589^d	540^e	450^c
	D	4.37^f		3.31^g	2.99^h

The values based on our chosen method together with experimental values are in bold.

^a Ref. [47].

^b Ref. [51].

^c Ref. [13].

^d Ref. [49].

^e Ref. [52].

^f Ref. [50].

^g Ref. [48].

^h Ref. [16].

followed by vibration frequency calculations to determine a stationary point obtained.

In order to choose the suitable computational method, we performed benchmark calculation on the two-atom clusters (S_2 , Fe_2 , FeS and FeS^-) with various exchange–correlation functionals and two Post-Hartree–Fock ab initio method (B3PW91[38–40], PW91 [38,40], B3LYP [38,41], TPSS [42], PBE [42], BP86 [41,43], MP3 and MP4 [44]) combined with 6-311+G* [45,46] basis set. The tested results together with the comparable experimental results [13,16,47–52] are summarized in Table 1. In a series of trials, it can be noted that the results for bond lengths (r), vibration frequencies (ω) and dissociation energies (D) are quite sensitive to the choices of B3PW91 methods. More specifically, the deviation between Fe–S distances is almost zero in FeS and only overestimates 3% in FeS^- . Moreover, the method B3PW91, which includes an exchange description constituted by contributions of local, nonlocal (Becke three-parameter), and Hartree–Fock exchange terms, is one of the most successful hybrid functionals. The triple- ξ basis set 6-311+G*, which include diffuse function and an f-type polarization function on iron atoms, is employed for our system. In addition, the reliability of present computational method was again validated by calculating the first VDEs ($\text{VDE} = E_{\text{neutral at optimized anion geometry}} - E_{\text{optimized anion}}$) and ADEs ($\text{ADE} = E_{\text{optimized neutral}} - E_{\text{optimized anion}}$)

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