Supporting Information for

# Fe-V Sulfur Clusters studied through Photoelectron Spectroscopy and Density

## **Functional Theory**

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Figure S1. Mass spectrum of  $Fe_mV_nS_xC_y$  cluster anions generated by laser ablation of a mixed iron/vanadium powder (Fe:V = 1:1) pressed target in the presence of a 0.1% CS<sub>2</sub> in helium carrier gas. Oxygen contamination peak positions of FeVSO<sup>-</sup> and FeVS<sub>2</sub>O<sup>-</sup> are marked by star in the mass spectrum. The features marked in red indicate the Fe/V/S clusters of interest to these studies.



Figure S2. DFT optimized structures of  $FeV_3S_4^-$  cluster at the BPW91/TZVP level. Relative energy (in eV), and spin multiplicity *M* are indicated on the structures. [Grey = V, blue = Fe, yellow = S]



Figure S3. NBO plots showing HOMO to HOMO-4 orbitals of  $FeVS_{1-3}$  cluster anions. The spin multiplicity (*M*) is listed as <sup>*M*</sup>FeVS\_{1-3</sub>. [Grey = V, blue = Fe, yellow = S]



Figure S4. NBO plots showing HOMO to HOMO-4 orbitals of  $FeV_2S_3^-$  and  $Fe_2VS_3^-$  cluster anions. The spin multiplicity (*M*) is listed as  ${}^{M}Fe_{m}V_{n}S_{m+n}^-$ . [Grey = V, blue = Fe, yellow = S]



Figure S5. NBO plots showing HOMO to HOMO-4 orbitals of  $\text{Fe}_m \text{V}_n \text{S}_{m+n}$  (m + n = 4, m > 0, n > 0) cluster anions. The spin multiplicity (*M*) is listed as  ${}^M\text{Fe}_m \text{V}_n \text{S}_{m+n}$ . [Grey = V, blue = Fe, yellow = S]

#### Section A. BROKEN SYMMETRY

The ground states of many transition-metal clusters (especially iron containing clusters) exhibit "antiferromagnetic" spin coupling, in which the spin vectors associated with the individual metal centers are aligned in opposing directions. Broken symmetry analysis, which was developed by Noodleman et al., has proved to be a good method to investigate such antiferromagnetic coupling in iron sulfur clusters. <sup>1, 2</sup> For the broken symmetry solution, the spin-unrestricted high spin (HS) solution is generated with all site spins ferromagnetically coupled in one direction (all spins up,  $\uparrow$ ). The  $\alpha$  ( $\uparrow$ ) and  $\beta$  ( $\downarrow$ ) electron densities, centered at these sites, which are expected to be antiferromagnetically coupled (spins both up and down,  $\uparrow+\downarrow$ ) to the total spin vector, are then exchanged for the earlier obtained HS solution. Because this approach often results in lowering the electronic symmetry of the system while retaining its structural symmetry, a solution obtained in this manner is often referred to as the broken symmetry (BS) state. In these Fe-V sulfur anion clusters, the metal centers can be antiferromagnetically coupled in low spin states. For instance, the spin densities for isomer I of  ${}^{5}\text{Fe}_{2}\text{VS}_{3}{}^{-}$ , give unpaired electrons on all V and Fe centers, with the V center (V6) having opposite spin with respect to the other two Fe center (Fe4 and Fe5). This case is presented in the table below."

Label	Ato	Mulliken	Spin	<sup>5</sup> Fe <sub>2</sub> VS <sub>3</sub> <sup>-</sup> structure with labels
	m	charges	densities	
1	S	-0.523076	0.050374	
2	S	-0.390246	0.290190	2
3	S	-0.368132	0.230285	
4	Fe	0.056405	2.765282	
5	Fe	0.092331	2.899111	
6	V	0.132718	-2.235241	
Sum		-1.00000	4.00000	

Table S1. The relative energy  $\Delta E$  (in eV) and the first calculated VDEs (in eV) for FeS<sup>-</sup> for selected spin multiplicity (*M*) calculated at different theoretical levels employing Gaussian 09 and MOLPRO programs, as well as the experimental first VDE result for comparison. Spin orbit coupling (SOC) corrected relative energies and VDEs are performed using MOLPRO. See details in the following discussion section.

Methods –		FeS <sup>-</sup>				
		Δ <i>Ε</i> (eV)		VDE (eV)		
		<i>M</i> = 4	<i>M</i> = 6	M = 4	Exp.	
G09	B3LYP/TZVP	0.00	0.18	1.43		
	B3LYP/aug-cc-PVQZ	0.00	0.06		1.85	
	BPW91/TZVP	0.00	0.17	1.12		
	BPW91/aug-cc-PVQZ	0.00	0.04			
	CASSCF/TZVP	0.00	0.06	1.75		
MOLPR	CASSCF/TZVP (SOC)	0.00	0.24	1.97		
0	CASSCF/aug-cc-PVQZ	0.00	0.03	1.88		
	CASSCF/aug-cc-PVQZ (SOC)	0.00	0.09	1.52		

Table S2. The relative energy  $\Delta E$  (in eV) and the first calculated VDEs (in eV) for Fe<sub>2</sub>S<sub>2</sub><sup>-</sup> for selected spin multiplicity (*M*) calculated at different theoretical levels employing Gaussian 09 and MOLPRO program, as well as the experimental first VDE result for comparison. Spin orbit coupling (SOC) corrected relative energies and VDEs are performed using MOLPRO. See details in the following discussion section.

Methods –		Fe <sub>2</sub> S <sub>2</sub> -			
		Δ <i>Ε</i> (eV)		VDE (eV)	
		<i>M</i> = 8	<i>M</i> = 2	<i>M</i> = 8	Exp.
G09	BPW91/TZVP	0.00	0.53	2.04	
	CASSCF/TZVP	0.00	0.15	2.46	2.34
MOLPR	CASSCF/TZVP (SOC)	0.00	0.14	2.39	
0	CASSCF/aug-cc-PVQZ	0.00	0.15	2.32	
	CASSCF/aug-cc-PVQZ (SOC)	0.00	0.13	2.21	

## DISCUSSION OF THE ABOVE CALCULATIONAL RESULTS IN TABLE S1 AND S2

In order to consider the effect of spin-orbit coupling (SOC), complete-active-space self-consistent field (CASSCF) methods coupled with different basis sets TZVP and aug-cc-PVQZ are employed to calculate the relative energy and first VDE of the  $(FeS)_{1,2}$ <sup>-</sup> clusters with selected spin multiplicities, using the MOLPRO program. <sup>3</sup> The relative energy of quartet and sextet FeS<sup>-</sup>, doublet and octet Fe<sub>2</sub>S<sub>2</sub><sup>-</sup>, and the first VDE of quartet FeS<sup>-</sup> and octet Fe<sub>2</sub>S<sub>2</sub><sup>-</sup>, with/without spin-orbit coupling, are calculated and displayed in Tables S1 and S2, respectively. The CASSCF levels employed are as follows: 3 valence electrons in 7

active orbitals, denoted as CASSCF(3,7) for quartet FeS<sup>-</sup>; CASSCF(5,9) for sextet FeS<sup>-</sup>; CASSCF(5,7) for doublet Fe<sub>2</sub>S<sub>2</sub><sup>-</sup>; and CASSCF(7,12) for octet Fe<sub>2</sub>S<sub>2</sub><sup>-</sup>. Spin-orbit coupling calculations employ the Breit-Pauli (BP) operator and the state interacting method. The calculated results using G09 without inclusion of SOC, and experimental results are also listed in these tables for comparison. As the results show in Table S1, the relative energies of spin state M = 4 of FeS<sup>-</sup> obtained at CASSCF/TZVP and CASSCF/aug-cc-PVQZ levels using MOLPRO are lower than those of spin state M = 6 of FeS<sup>-</sup>, both with and without consideration of spin-orbit coupling. These results suggest the relative energy order of different spin state (M = 4 and M = 6) of FeS<sup>-</sup> cluster is not affected by spin-orbit coupling. These MOLPRO results also agree with the G09 results at different theoretical levels without consideration of SOC (also displayed in Table S1). The SOC corrected first VDE of the lowest energy spin state (M = 4) FeS<sup>-</sup> cluster is obtained at CASSCF/TZVP (1.97 eV) and CASSCF/aug-cc-PVQZ (1.52 eV) levels. Without SOC, the calculated first VDE of the FeS<sup>-</sup> (M = 4) cluster is 1.75 eV and 1.88 eV at a CASSCF/TZVP and CASSCF/aug-cc-PVQZ level, respectively. All the above calculated results are in reasonable agreement with the experimental result for the FeS<sup>-</sup> cluster. Thus, neglect of SOC for the first VDE calculation apparently does not affect the assignment accuracy for the FeS<sup>-</sup> cluster.

The relative energies of spin states M = 2 and M = 8 of Fe<sub>2</sub>S<sub>2</sub><sup>-</sup> and the calculated first VDE of Fe<sub>2</sub>S<sub>2</sub><sup>-</sup> (M = 8) obtained at CASSCF/TZVP and CASSCF/aug-cc-PVQZ levels are presented in Table S2. The differences between the SOC corrected first VDE, relative energies of different spin state results, and the relative results without SOC are also small. For example, the calculated first VDE of Fe<sub>2</sub>S<sub>2</sub><sup>-</sup> (M = 8) is 2.32 eV at CASSCF/aug-cc-PVQZ level, and the relative SOC corrected result is 2.21 eV. This ~ 0.1 eV difference is insignificant for the assignment of the experimental first VDE result for the Fe<sub>2</sub>S<sub>2</sub><sup>-</sup> cluster (2.34 eV). Thus, SOC corrections are not important for calculation of relative energies of the spin states and the first VDEs of (FeS)<sub>1,2</sub><sup>-</sup> clusters at the present level of theory and experiment.

### References

(1) Noodleman, L.;Peng, C. Y.;Case, D. A.;Mouesca, J. M. Orbital Interactions, Electron Delocalization and Spin Coupling in Iron-Sulfur Clusters. *Coord Chem Rev* **1995**, *144*, 199.

(2) Noodleman, L.; Case, D. A.; Aizman, A. Broken Symmetry Analysis Of Spin Coupling in Iron Sulfur Clusters. J Am Chem Soc **1988**, *110*, 1001.

(3) Werner, H.-J.;Knowles, P. J.;Knizia, G.;Manby, F. R.;Schütz, M. Molpro: A General-Purpose Quantum Chemistry Program Package. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2012**, *2*, 242.