Structures of manganese polysulfides: mass-selected photodissociation and density functional calculations†

Yu-Chao Zhao, Jinyun Yuan, Zeng-Guang Zhang, Hong-Guang Xu and Weijun Zheng*

Received 7th September 2010, Accepted 8th December 2010
DOI: 10.1039/c0dt01179g

Manganese polysulfide cations, MnSₙ⁺ (ₓ = 1–10), were studied with mass-selected photodissociation experiments and density functional calculations. We found that MnS⁺, MnS₂⁺ and MnS₃⁺ undergo dissociation at 355 nm by loss of S, S₂ and S₃, respectively. The dissociation of larger clusters is relatively complex because of the existence of multiple isomers and multiple dissociation channels. The geometric structures of the low-lying isomers found by theoretical calculations are consistent with the dissociation channels observed in the experiments. The dissociation of MnSₓ⁺ clusters occurs mainly by breaking of the Mn–S bonds since they are weaker than the S–S bonds.

1. Introduction

Transition-metal sulfides have been studied by many research groups in the past decades as they have important applications in superconductors,¹,² biochemical systems,³ and catalytic processes.⁴ Dance and co-workers generated many transition-metal sulfides using the laser ablation method and analyzed them by Fourier-transform ion cyclotron resonance (FTICR) mass spectrometry.⁵–¹¹ Liang et al. investigated the sulfides of group 4–6, 8 and 10 transition metals using matrix-isolation infrared spectroscopy and DFT calculations.¹²–¹⁶ Nakajima and co-workers conducted anion photoelectron spectroscopy studies of iron–sulfur and manganese–sulfur clusters.¹⁷–¹⁹ Gemming et al. investigated the structures of molybdenum sulfide clusters,²⁰ Gao and co-workers studied the photodissociation of tantalum–sulfur,²¹ iron–sulfur,²² cobalt–sulfur cluster ions,²³ and many other transition-metal sulfides.²⁴–²⁸ Kretzschmar et al. investigated the thermochemistry and reactivity of a number of transition-metal sulfides (M–V, Mo, Sc, Ti) in the gas phase.²⁹,³₀ Bernstein and co-workers studied the formation and stability of neutral vanadium–sulfide clusters using multiphoton ionization.³¹

Among the transition-metal sulfides, transition-metal polysulfides belong to a special category showing novel structural and reactive properties.³²–³⁵ They have potential applications in chemical industrial catalysis³⁶ and in battery cathodes,³⁷ and thus have attracted particular attention. Photodissociation, collision-induced dissociation and ion–molecule reaction experiments were used to study FeSₓ⁺⁺ clusters.³⁸ FeSₓ⁻ cluster anions were studied with photoelectron spectroscopy.³⁹ FeSₓ⁺⁺ (n = 2–8), TaSₓ⁺⁺ (n = 4–10), and CoSₓ⁺⁺ (n = 4, 6) were explored by photodissociation experiments.⁴¹ The formation and structures of the polysulfides of many other transition metals (except Tc) were investigated using laser ablation and FTICR mass spectrometry.⁴² As for manganese, its sulfides and polysulfides were generated in the gas phase by laser ablation of solid MnS and were investigated using collision-induced dissociation method and density functional calculations.⁴³,⁴⁴ Nevertheless, our knowledge about the properties of manganese polysulfides is not conclusive. To further explore the structural properties of manganese polysulfides, here we investigated MnSₓ⁺⁺ (n = 1–10) by mass-selected photodissociation experiments and density functional calculations.

2. Experimental and theoretical methods

The experiments were conducted on a home-built reflection time-of-flight mass spectrometer (RTOF-MS) which has been described elsewhere.⁴² Briefly, the manganese–sulfur clusters were generated in the source chamber by ablating a rotating and translating Mn/S mixture disk target (13 mm diameter, Mn/S molar ratio 1:2) using the second harmonic output (532 nm, 10 mJ pulse⁻¹, 5 Hz) of an Nd:YAG laser. The resulting plasma was cooled with argon carrier gas expanded through a pulsed valve (General Valve Series 9) at 3–5 atm backing pressure. The produced Mn/S cluster ions were mass-analyzed with the RTOF-MS. A selection–deceleration–dissociation–reacceleration method was used in the dissociation experiments. The MnSₓ⁺⁺ (n = 1–10) cluster ions were mass-selected with a mass-gate at the first space focus point of the RTOF-MS, decelerated with a electric field, and dissociated with a second Nd:YAG laser (Continuum Surelite II-10) at 532 (69 mJ pulse⁻¹, 5 ns) and 355 nm (21 mJ pulse⁻¹, 5 ns) wavelengths without focusing the laser beam. The fragment ions and surviving
parent ions were then reaccelerated and detected by the MCP (microchannel plate) detector of the RTOF-MS. The ion signals were amplified with a broadband amplifier and recorded with a 100 MHz digital card, and were then collected in a laboratory computer with home-made software.

*Ab initio* calculations were performed using the Gaussian 03 package. The geometric optimizations were conducted using Becke's three parameters hybrid functional and the Lee, Yang and Parr correlation functional (B3LYP) in conjunction with the 6-31g(d) basis set. The single-point energies of all optimized structures were calculated at the B3LYP theory level in conjunction with the mixed basis sets (S: aug-cc-pvqz; Mn: 6-311++G(3df)). The frequency analysis and zero-point energy corrections (ZPE) were also implemented at the same method as that of structural optimizations. It has been verified that all of the optimized structures have no imaginary frequencies. We have tested the theoretical method by calculating the bond dissociation energies (BDEs) of MnS+ and S+, as well as the ionization energy of S+. Our calculations show that the BDEs of MnS+ and S+ are 2.48 and 4.38 eV respectively, in agreement with the experimental values (2.52 ± 0.24 eV for MnS+, and 4.41 ± 0.13 eV for S+, in the literature. The calculated ionization energy of S+ is about 9.56 eV, which is also close to the experimental value of 9.36 ± 0.02 eV. Thus, the comparison of theoretical calculations and experimental values demonstrated that the method chosen here is suitable for Mn–S clusters.

### 3. Experimental results

Fig. 1 shows a typical and reproducible mass spectrum of MnS+x cluster ions generated in the experiments. There are three series of clusters, S+x (x = 2–13), MnS+x (x = 0–14), and Mn2S+x (x = 0–12). In these three series, the predominant mass peaks in the spectrum are those of S+x and MnS+x. The mass peaks of the MnS+x clusters are weaker than those of S+x and MnS2+x.

![Mass spectrum of MnS+x cluster ions.](image)

Fig. 2 and Fig. 3 show the photodissociation mass spectra of the MnS+x+ (x = 1–10) clusters at 355 and 532 nm wavelengths, respectively. Generally, the efficiency of photodissociation at 532 nm is much lower than that at 355 nm. No dissociation fragments have been observed for MnS5+x and MnS6+x.

MnS+x, MnS2+x and MnS3+x undergo dissociation at 355 nm by loss of S, S2, and S3, respectively. They all produced Mn+ fragment ions but with very low efficiency. At 352 nm, Mn+ fragment ion was detected for MnS4+x but no fragment ion has been detected for MnS5+x and MnS6+x.

MnS+x, MnS2+x and MnS3+x undergo dissociation at 355 nm by loss of S units until reaching the smallest fragment ion, Mn+. MnS4+x and MnS5+x undergo dissociation at 355 nm by loss of S units until reaching the fragment ion, MnS3+x, then the fragment ion MnS3+x loses S to generate Mn+. A very tiny amount of MnS+x and MnS2+x fragment ions for MnS3+x as well as MnS+x fragment ions for MnS3+x are barely distinguishable. At 352 nm, the dissociation of MnS4+x still shows the same trend except that the MnS+x fragment ion was not detected for MnS4+x. The smallest fragment ion at 352 nm for MnS5+x and MnS6+x is MnS3+x instead of Mn+. The smallest fragment ion at 352 nm for MnS4+x and MnS5+x is MnS3+x instead of Mn+. These results are consistent with the low dissociation efficiency or non-dissociation of MnS2+x and MnS3+x at 352 nm.

The major fragment ions of MnS+x at 355 nm are MnS5+x, MnS6+x, MnS7+x and Mn+ while the minor ones are MnS+x and MnS2+x. More likely, the photodissociation of MnS+x occurs first by loss of an S or S2 unit. Then, the MnS+x and MnS2+x fragments are further photodissociated to generate other fragment ions. However, it is worth noting that the sub-dissociation of MnS+x fragment of MnS+x might be different from that of the MnS+x parent ion, because the signal of the MnS+x fragment ion in the MnS+x spectrum is much lower than that in the MnS+x spectrum. Photodissociation of MnS+x produces MnS+x+, MnS2+x, MnS3+x and Mn+ fragments. The photodissociation of MnS+x probably occurs by initial loss of an S unit.
4. Theoretical results and discussion

Fig. 4 shows the structures of the low-lying isomers of MnS$_x^+$ ($x = 1–8$) clusters with the most stable ones on the left.

**MnS$_1^+$**

The most stable structure of MnS$_1^+$ is isomer 1A in the $^3S_g$ state. Isomer 1B is in the $^5S_g$ state, which is 0.33 eV higher in energy. Our calculations show that the bond dissociation energy (BDE) of isomer 1A is 2.48 eV which is in agreement with the experimental value of 2.52 eV, and that of isomer 1B is 2.18 eV. A 355 nm photon is able to dissociate isomer 1A and 1B. A 532 nm photon can only dissociate isomer 1B. In our spectra, the relative intensity of the fragment ion Mn$^+$ at 355 nm (Fig. 2) is higher than that at 532 nm (Fig. 3). We suggest that both isomers 1A and 1B exist in our experiment. The intensity of the fragment ion Mn$^+$ at 355 nm probably is contributed by both isomers 1A and 1B, while that at 532 nm probably is contributed by isomer 1B only.

**MnS$_2^+$**

The most stable structure of MnS$_2^+$ is isomer 2A in the $^7A_2$ state. Isomers 2B and 2C are in $^5A_2$ and $^5A''_2$ states, respectively, which are
0.35 and 0.52 eV higher than isomer 2A in energy. Isomers 2D and 2E are higher than isomer 2A by 0.72 and 0.96 eV, respectively. All of them are of type Mn⁻–S₂. That is in agreement with the loss of an S₂ unit in the dissociation experiment. Zhang et al. suggest that the MnS₂ neutral has two types of isomers, Mn–S₂ and S%Mn%S. We found the S%Mn%S linear structure is much more unstable than isomer 2A being higher in energy than isomer 2A by at least 1.7 eV. Since isomers 2C, 2D and 2E are much higher in energy, they are unlikely to be populated in our experiments, and isomers 2A and 2B are likely to be the major products in our experiments.

MnS₃⁺

The most stable structure of MnS₃⁺ is isomer 3A in the ℏA₂ state. Our calculation shows that the BDE of 3A is 2.70 eV. It can be only dissociated at the 355 nm wavelength in accordance with the dissociation experiments. We suggest that isomer 3A exists in our
experiment. Isomers 3B and 3C would undergo dissociation by loss of S2 to produce MnS* fragment ion. However, the MnS* fragment has not been observed in our experiments. Also, the isomers 3B and 3C are less stable than isomer 3A since their energies are much higher than that of isomer 3A. Thus, isomers 3B and 3C probably are not observed in the experiments.

MnS*+

The most stable structure of MnS*+ is isomer 4A in the 1B2u state. We found that the BDE value for loss of the first S, is 2.08 eV and for the second S, is 1.70 eV. Thus, both 355 and 532 nm photons are able to dissociate isomer 4A to produce MnS*+ and Mn* fragment ions. That is in agreement with our experimental observation. We suggest that isomer 4A is present in our experiment. Isomer 4B is in the 1A1 state which is 0.28 eV higher than isomer 4A in energy. Our calculations show that it takes about 3.07 eV to dissociate isomer 4B into Mn* and S4. Thus, a 355 nm photon is able to dissociate isomer 4B to generate the Mn* fragment, but a 532 nm photon cannot. Since the energy of isomer 4B is only 0.28 eV higher than isomer 4A, we suspect that it might also be present in our experiments.

MnS*-

The most stable structure of MnS*+ is isomer 5A in the 3A1 state. Isomers 5B and 5C are in 1A1 and 5A1 states respectively, whose structures are analogous to that of isomer 5A. They are 0.22 and 0.34 eV higher than isomer 5A in energy, respectively. The energy of isomers 5D, 5E and 5F are much higher than isomer 5A and probably are not observed in the experiments. For isomers 5A, 5B and 5C, the BDE of the loss of S2 is lower than that of the loss of S4. Thus, the most probable dissociation pattern is that isomers 5A, 5B and 5C first undergo dissociation by the loss of S2 to produce the MnS* fragment, and then the MnS* fragments undergo dissociation by loss of S4 to produce Mn*. This is in agreement with the observation of MnS*+ and Mn* in the dissociation experiment of MnS*+ at 355 nm. As shown earlier, MnS*+ cannot be dissociated by a 532 nm photon, thus, no Mn* was produced in the dissociation of MnS*+ at 532 nm.

MnS*-

The low-lying isomers of MnS* are very close in energy and are all probably present in our experiments. Isomers 6A and 6C have similar structures but are in different electronic states. Both of them can undergo dissociation by sequential loss of S4 units to produce MnS*+, MnS*+ and Mn* fragments. Our calculations show that isomers 6B, 6D, 6E and 6F all can undergo dissociation by sequential loss of S4 units. Loss of S4 is also possible for isomer 6E. These are consistent with the observation of MnS*+, MnS*+ and Mn* fragments at 355 nm in our experiments. Isomer 6F probably can also lose S4 to generate Mn* directly at 355 nm. No Mn* fragment has been detected at 532 nm probably because the energy of 532 nm photons is too low to generate Mn* directly from isomer 6F, or to generate Mn* indirectly from the MnS*+ fragment ion.

MnS*+

Isomers 7A and 7D photodissociated by 355 nm photons can lose S4 to produce the Mn* fragment directly. Isomers 7B and 7F have similar structures but are in different electronic states and they all can generate the MnS*+ fragment by loss of S4. Isomer 7C can be dissociated to produce MnS*+ and MnS*+ fragments by loss of S2 or S4 units. Isomer 7E probably has the same photodissociation pattern as isomer 7C since their geometric structures are similar, that is, they consist of S2 and S4 units.

MnS*+

Our calculations show that isomers 8A and 8D can be dissociated by loss of one S2 unit or by loss of S4 units. Isomers 8C and 8E can be dissociated by loss of four S4 units sequentially. Thus, they are able to produce MnS*+, MnS*+, MnS*+ and Mn* fragment ions at 355 nm. Isomers 8B and 8F might be able to generate a Mn* fragment by loss of S4 at 355 nm. No Mn* fragment has been observed at 532 nm because a 532 nm photon is not able to initiate loss of S4 from isomers 8B and 8F or loss of S4 from the MnS2* fragment ion. The calculated structures of MnS*+ are consistent with dissociation products detected in the experiments.

MnS*+ and MnS10+

As shown in the experiments (Fig. 2), the first step of photodissociation of MnS*+ is dissociation of the S or S2 unit to produce the fragment ions MnS*+ or MnS*+, respectively. Then, the fragment ion MnS*+ can be photodissociated to produce the fragment ions MnS*+ and MnS*+ and finally the fragment ion MnS*+ may be photodissociated to produce the Mn*+, and the fragment ion MnS*+ may be also photodissociated to generate the ions MnS*+ and Mn*, in which the yield of Mn*+ is larger than that of MnS*+.

According to the photodissociation experimental results, it might be possible that MnS*+ is composed of S2 and MnS*+ units and the structural unit MnS*+ might consist of S4 and MnS*+ units. MnS10+ is firstly photodissociated by loss of an S4 unit to produce the MnS*+ fragment ion at 355 nm. Subsequently, the daughter ion MnS*+ can be further photodissociated to produce the other fragment ions such as MnS*+, MnS*+ and Mn*. Therefore, we speculate that MnS10+ would be composed of S4 and MnS*+ units. Multiple isomers probably also exist for MnS*+ and MnS10+.

Dance and co-workers calculated the molecular structures of MnS, neutrals. They found the most stable structure of MnS neutral is linear and that of MnS neutral has a triangular structure formed by the three S atoms and the Mn atom is at the center of the triangle. Our calculations show that the linear structure of MnS neutral is unstable for MnS*. The planar triangular isomer found for MnS neutral is unstable for MnS*. Gao and co-workers reported the photodissociation of TaS*+, FeS*+ and MnS10+ clusters using 248 nm photons. In the photodissociation of TaS*+, clusters, the main dissociation channel is the loss of S4 or S2, however, the loss of S4 can also occur for TaS*+. The channels for loss of a sulfur atom were also observed for FeS*+, FeS*+, FeS*+ and FeS*+. The dissociation channel of CoS*+ is loss of S4, while that of CoS*+ is loss of S2. Both the dissociations of CoS*+ and CoS*+ are of very low efficiency. In our experiments of MnS*+, clusters, no dissociation channel for loss of S atom has been observed except for MnS*+. The dissociations of MnS*+, MnS*+ and other
larger clusters are much more efficient than those of TaS$_x^+$, FeS$_x^+$ and CoS$_x^+$ clusters. The intensities of the fragment ions of MnS$_x^+$ clusters at 355 nm are close to or higher than that of the remaining parent ions, which means the dissociation ratios are higher than 50%. For MnS$_2^+$ with an even number of sulfur atoms, the main dissociation channel is the loss of S$_2$ or S$_4$. For MnS$_4^+$ with an odd number of sulfur atoms, the main dissociation channel is the loss of S$_2$ units followed by loss of S$_3$. For the larger clusters, such as MnS$_9^+$ and MnS$_{10}^+$, the loss of S$_2$ can also happen.

As reported in the literature, the BDE of MnS$^+$ is 2.52 ± 0.24 eV, and that of S$_2$ is 4.41 ± 0.13 eV. The S–S bonds are stronger than the Mn–S bonds. This implies that the dissociation of MnS$_x^+$ clusters would occur mainly by breaking of the Mn–S bonds. That is consistent with what is observed in the dissociation experiments (Fig. 2 and 3). We found that for the most probable isomers of MnS$_2^+$ and MnS$_3^+$, the coordination number of Mn$^+$ is 2. For MnS$_n^+$ (n = 4–8) clusters, the coordination number of Mn$^+$ can be 2, 4 or 6. Among them, the clusters have more inclination to form four-coordinated structures.

5. Conclusions

We studied the photodissociation of MnS$_x^+$ (x = 1–10) clusters and calculated the geometric structures of MnS$_n^+$ (n = 1–8) using density functional method. We found that MnS$_n^+$, MnS$_x^+$ and MnS$_{n+2}^+$ undergo dissociation at 355 nm by loss of S, S$_2$ and S$_3$, respectively. Dissociation of MnS$_4^+$ and MnS$_6^+$ at 355 nm first generated MnS$_x^+$ by loss of S$_2$ units, then generated Mn$^+$ by loss of an S unit. The clusters with an even number of sulfur atoms, such as MnS$_n^+$, MnS$_x^+$ and MnS$_{n+2}^+$, undergo dissociation mainly by sequential loss of S$_2$ or S$_3$ units. Comparison of the experimental data and theoretical calculations suggests that the MnS$_n^+$ clusters coexist as multiple isomers. The structures of the low-lying isomers of MnS$_n^+$ clusters are characterized by addition of S$_n$ (n ≥ 3) to units to the Mn$^+$ ion. The Mn$^+$ ion coordinates with the S atoms at the two ends of the S$_n$ units to form (n + 1)-membered rings. The number of S$_n$ units connecting to the Mn$^+$ ion can be two, one or three, with more inclination towards two; hence, most of the isomers have double ring structures. The most stable isomer of MnS$_n^+$ has a (S$_n$)Mn(S$_n$) style double five-membered ring structure.

Acknowledgements

W. J. Z. acknowledges the Institute of Chemistry, Chinese Academy of Sciences for start-up funds. We are grateful to Professor Zhen Gao for valuable discussions. We thank the Supercomputing Center of Chinese Academy of Sciences for allowing us to use the ScGrid for theoretical calculations.

References
