Activation of H₂S by Atomic Cr, Mn, and Fe: Matrix Infrared Spectra and Quantum Chemical Calculations

Jie Zhao and Xuefeng Wang *

ABSTRACT: Hydrogen sulfide is toxic and corrosive gas abundantly available in nature. The activation of hydrogen sulfide to produce hydrogen and elemental sulfur is of great significance for possible applications in toxic pollutant control and hydrogen energy regeneration. The activation of H₂S by transition metal atoms (M = Cr, Mn, and Fe) has been studied by low-temperature matrix isolation infrared spectroscopy and quantum chemical calculations. Experimental and theoretical results indicate that the reaction between ground-state M atoms and H₂S is inhibited by the repulsive interactions between the reactants. After being excited upon photolysis, the corresponding excited-state M atoms react with H₂S molecules spontaneously. The produced insertion product HMSH further decomposed to metal sulfides upon full-arc mercury lamp irradiation by the splitting of hydrogen.

INTRODUCTION

Toxic hydrogen sulfide originates from nature, and industrial waste gases are responsible for the formation of aerosols and acid rain. The common process utilized to dispose hydrogen sulfide is the Claus process. Meanwhile, the potential for hydrogen generation from hydrogen sulfide is lost in the Claus process. The splitting of hydrogen sulfide to produce hydrogen and sulfur is of great significance for toxic pollution control as well as hydrogen energy regeneration. Numerous materials such as metals, metal oxides, and metal sulfides have been explored as possible catalysts for hydrogen sulfide decomposition. The low-temperature matrix isolation technique is useful in the reaction mechanism study. The activation of H₂S by laser-ablated group 4 and group 5 transition metal atoms in a low-temperature argon matrix takes place spontaneously, and the produced insertion products decompose to metal sulfides and hydrogen upon photoirradiation. Laser-ablated Th and U atoms react with H₂S on the annealing processes to produce H₂ThS and H₂US, respectively. The products further decompose to metal sulfides and hydrogen on broadband mercury lamp irradiation.

For the purpose of obtaining more possible catalysts for the activation of H₂S, matrix isolation infrared spectroscopy and quantum calculations were employed to study the reaction mechanisms of transition metal atoms (M = Cr, Mn, and Fe) with hydrogen sulfide molecules in this work. We will show that laser-ablated Cr, Mn, and Fe atoms react with H₂S molecules in solid argon upon photolysis to produce the insertion product HMSH.

EXPERIMENTAL AND THEORETICAL METHODS

The experimental setup for laser ablation and matrix isolation infrared spectroscopy has been described in detail previously. Briefly, a fundamental Nd:YAG laser (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on a rotating metal target. The laser-ablated Cr, Mn, or Fe metal atoms were co-deposited with hydrogen sulfide diluted in an argon matrix (typically 0.3%) on a 5 K CsI window for 1 h. After sample co-deposition, the Fourier transform infrared spectra were recorded between 400 and 4000 cm⁻¹ at 0.5 cm⁻¹ resolution using a Bruker 80 V spectrometer with a liquid nitrogen-cooled broadband MCT detector. Then, samples were annealed to the desired temperature and exposed to light with selected wavelengths to induce further reaction. A mercury lamp (75 W, without a globe) was used as a light source in the photolysis process with the aid of band filters to allow light of selected wavelength to pass through.

All the calculations were performed with the Gaussian 09 software package. The def2-TZVPP basis sets were employed for all atoms. Structures of relative species were fully optimized, and harmonic frequencies were calculated analytically on the optimized structures. Transition states were characterized with one imaginary frequency and confirmed to
link the corresponding products and reactants by intrinsic reaction coordinate calculations (IRC). Time-dependent density functional theory (TDDFT) at the B3LYP theoretical level was used to calculate the potential energy surfaces for the excited states.

**RESULTS**

Matrix isolation infrared spectroscopy was employed to study the reaction of laser-ablated transition metal atoms M (M = Cr, Mn, and Fe) with H₂S molecules diluted in the argon matrix (typically 0.3%). Besides the absorptions due to reactants and impurities such as water existing in all our experiments, absorptions due to chromium hydrides (CrH and CrH₂) and chromium sulfides (CrS and CrS₂) and two new absorptions at 1661.8 and 1683.4 cm⁻¹ were identified in the experiments of Cr + H₂S in the solid argon matrix.

Absorptions contributed from MnH, MnH₂, and MnS and a new absorption at 1661.6 cm⁻¹ were identified in the experiments of Mn with H₂S by infrared spectroscopy. In the reaction of Fe + H₂S in the solid argon matrix, absorptions due to FeH₂, FeS, and FeS₂ and two new absorptions at 1731.6 and 1688.9 cm⁻¹ were identified. The assignments of the absorptions will be discussed in detail below.

**HCrSH and HCr(SH)₂.** The spectra in selected regions from reactions of laser-ablated Cr atoms with H₂S are presented in Figure 1 and Figure s1 in the Supporting Information.

Upon full-arc mercury lamp irradiation, absorption at 1661.8 cm⁻¹ was nearly destroyed, accompanied by the appearance of absorption due to CrS (476.4 cm⁻¹), indicating the conversion from the complex contributing to the 1661.8 cm⁻¹ absorption to CrS upon photolysis. We assigned this absorption to HCrSH.

Absorption at 1683.4 cm⁻¹ appeared as weak absorption after the annealing of the sample to 25 K and tripled upon the following >400 nm photolysis. The 1683.4 cm⁻¹ absorption is 21.6 cm⁻¹ higher than the Cr−H stretching mode of HCrSH. This absorption is suitable for the Cr−H stretching mode. No other absorption was observed to track with this absorption. It suggests the existence of a Cr−H subunit in the complex. Absorption at 1683.4 cm⁻¹ was nearly destroyed, and absorption due to CrS2 appeared upon full-arc mercury lamp irradiation, indicating the conversion of the complex to CrS₂. Accordingly, the 1683.4 cm⁻¹ absorption is assigned to HCr(SH)₂.

Density functional theory calculations at the B3LYP theoretical level were carried out to further prove our assignments (Table 1). HCrSH was calculated to have a ³A ground state with Cr−H stretching vibration predicted at 1708.2 cm⁻¹ by harmonic frequency calculation (overestimated the experimental value by 2.8%). The predicted H/D isotopic ratio (1.3999) matches the experimental value (1.3862) well. The Cr−H stretching vibration of HCr(SH)₂ predicted at 1740.1 cm⁻¹ by B3LYP calculations overestimates the experimental value (1683.4 cm⁻¹) by 3.4%. The predicted H/D isotopic ratio of 1.3994 is consistent with the experimental value of 1.3863.

**HMnSH.** Figure 3 presents the infrared spectra in selected regions from the reaction of laser-ablated Mn atoms with H₂S in solid argon. After annealing to 25 K, weak absorption at 1661.6 cm⁻¹ sharpened and absorptions due to MnH₂ (1592.3 cm⁻¹) and MnH (1477.9 cm⁻¹) appeared. The 1661.6 cm⁻¹ absorption enhanced by about 10% upon >350 nm irradiation and increased by about 10% again upon >300 nm photolysis. After being exposed to full-arc mercury lamp irradiation, the absorption decreased by about 10% accompanied by the enhancement of absorption due to MnS at 507.1 cm⁻¹. In the reaction with the mixture of H₂S, HDS, and...
D$_2$S as reagents (Figure 4), the deuterium counterpart of 1661.6 cm$^{-1}$ appeared at 1195.7 cm$^{-1}$, defying the H/D isotopic ratio of 1.3896. The 1661.6 cm$^{-1}$ absorption is slightly lower than the Mn–H stretching mode of HMnOH (1663.4 cm$^{-1}$). The band position and H/D isotopic ratio are suitable for the Mn(II)–H stretching vibration, and this absorption is assigned to the Mn–H stretching mode of HMnSH.

DFT calculations predict HMnSH to have a C$_s$ symmetric structure at the 6$^a$A$'$ ground state. The Mn–H stretching vibration predicted at 1695.0 cm$^{-1}$ overestimates the experimental value by 2.0% (Table 2). The predicted H/D isotopic ratio (1.4015) is in good agreement with the experimental value of 1.3896.

HFeSH and HFeSH$_2$. In the reaction of laser-ablated Fe atoms with H$_2$S in solid argon (Figure 5), absorption at 1731.6 cm$^{-1}$ appeared as weak absorption after co-deposition and doubled on annealing to 25 K. The absorption negligibly changed on >400 nm photolysis but sharply increased (by over 500%) on >350 nm photolysis. Upon full-arc mercury lamp irradiation.

**Table 1. Observed and Calculated Vibrational Frequencies (cm$^{-1}$) at B3LYP for HCrSH and HCr(SH)$_2$**

|                  | B3LYP obsd | B3LYP obsd | description |
|------------------|------------|------------|-------------|
| HCrSH            | 2649.2(1)  | 1901.9(0)  | S–H str     |
|                  | 1708.2(224)| 1220.2(118)| Cr–H str    |
|                  | 498.5(4)   | 348.1(12)  | H–S–Cr bend|
|                  | 405.7(154) | 394.4(49)  | Cr–S str    |
|                  | 351.8(13)  | 269.8(44)  | H–Cr–S bend|
|                  | 275.3(58)  | 198.1(32)  | HCrSH def   |
| HCr(SH)$_2$      | 2642.4(0)  | 1897.1(0)  | S–H str     |
|                  | 2641.8(3)  | 1896.6(2)  | S–H str     |
|                  | 1740.1(110)| 1683.4     | Cr–H str    |
|                  | 565.3(13)  | 492.0(53)  | Cr–H bend   |
|                  | 520.4(1)   | 391.7(4)   | S–H bend    |
|                  | 509.0(14)  | 371.5(8)   | S–H bend    |
|                  | 394.9(57)  | 338.4(2)   | Cr–S str    |
|                  | 356.7(6)   | 321.6(19)  | Cr–S str    |
|                  | 255.6(11)  | 185.2(5)   | S–H bend    |
|                  | 250.4(19)  | 181.1(11)  | S–H bend    |
|                  | 102.7(60)  | 79.2(35)   | Cr–H bend   |
|                  | 90.7(0)    | 88.7(0)    | S–Cr–S bend|

*Calculated intensities (km/mol) are given in parentheses.

**Table 2. Observed and Calculated Vibrational Frequencies (cm$^{-1}$) at B3LYP for HMnSH**

|                  | B3LYP obsd | B3LYP obsd | description |
|------------------|------------|------------|-------------|
| HMnSH            | 2655.9(2)  | 1906.6(1)  | S–H str     |
|                  | 1695.0(325)| 1661.6     | Mn–H str    |
|                  | 493.3(9)   | 337.2(8)   | H–Mn–S str  |
|                  | 367.2(39)  | 385.4(38)  | Mn–S str    |
|                  | 230.9(143)| 168.7(79)  | H–Mn–S bend|
|                  | 205.2(160)| 149.3(86)  | HMnSH def   |

*Calculated intensities (km/mol) are given in parentheses.
irradiation (>220 nm), the 1731.6 cm\(^{-1}\) absorption decreased by about 10% along with the enhancement of absorptions due to FeS (523.2 cm\(^{-1}\)) and FeS\(_2\) (471.1 cm\(^{-1}\)).\(^15\) It suggests that the composite contributing to the 1731.6 cm\(^{-1}\) absorption converts to FeS upon full-arc mercury lamp irradiation. The 1731.6 cm\(^{-1}\) absorption shifts to 1246.2 cm\(^{-1}\) in the reaction with D\(_2\)S as a reagent (Figure 6), giving an H/D isotopic ratio of 1.3895. Compared with the Fe–H stretching vibration of HFeOH\(^{17}\) (1731.9 cm\(^{-1}\)), FeH\(_2\) (1694 cm\(^{-1}\)), and FeH\(_3\) (1646.1 cm\(^{-1}\))\(^15\) in the solid argon matrix, the 1731.6 cm\(^{-1}\) absorption is suitable for the Fe(II)–H stretching vibration. Accordingly, this absorption is assigned to HFeSH.

Absorption at 1688.9 cm\(^{-1}\) increased upon >270 nm photolysis. In the experiments with D\(_2\)S as the reagent, the absorption shifts to 1216.3 cm\(^{-1}\), defying the H/D isotopic ratio of 1.3886. This absorption lies close to the Fe–H stretching vibration of HFeSH. The band position and H/D isotopic ratio are appropriate to the Fe(II)–H stretching vibration. The 1688.9 cm\(^{-1}\) absorption showed the same behaviors as the 1731.6 cm\(^{-1}\) absorption in the annealing and photochemical processes. This absorption is suitable for the Fe–H stretching vibration of HFeSH\(_2\).

HFeSH is predicted to have a \(\text{Cs}^+\) symmetric structure at the \(\text{S}^\text{A}\) ground state by DFT calculations. The Fe–H stretching vibration of HFeSH predicted at 1757.7 cm\(^{-1}\) is in good consistency with the experimental value of 1731.6 cm\(^{-1}\) (Table 3). The predicted H/D isotopic ratio of 1.4012 is also in good agreement with the experimental value of 1.3895. The Fe–H stretching vibration of HFeSH\(_2\) predicted at 1718.4 cm\(^{-1}\) overestimates the experimental value (1688.9 cm\(^{-1}\)) by 1.7%. Theoretical calculations give additional evidence for our assignments.

**DISCUSSION**

The reactions of laser-ablated transition metal atoms M (M = Cr, Mn, and Fe) with hydrogen sulfide in the low-temperature argon matrix were conducted, and the products were identified by infrared spectroscopy. Figures 7 and 8 present the optimized structures of relative species and energy profiles along the reaction coordinate from M + H\(_2\)S to HSMH. The insertion of one M atom into one S–H bond of H\(_2\)S is thermodynamically driven. The reaction of ground-state Cr\(^{2+}\)(3d\(^5\)4s\(^3\)) with H\(_2\)S releases heat of 23.3 kcal/mol, but the reaction is hindered by a reaction barrier of 12.6 kcal/mol on the ground-state surface. In the low-temperature argon matrix, absorptions assigned to HCrSH exhibited no change but greatly increased upon >400 nm photolysis. The z\(^\rightarrow\)P ← S transition of Cr atoms occurred at 396 nm in a low-temperature krypton matrix.\(^21\) The experimental results indicate that the first step for the insertion reaction is the formation of the MSH\(_2\) complex by the approaching of transition metal atoms to H\(_2\)S molecules. As shown in Figure 9, the interaction energy between ground-state Cr and H\(_2\)S is 1.36 kcal/mol at a Cr–S distance of 3.1 Å, which is assigned to the van der Waals force. A stable complex could be formed between excited-state Cr\(^{2+}\)(3d\(^5\)4p\(^3\)) atoms

**Table 3. Observed and Calculated Vibrational Frequencies (cm\(^{-1}\)) at B3LYP for HFeSH and HFeSH\(_2\)**

| B3LYP obsd | B3LYP obsd | description   |
|------------|------------|---------------|
| HFeSH      | DFeSD      | S–H str       |
| 2648.8(2)  | 1901.8(1)  | S–H str       |
| 1757.7(22) | 1731.6     | Fe–H str      |
| 615.3(14)  | 452.3(10)  | HFeSH def     |
| 401.0(89)  | 287.3(44)  | H–S–Fe bend   |
| 381.3(36)  | 378.2(36)  | Fe–S str      |
| 69.1(159)  | 50.8(87)   | H–Fe–S bend   |
| HFeSH\(_2\) | DFeSD\(_2\) |               |
| 2686.1(7)  | 1927.3(3)  | S–H str       |
| 2671.6(6)  | 1918.4(0)  | S–H str       |
| 2667.9(1)  | 1915.3(2)  | S–H str       |
| 1718.4(347)| 1688.9     | Cr–H str      |
| 1205.0(1)  | 863.2(0)   | SH\(_2\) str   |
| 508.5(3)   | 382.2(27)  | H–S–Fe bend   |
| 437.9(17)  | 353.3(28)  | SH\(_2\) str   |
| 396.3(14)  | 308.3(4)   | SH\(_2\) str   |
| 360.8(42)  | 287.9(14)  | Fe–S str      |
| 302.5(113) | 215.9(42)  | HFeSH def     |
| 223.8(126) | 170.6(21)  | S–Fe–H bend   |
| 164.7(10)  | 149.9(94)  | Fe–S str      |
| 125.0(13)  | 85.4(7)    | HFeSH def     |
| 62.3(1)    | 62.7(4)    | S–Fe–S bend   |
| 32.1(15)   | 38.2(5)    | FeH\(_2\) def |

\(^a\)Calculated intensities (km/mol) are given in parentheses.

![Figure 6. Spectra in selected regions from the reaction of Fe with 0.1% H\(_2\)S + 0.1% HDS + 0.1% D\(_2\)S in the argon matrix: (a) 1 h co-deposition, (b) 25 K annealing, (c) 5 min >400 nm photolysis, (d) 5 min >270 nm photolysis, and (e) 5 min full-arc mercury lamp irradiation.](image)

![Figure 7. Optimized structures of relative species by B3LYP calculations. The bond lengths and angles are in angstroms and degrees, respectively.](image)
and H$_2$S with a binding energy of 31.6 kcal/mol at a Cr–S bond length of 2.35 Å (Figure 9). The formed excited-state MSH$_2$ rearranges to HCrSH spontaneously on the heptet state surface followed by spin-forbidden surface crossing and nonradiative decay to a quintet ground state. As shown in Figure 8, the quintet ground-state HCrSH($^5$A) is 35.3 kcal/mol lower in energy compared with heptet ground-state HCrSH($^7$A'). The transition state linking the reactants and insertion products on the quintet state is 10.2 kcal/mol lower in energy compared with that on the heptet state surface. It suggests that the spin-forbidden surface crossing occurred before the transition state.

Reactions of Mn and Fe with H$_2$S are spin-conserved. As shown in Figure 9, interactions between ground-state Mn and Fe atoms and H$_2$S are totally repulsive. The repulsive interaction hindered the approaching of the two reactants for further reaction. The reaction barriers of 14.0 and 6.2 kcal/mol for the reactions of ground-state Mn:$^6$S(3d$^5$4s$^2$) and Fe:$^5$D-(3d$^6$4s$^1$4p$^1$) with H$_2$S also inhibited the occurrences of the reactions. Absorptions assigned to HMnSH start to increase on >350 nm photolysis. The a$^6$S $\rightarrow$ z$^2$p transition of manganese atoms occurred at 397.4 nm. In our experiments, excited-state Mn:z$^2$p(3d$^4$4s$^4$p$^1$) atoms produced upon >350 nm photolysis become attractive to H$_2$S, leading to the formation of the complex MSH$_2$ on the excited state. The produced hot complex [MSH$_2$]$^*$ can further rearrange to insertion products by surmounting the reaction barrier on the ground-state surface. Experimental and theoretical studies conclude that the formation of a stable complex by the approaching of transition metal atoms to H$_2$S molecules is the vital process for the activation of H$_2$S. H$_2$S can be activated by a metal atom that is attractive to a H$_2$S molecule to produce the stable complex MSH$_2$ for further reaction.
Upon full-arc mercury lamp irradiation, absorptions assigned to HMSH (M = Cr, Mn, and Fe) decreased along with the enhancement of absorptions due to MS. The experimental results indicate that the MS molecules are produced by the elimination of hydrogen from HMSH upon photolysis. As shown in Figure 8, the elimination of hydrogen from HMSH is endothermic. The energy needed for the splitting of hydrogen from HMSH could be supplied by photolysis. In the argon matrix, metal sulfdies and hydrogen are produced by the reaction of M atoms with H₂S upon photolysis, which delivers a possible way to reproduce hydrogen from H₂S with the participation of transition metal atoms.

■ CONCLUSIONS
Matrix isolation infrared spectroscopy and quantum chemical calculations were employed to study the reaction of laser-ablrated M (M = Cr, Mn, and Fe) atoms with hydrogen sulfide in a 5 K argon matrix. Experimental and theoretical results indicate that the activation of H₂S by M atoms takes place upon photolysis. The ground-state Mn and Fe atoms are repulsive to hydrogen sulfide molecules, and ground-state Cr atoms were slightly attractive to H₂S molecules by van der Waals force. The excited-state Cr:ZP(3d⁴4p¹), Mn:yP: (3d⁴4s⁴p¹), and Fe:ZpD(3d⁴4s⁴p¹) atoms produced on photolysis become attractive to H₂S molecules with relatively large binding energies. The activation of H₂S by Cr atoms takes place upon irradiation at longer wavelength compared with Mn and Fe. It suggests that Cr atoms are more suitable for the photochemical activation of H₂S among the three kinds of metal atoms investigated in this work. The formed MSH₂ rearranges to HMSH spontaneously. Upon full-arc mercury lamp irradiation, metal sulfdies were produced by the elimination of hydrogen from HMSH molecules.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03594.
Spectra in selected regions from the reaction of Cr atoms with H₂S (PDF)

■ AUTHOR INFORMATION

Corresponding Author
Xuefeng Wang – School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China; orcid.org/0000-0001-6588-997X; Email: xfwang@tongji.edu.cn

Author
Jie Zhao – School of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550025 Guizhou, China; School of Chemical Science and Engineering, Tongji University, Shanghai 200092, China; orcid.org/0000-0002-8463-5913

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.2c03594

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS
This work is supported by the Science and Technology Fund of Guizhou Province (no. 2020-1Y046).

■ REFERENCES

1. Schreiner, B. Der Claus-Prozess. Reich an Jahren und bedeutender denn je. Chem. unserer Zeit 2008, 42, 378–392.
2. Reddy, S.; Nadgouda, S. G.; Tong, A.; Fan, L. S. Metal sulfide-based process analysis for hydrogen generation from hydrogen sulfide conversion. Int. J. Hydrogen Energy 2019, 44, 21336–21350.
3. Guldal, N. O.; Figen, E. H.; Baykara, S. Z. Peroxideslute catalysts for hydrogen production from hydrogen sulfide. Int. J. Hydrogen Energy 2018, 44, 1038–1046.
4. Kwock, K. M.; Ong, S. W. D.; Chen, L.; Zeng, H. C. Constrained Growth of MoS₂ Nanosheets within a Mesoporous Silica Shell and Its Effects on Defect Sites and Catalyst Stability for H₂S Decomposition. ACS Catal. 2018, 8, 714–724.
5. Wang, Q.; Zhao, J.; Wang, X. Reactions of Ti, Zr, and Hf atoms with hydrogen sulfide: argon matrix infrared spectra and theoretical calculations. J. Phys. Chem. A 2015, 119, 2244–2252.
6. Zhao, J.; Xu, B.; Yu, W. J.; Wang, X. F. Reactions of Group V Metal Atoms with Hydrogen Sulfide: Argon Matrix Infrared Spectra and Theoretical Calculations. Chin. J. Chem. Phys. 2016, 29, 10–20.
7. Wang, X.; Andrews, L.; Thanthirivatte, K. S.; Dixon, D. A. Infrared spectra of H₂ThS and H₂US in noble gas matrices: enhanced H-An-S covalent bonding. Inorg. Chem. 2013, 52, 10275–10285.
8. Zhao, J.; Ji, T.; Xiao, X.; Wang, X.; Beckers, H.; Riedel, S. Charge-Inverted Hydrogen-Bridged Bond in HCA(μ-H): E (E = Si, Ge, and Sn): Matrix Isolation Infrared Spectroscopic and Theoretical Studies. Inorg. Chem. 2020, 59, 14355–14366.
9. Ji, T.; Zhu, B.; Zhao, J.; Yu, W.; Wang, X. Infrared Spectra and Theoretical Calculations of BSe₄ and BSe₆: The Pseudo-Jahn–Teller Effect. J. Phys. Chem. A 2021, 125, 3606–3613.
10. Frisch, M. J. T. G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenhuth, R.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakah, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford CT, 2009.
11. Wang, X.; Andrews, L. Chromium Hydrides and Di Hydrogen Complexes in Solid Neon, Argon, and Hydrogen: Matrix Infrared Spectra and Quantum Chemical Calculations. J. Phys. Chem. A 2003, 107, 570–578.
12. Liang, B.; Andrews, L. Infrared Spectra and Density Functional Theory Calculations of Group 6 Transition Metal Sulfdies in Solid Argon. J. Phys. Chem. A 2002, 106, 6945–6951.
13. Wang, X.; Andrews, L. Matrix Infrared Spectra and Density Functional Theory Calculations of Manganese and Rhenium Hydrides. J. Phys. Chem. A 2003, 107, 4081–4091.
14. DeVore, T. C., SPECTROSCOPY OF TRANSITION METAL SPECIES IN RARE GAS MATRICES: I. VANADIUM METAL. II. SULFIDES. III. CARBONYL COMPLEXES. IV. DINITROGEN COMPLEXES. V. HOMONUCLEAR DIATOMIC COMPOUNDS. 1975: Iowa State University.
15. Cherthı̈n, G. V.; Andrews, L. Infrared Spectra of FeH, FeH₂, and FeH₃ in Solid Argon. J. Phys. Chem. 1995, 99, 12131–12134.
16. Liang, B.; Wang, X.; Andrews, L. Infrared Spectra and Density Functional Theory Calculations of Group 8 Transition Metal Sulfdie Molecules. J. Phys. Chem. A 2009, 113, 5375–5384.
17. Kaufman, J. W.; Hauge, R. H.; Margrave, J. L. Studies of reactions of atomic and diatomic chromium, manganese, iron, cobalt, nickel, copper, and zinc with molecular water at 15 K. J. Phys. Chem. 1985, 89, 3541–3547.
(18) Wang, X.; Andrews, L. Silylidyne, HSi≡MoH$_3$ and HSi≡WH$_3$, and Silyl Metal Hydride, SiH$_3$-CrH, Products in Silane Reactions. *J. Am. Chem. Soc.* **2008**, *130*, 6766–6773.

(19) Wang, X.; Andrews, L. Infrared Spectra, Structure, and Bonding of the GeH$_3$—CrH, HGe≡MoH$_3$, and HGe≡WH$_3$ Molecules in Solid Neon and Argon. *Inorg. Chem.* **2008**, *47*, 8159–8166.

(20) Zhou, M.; Zhang, L.; Shao, L.; Wang, W.; Fan, K.; Qin, Q. Reactions of Mn with H$_2$O and MnO with H$_2$. Matrix-Isolation FTIR and Quantum Chemical Studies. *J. Phys. Chem. A* **2001**, *105*, 5801–5807.

(21) Pellin, M. J.; Gruen, D. M.; Fisher, T.; Foosnaes, T. Emission, optical–optical double resonance, and excited state absorption spectroscopy of matrix isolated chromium and molybdenum atoms. *J. Chem. Phys.* **1983**, *79*, 5871–5886.

(22) Zhao, J.; Wang, Q.; Yu, W.; Huang, T.; Wang, X. M–S Multiple Bond in HMSH, H$_2$MS, and HMS Molecules (M = B, Al, Ga): Matrix Infrared Spectra and Theoretical Calculations. *J. Phys. Chem. A* **2018**, *122*, 8626–8635.

(23) Mann, D. M.; Broida, H. P. Ultraviolet Absorption Spectra of Transition Metal Atoms in Rare-Gas Matrices. *J. Chem. Phys.* **1971**, *55*, 84–94.

(24) Pan, Z.; Liu, X.; Zhao, J.; Wang, X. Infrared spectra of HMSH and HMMSH (M=Zn, Cd, Hg) in solid argon. *J. Mol. Spectrosc.* **2015**, *310*, 16–22.