4-30-2019

Coinage Metal–Sulfur Complexes: Stability on Metal(111) Surfaces and in the Gas Phase

Jiyoung Lee  
*Iowa State University and Ames Laboratory*

Theresa L. Windus  
*Iowa State University*, twindus@iastate.edu

Patricia A. Thiel  
*Iowa State University and Ames Laboratory*, pthiel@ameslab.gov

James W. Evans  
*Iowa State University and Ames Laboratory*, jevans@ameslab.gov

Da-Jiang Liu  
*Ames Laboratory*, dajiang@ameslab.gov

Follow this and additional works at: https://lib.dr.iastate.edu/chem_pubs

Part of the Condensed Matter Physics Commons, Metallurgy Commons, and the Physical Chemistry Commons

The complete bibliographic information for this item can be found at https://lib.dr.iastate.edu/chem_pubs/1126. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Coinage Metal–Sulfur Complexes: Stability on Metal(111) Surfaces and in the Gas Phase

Abstract
We provide a comprehensive theoretical assessment at the level of density functional theory (DFT) of the stability of various coinage metal–sulfur complexes, both in the gas phase and also for the complexes adsorbed on the (111) surface of the same coinage metal. Our primary interest lies in the latter where earlier scanning tunneling microscopy (STM) experiments were interpreted to suggest the existence of adsorbed S-decorated metal trimers, sometimes as a component of more complex adlayer structures. Recent STM studies at 5 K directly observed other isolated adsorbed metal–sulfur complexes. For these adsorbed species, we calculate various aspects of their energetics including a natural measure of stability corresponding to their formation energy from sulfur adsorbed on terraces and from metal atoms that are in thermal equilibrium with the substrate. From this perspective, our DFT analysis shows that all of Ag2S3, Ag3S3, and many larger complexes on Ag(111) are strongly stable, Cu2S3 is stable, and some larger complexes are marginally stable on Cu(111), but only Au4S4 on Au(111) is stable. Results are consistent with STM observations for Cu(111) and Ag(111) surfaces but appear to deviate slightly for Au(111). A systematic analysis relating stability in the gas phase with that of adsorbed species is achieved within the framework of Hess's law. This analysis also unambiguously elucidates various energetic contributions to stability.

Disciplines
Condensed Matter Physics | Metallurgy | Physical Chemistry

Comments
This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in Journal of Physical Chemistry C, copyright © American Chemical Society after peer review. To access the final edited and published work see DOI: 10.1021/acs.jpcc.9b03770. Posted with permission.
Coinage Metal-Sulfur Complexes: Stability on Metal(111) Surfaces and in the Gas Phase

Jiyoung Lee,†‡ Theresa L. Windus,†‡ Patricia A. Thiel,†‡¶ James W. Evans,†§ and Da-Jiang Liu*,†

†Ames Laboratory – USDOE, Iowa State University, Ames, Iowa 50011
‡Department of Chemistry, Iowa State University, Ames, Iowa 50011
¶Department of Materials Science & Engineering, Iowa State University, Ames, Iowa 50011
§Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

E-mail: dajiang@ameslab.gov

Abstract

We provide a comprehensive theoretical assessment at the level of Density Functional Theory (DFT) of the stability of various coinage metal-sulfur complexes, both in the gas-phase and also for these complexes adsorbed on the (111) surface of the same coinage metal. Our primary interest is in the latter where earlier STM experiments were interpreted to suggest the existence of adsorbed S-decorated metal trimers, sometimes as a component of more complex adlayer structures. Recent STM studies at 5 K directly observed other isolated adsorbed metal-sulfur complexes. For these adsorbed species, we calculate various aspects of their energetics including a natural measure of stability corresponding to their formation energy from sulfur adsorbed on terraces and from metal atoms that are in thermal equilibrium with the substrate. From this perspective, our DFT analysis shows that all of Ag₂S₃, Ag₃S₃, and many larger complexes on Ag(111) are strongly stable, Cu₂S₃ is stable and some larger complexes are marginally stable on Cu(111), but only Au₄S₄ on Au(111) is stable. Results are consistent
with STM observations for Cu(111) and Ag(111) surfaces, but appear to deviate slightly for
Au(111). A systematic analysis relating stability in the gas-phase with that of adsorbed species
is achieved within the framework of Hess’s law. This analysis also unambiguously elucidates
various energetic contributions to stability.

1 Introduction

Over the last decade, there have been several observations from Scanning Tunneling Microscopy
(STM) analysis of small stable metal (M)-chalcogenide complexes, and in particular M-S com-
plexes, adsorbed on hexagonal close-packed (111) surfaces of the same or different metals. Per-
haps the most definitive observation is from STM at 5 K of heart-shaped Cu$_2$S$_3$ complexes on
Cu(111).$^1$ In addition, adlayer clusters formed after exposure of Ni(111) to H$_2$S were proposed
to be composed of Ni$_3$S$_3$ complexes,$^2$ and massive S-induced transformation of nm-sized Co-
nanoparticles on Au(111) was found to be mediated exclusively by the formation and detachment
of Co$_3$S$_4$ complexes.$^3$ More speculative STM studies suggested the presence of Au$_3$S$_3$ complexes
after adsorption of S on Au(111) at liquid nitrogen temperatures,$^4$ and of Cu$_3$S$_3$ complexes as a
component of intricate adlayer structures near step edges on Cu(111) observed down to 50 K.$^5$
However, the latter interpretation was not supported by more recent studies at 5 K.$^6$ In some
cases, significantly larger complexes were also observed at 5 K with a linear “polymeric” struc-
ture: Ag$_{16}$S$_{13}$ and Ag$_{13n+3}$S$_{9n+4}$ for $n > 1$ on Ag(111);$^7$ and Cu$_n$S$_{n+1}$ for $n > 2$ on Cu(111).$^6$
Beyond the observed structures, other small complexes have been suggested to occur as stable ab-
sorbed moieties: $MS_2$, $MS_3$, $M_3S_3$, etc. on M(111) for coinage metals $M = Cu$ and Ag.$^{1,8,9}$ The
smaller complexes have been implicated as carriers in dramatically enhanced metal mass transport
observed on some surfaces, e.g., in the form of accelerated decay of smaller 2D metal nanoclus-
ters.$^{1,8-11}$ Such enhancement can occur in the presence of even trace amounts of chalcogen.

Still considering metal (M)-chalcogen systems, we note that M-O complexes have long been
speculated to play a role in the degradation through coarsening of supported catalyst nanoparticles,
particularly PtO$_2$ for supported Pt nanoparticles.$^{12-14}$ Degradation might occur via transport either
across the surface or through the gas phase. Also, Ag-O complexes have been suggested to play a role in surface mass transport on Ag(100) surfaces.\textsuperscript{11,15} With regard to other classes of systems, $M$-hydrogen,\textsuperscript{16,17} $M$-halide,\textsuperscript{18–20} and $M$-CO\textsuperscript{21–23} complexes have all been considered. In fact, long ago it was proposed that formation of mobile adsorbate-metal complexes might occur whenever electronegative adsorbates interact with “soft” metals.\textsuperscript{19} Also of relevance is that various $M$-halide and $M$-chalcogenide molecules in the gas phase are found to be end products of dry etching processes.\textsuperscript{24} Finally, we mention that $X$-$\text{Au}$-$X$ complexes with $X = \text{alkylthiolate}$ have been proposed to play a role in molecular self-assembly on Au surfaces. These have been observed directly in the case of $X = \text{CH}_3\text{S}$\textsuperscript{25} for which stability has been confirmed by DFT analysis.\textsuperscript{18}

However, what has been lacking is a comprehensive theoretical exploration of the stability of these various adsorbed complexes. This exploration might naturally compare at least trends in stability for adsorbed complexes with those in the gas phase. In fact, the latter comparison can be made systematic within a Hess’s law framework. We pursue this goal here for $M$-$\text{S}$ complexes on the low-index $M$(111) surface of the same coinage metal for $M = \text{Cu}$, Ag, or Au. We have previously studied $M_3\text{S}_3$ complexes, and assess whether it is reasonable to assign experimentally observed features on the metal surface exposed to sulfur to this particular complex.\textsuperscript{26} In this work, we greatly expand consideration to a set of nine distinct complexes for each of three different coinage metals. Comparison with previous analysis is made.

The contents of the paper is as follows. The methodology for our Density Functional Theory (DFT) based analysis is described in Sec. 2. Although our primary interest and focus is on adsorbed complexes, results for calculations of gas-phase stability are first presented in Sec. 3, as these will be utilized in subsequent analysis. Next, results for adsorbed $M$-$\text{S}$ complexes are presented in Sec. 4. Section 5 relates the stabilities of adsorbed complexes with the gas-phase energetics within the framework of Hess’s law, as mentioned above. Concluding remarks are given in Sec. 6.
2 Methodology

DFT calculations are generally carried out using two different types of basis sets. For extended and periodic systems, it is most natural to use a plane-wave (PW) basis set. For such analyses, in this paper, we use the VASP package (v5.4)\(^{27,28}\) and the standard PAW potentials\(^{29,30}\) that are included in the package. The PBE\(^{31}\) functional is used for slab calculations probing the energetics of adsorbed complexes. In these calculations, the surface is represented by a periodic array of slabs, separated by 1.2 nm of vacuum. Lattice constants for the fcc metal substrates are taken as theoretical values obtained with the energy cutoff 280 eV for the PBE functional. S and \(M-S\) complexes are adsorbed on top of each slab (rather than on both sides). The total energy of the system is then minimized allowing both the adsorbate and metal substrate or slab atoms to relax, except for the bottom layer of the slab. The convergence criterion requires that all forces are below 0.02 eV/Å. All surface energetics are obtained from averages over 4 to 7 layer slabs which has the effect of minimizing quantum size effects associated with electron confinement in thin slabs. Most calculations involving adsorbed complexes are carried out with \((4 \times 4)\) lateral supercells.

For analysis of gas-phase energetics, we also somewhat unconventionally calculate energetics using the same PW basis set which allows consistent comparison with the analysis of adsorbed complexes. Gas-phase complexes are simulated using 3D orthogonal periodic cells. In addition to the PBE functional used extensively for surface calculations, the hybrid PBE0\(^{32}\) meta-GGA SCAN,\(^{33}\) and optB88-vdW\(^{34,35}\) functionals are used for the gas phase analyses. These PW results are compared with the local basis calculations described below, thereby facilitating the validation of both approaches.

Since the PW DFT calculations involve different bulk, surface, and gas phases, different choices of smearing of the electron occupancy are needed. For bulk, we use the tetrahedron method with Blöchl corrections.\(^{36}\) For gas phase forms of individual atoms, diatomic \(S_2\), and complexes, Gaussian smearing of width 0.002 eV is used. For surface calculations, the first-order Methfessel-Paxton smearing of width 0.2 eV is used. Non-spin polarized DFT is used for bulk and slab calculations, and spin polarized DFT is used for atoms and complexes in the gas phase. For each supercell,
we use a $k$-point mesh that is closest to the equivalent of $(24 \times 24 \times 1)$ for the unit surface cell. Selected calculations with spin-polarized DFT adsorbed complexes show that the ground state of Cu, Ag, and Au slabs with adsorbed S or metal-sulfur complexes have no magnetic moment.

For gas-phase atoms and complexes, atomic or Gaussian-type orbitals (GTO) constitute more natural basis sets. Thus, DFT calculations with GTO basis sets are performed with the NWChem software. All structures are optimized to minimize energy with PBE$^{31}$ and PBE0$^{32}$ functionals using three different basis sets. For the smallest basis set, we use Los Alamos National Laboratory double zeta (LANL2DZ) with effective core potentials (ECPs)$^{38-40}$ for metals and 6-311++G(d,p)$^{41-43}$ for S. It is denoted by DZ/TZ. For two larger basis sets, we use def2-NZVP for metals$^{44,45}$ (small ECP is used for heavier atoms, Ag and Au) and def2-NZVPPD for S$^{46}$ (N=T, Q). They are denoted by TZ/TZ and QZ/QZ, respectively. Spherical functions are used for N=Q to eliminate linear dependence problems. To find minimum energy states, initial $M_nS_m$ complexes are optimized at different possible spin multiplicities using DZ/TZ basis sets. For instance, if the number of metals is even (odd), multiplicities such as doublet, quartet, sextet, etc. (singlet, triplet, quintet, etc.) are explored and the spin state with the lowest energy is chosen. Some of our analysis will require energies, $E[M_m\text{ (gas)}]$, for metal clusters in the gas phase, for which we use a similar approach. For the S atom, the triplet state is used. After the spin states are determined, complexes are optimized with the smallest basis sets DZ/TZ first and reoptimized later with larger basis sets. Restricted open-shell DFT (RODFT) is used for open-shell systems with the number of radial grid points and angular points in the Lebedev grid being chosen as 99 and 590, respectively.

3 Energetics of Gas-Phase Complexes

The list of metal-sulfur complexes considered here is motivated by their existence (either proposed or confirmed) on (111) surfaces, and also by their anticipated stability in the gas phase. However, we exclude those configurations that include S-S bonds since we are mostly concerned with low S coverages for surface systems where it is generally more energetically favorable for disulfur to
dissociate and to bond with metal atoms. Figure 1 shows the nine types of $M_mS_n$ complexes, $MS$, $MS_2$, $M_2S_2$, $MS_3$, $M_2S_3$, $M_3S_3$, $M_3S_4$, $M_4S_4$, and $M_4S_5$, which we analyze. Geometries shown are optimized using the PBE functional and the VASP code.

$$E_a(M_mS_n)(\text{gas}) = mE[M(\text{gas})] + nE[S(\text{gas})] - E[M_mS_n(\text{gas})],$$

where $E[X(\text{gas})]$ denotes the energy of species $X$ in the gas phase. Table 1 lists $E_a(\text{gas})$ for these gas-phase complexes from PW DFT calculations. These results show that for complexes with more than one metal atom ($m > 1$), the atomization energy is the lowest for Ag and higher for Au and Cu. This correlates with the bulk cohesive energies, $E_c^M$, of the metals (theoretical values for which are reported below). The atomization energy also generally increases as the size of the complex increases, the main exception being that $M_4S_4$ (rather than $M_4S_5$) has the largest atomization energy amongst all configurations.
Table 1 also lists the atomization energies using the hybrid PBE0, meta-GGA SCAN,\textsuperscript{33} and optB88-vdW functionals. The PBE0 atomization energies are consistently lower than the corresponding PBE values. This trend has been found before, e.g., for the G2-1 test set,\textsuperscript{47,48} and inclusion of coinage metals here conforms with this trend. On the other hand, the differences between PBE and SCAN values are rather small, with SCAN values being slightly smaller, but with some exceptions. Also note that the trigonal AuS\textsubscript{3} configuration is not (locally) stable for either PBE0 or SCAN functionals. Results using optB88-vdW are almost identical to those from PBE, indicating that dispersion interactions are not significant for these gas-phase complexes.

The atomization energies for diatomic MS can be compared with available experimental values: 2.80 eV for CuS, 2.21 eV for AgS, and 2.59 eV for AuS.\textsuperscript{49} All functionals reproduce the experimental sequence of Cu > Au > Ag, with PBE0 closest to experimental values. However, one should not assess validity of a functional based solely on its prediction for the energy of a diatomic bond.

Table 1: The atomization energy $E_a$(gas) (in eV) of the gas-phase $M_mS_n$ complex, obtained using the VASP code. Missing values correspond to unstable complexes.

<table>
<thead>
<tr>
<th></th>
<th>$M_S$</th>
<th>$M_S^2$</th>
<th>$M_S^2S_2$</th>
<th>$M_S^3$</th>
<th>$M_S^2S_3$</th>
<th>$M_S^3S_3$</th>
<th>$M_S^3S_4$</th>
<th>$M_S^4S_4$</th>
<th>$M_S^4S_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>Cu 3.23</td>
<td>5.82</td>
<td>10.02</td>
<td>7.75</td>
<td>11.87</td>
<td>16.63</td>
<td>17.34</td>
<td>23.06</td>
<td>22.41</td>
</tr>
<tr>
<td></td>
<td>Ag 2.46</td>
<td>4.52</td>
<td>7.44</td>
<td>5.79</td>
<td>9.06</td>
<td>12.69</td>
<td>13.32</td>
<td>17.49</td>
<td>17.34</td>
</tr>
<tr>
<td></td>
<td>Au 2.94</td>
<td>5.92</td>
<td>8.49</td>
<td>7.51</td>
<td>11.51</td>
<td>14.92</td>
<td>16.41</td>
<td>21.60</td>
<td>20.87</td>
</tr>
<tr>
<td>PBE0</td>
<td>Cu 2.92</td>
<td>5.18</td>
<td>8.99</td>
<td>6.17</td>
<td>10.52</td>
<td>15.04</td>
<td>15.47</td>
<td>20.47</td>
<td>20.06</td>
</tr>
<tr>
<td></td>
<td>Ag 2.29</td>
<td>3.87</td>
<td>6.70</td>
<td>4.25</td>
<td>8.00</td>
<td>11.82</td>
<td>11.57</td>
<td>16.46</td>
<td>15.87</td>
</tr>
<tr>
<td></td>
<td>Au 2.62</td>
<td>5.18</td>
<td>7.68</td>
<td>10.08</td>
<td>13.56</td>
<td>14.41</td>
<td>19.48</td>
<td>18.71</td>
<td></td>
</tr>
<tr>
<td>SCAN</td>
<td>Cu 3.16</td>
<td>5.34</td>
<td>9.95</td>
<td>7.54</td>
<td>11.80</td>
<td>16.77</td>
<td>17.43</td>
<td>23.41</td>
<td>22.74</td>
</tr>
<tr>
<td></td>
<td>Ag 2.34</td>
<td>4.40</td>
<td>7.16</td>
<td>5.39</td>
<td>8.66</td>
<td>12.75</td>
<td>13.19</td>
<td>17.65</td>
<td>17.27</td>
</tr>
<tr>
<td></td>
<td>Au 3.05</td>
<td>6.01</td>
<td>8.67</td>
<td>12.07</td>
<td>15.84</td>
<td>17.28</td>
<td>22.96</td>
<td>22.26</td>
<td></td>
</tr>
<tr>
<td>optB88-vdW</td>
<td>Cu 3.20</td>
<td>5.82</td>
<td>9.88</td>
<td>7.72</td>
<td>11.72</td>
<td>16.46</td>
<td>17.20</td>
<td>22.80</td>
<td>22.33</td>
</tr>
<tr>
<td></td>
<td>Ag 2.47</td>
<td>4.52</td>
<td>7.52</td>
<td>5.91</td>
<td>9.10</td>
<td>12.79</td>
<td>13.44</td>
<td>17.76</td>
<td>17.62</td>
</tr>
<tr>
<td></td>
<td>Au 2.95</td>
<td>5.95</td>
<td>8.56</td>
<td>7.60</td>
<td>11.52</td>
<td>15.04</td>
<td>16.54</td>
<td>21.75</td>
<td>21.08</td>
</tr>
</tbody>
</table>

We also calculate the atomization energies for a subset of the above large set of gas-phase com-
plexes using atomic or GTO basis sets. This subset is selected to include all smaller complexes which likely exist on surfaces. Results with three different basis sets (as described in detail in Sec. 2), and with the PBE and PBE0 functionals, are listed in Table 2. The values using double-

zeta basis sets for metals (DZ/TZ) are significantly lower than the two larger basis sets (TZ/TZ and QZ/QZ). With the PBE functional, results using the largest basis set (QZ/QZ) are in excellent agreement with PW-DFT results listed in Table 1. The agreement between PW-DFT and the GTO-DFT is slightly less satisfactory for the PBE0 functional. However, the trend that PBE0 atomization energies are lower than the PBE atomization energies occurs in both GTO and PW sets of calculations.

Next, we comment on the stability of gas-phase complexes based upon the above atomization energies. Since all these energies are positive, the complexes are stable against complete fragmentation into atomic constituents. However, since \( E_a(\text{gas}) \) is always lower for \( M_4S_5 \) than for \( M_4S_4 \), this means that the former is thermodynamically unstable against detachment of an S. In contrast, we note that \( M_4S_5 \) is stable against fragmentation into \( M_2S_2 \) and \( M_2S_3 \), and also usually against fragmentation into \( MS_2 \) and \( M_3S_3 \) (so that instead detachment of an S from \( M_4S_5 \) is always favored). Comparing relevant energies, we also find that: \( M_4S_4 \) is stable against fragmentation into two \( M_2S_2 \), or into \( MS \) and \( M_3S_3 \); \( M_3S_4 \) is stable against detachment of an S (discounting PBE0 Ag results) and against fragmentation into \( MS \) and \( M_2S_3 \), or into \( MS_2 \) and \( M_3S_2 \); \( M_2S_3 \) is stable against fragmentation into \( MS \) and \( MS_2 \). So generally, complexes are stable (except \( M_4S_5 \)). A complete accounting of energy changes for the various fragmentation process described above is provided in the Supporting Information.

For completeness, we note that it is also common to calculate the formation energy, \( E_f(M_mS_n)(\text{gas}) \) of gas-phase complexes from gas phase \( S_2 \) and bulk metal. This quantity is defined as

\[
E_f(M_mS_n)(\text{gas}) = E[M_mS_n(\text{gas})] - mE[M(\text{bulk})] - \frac{n}{2}E[S_2(\text{gas})].
\]

Here, \( E[M(\text{bulk})] \) is the energy per metal atom in the bulk phase, and \( E[S_2(\text{gas})] \) the energy of
Table 2: The atomization energy $E_a$(gas) (in eV) of the gas-phase $M_mS_n$ complex, obtained using the NWChem code with three different basis sets. Results from plane wave VASP analysis (PW) are also included for convenient comparison.

<table>
<thead>
<tr>
<th></th>
<th>$MS_2$</th>
<th>$MS_3$</th>
<th>$M_2S_3$</th>
<th>$M_3S_4$</th>
<th>$M_4S_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>5.12</td>
<td>6.97</td>
<td>10.85</td>
<td>15.38</td>
<td>16.10</td>
</tr>
<tr>
<td></td>
<td>5.73</td>
<td>7.65</td>
<td>11.65</td>
<td>16.38</td>
<td>17.02</td>
</tr>
<tr>
<td></td>
<td>5.78</td>
<td>7.70</td>
<td>11.71</td>
<td>16.46</td>
<td>17.10</td>
</tr>
<tr>
<td></td>
<td>5.82</td>
<td>7.75</td>
<td>11.87</td>
<td>16.63</td>
<td>17.34</td>
</tr>
<tr>
<td>PBE0</td>
<td>4.55</td>
<td>5.51</td>
<td>9.28</td>
<td>13.39</td>
<td>13.97</td>
</tr>
<tr>
<td></td>
<td>4.95</td>
<td>6.15</td>
<td>10.01</td>
<td>14.31</td>
<td>14.81</td>
</tr>
<tr>
<td></td>
<td>4.98</td>
<td>6.20</td>
<td>10.08</td>
<td>14.41</td>
<td>14.88</td>
</tr>
<tr>
<td></td>
<td>5.18</td>
<td>6.17</td>
<td>10.52</td>
<td>15.04</td>
<td>15.47</td>
</tr>
<tr>
<td><strong>Ag</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>4.11</td>
<td>5.22</td>
<td>8.26</td>
<td>11.66</td>
<td>12.25</td>
</tr>
<tr>
<td></td>
<td>4.57</td>
<td>5.90</td>
<td>9.19</td>
<td>12.84</td>
<td>13.49</td>
</tr>
<tr>
<td></td>
<td>4.55</td>
<td>5.96</td>
<td>9.27</td>
<td>12.96</td>
<td>13.60</td>
</tr>
<tr>
<td></td>
<td>4.52</td>
<td>5.79</td>
<td>9.06</td>
<td>12.69</td>
<td>13.32</td>
</tr>
<tr>
<td>PBE0</td>
<td>3.47</td>
<td>3.93</td>
<td>7.10</td>
<td>10.49</td>
<td>10.68</td>
</tr>
<tr>
<td></td>
<td>3.91</td>
<td>4.56</td>
<td>7.92</td>
<td>11.51</td>
<td>11.83</td>
</tr>
<tr>
<td></td>
<td>3.96</td>
<td>4.66</td>
<td>8.01</td>
<td>11.63</td>
<td>11.95</td>
</tr>
<tr>
<td></td>
<td>3.87</td>
<td>4.25</td>
<td>8.00</td>
<td>11.82</td>
<td>11.57</td>
</tr>
<tr>
<td><strong>Au</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBE</td>
<td>5.19</td>
<td>6.40</td>
<td>10.13</td>
<td>13.49</td>
<td>14.53</td>
</tr>
<tr>
<td></td>
<td>5.88</td>
<td>7.47</td>
<td>11.33</td>
<td>14.77</td>
<td>16.14</td>
</tr>
<tr>
<td></td>
<td>5.96</td>
<td>7.57</td>
<td>11.48</td>
<td>14.95</td>
<td>16.35</td>
</tr>
<tr>
<td></td>
<td>5.92</td>
<td>7.51</td>
<td>11.51</td>
<td>14.92</td>
<td>16.41</td>
</tr>
<tr>
<td>PBE0</td>
<td>4.41</td>
<td>4.56</td>
<td>8.86</td>
<td>12.02</td>
<td>13.02</td>
</tr>
<tr>
<td></td>
<td>4.94</td>
<td>5.76</td>
<td>9.91</td>
<td>13.36</td>
<td>14.41</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>5.88</td>
<td>10.04</td>
<td>13.55</td>
<td>14.58</td>
</tr>
<tr>
<td></td>
<td>5.18</td>
<td>10.08</td>
<td>13.56</td>
<td>14.41</td>
<td>18.71</td>
</tr>
</tbody>
</table>
the $S_2$ molecule in the gas-phase. Note that here we use $S_2$ (disulfur) gas as the reference state, even though under standard conditions the most stable phase of sulfur is solid. This definition is partly motivated by the observation that the source of elemental sulfur is predominantly $S_2$(gas) generated by an electrochemical cell used in many of the experiments.\textsuperscript{50} The choice is also partly due to the fact the solid phase of sulfur is particularly complicated, e.g., the orthorhombic $\alpha$ phase has 128 atoms in a single unit cell, such that it poses a significant challenge for computation. That said, it may be more desirable to use a theoretical gas-phase $S_8$ (cyclo-octasulfur) for the reference energy, since it is the dominant molecular species for solid sulfur\textsuperscript{51} with more S-S bonds than $S_2$(gas). A comprehensive set of values for $E_f$(gas) with $S_8$ as the reference are reported in the Supporting Information. However, these can also be readily obtained by modifying results based upon Eq. (2) using $S_2$ as a reference. If one sets $\delta E = E[S_2$(gas$)]/2 – E[S_8$(gas$)]/8 = 0.53$ eV (PBE), 0.51 eV (PBE0), 0.48 eV (SCAN), and 0.56 eV (optB88-vdW), then formation energies with the $S_8$ reference are just $n \times \delta E$ above those with the $S_2$ reference.

Table 3 lists $E_f$(gas) values for various gas-phase complexes using different functionals. Note that for the PBE0 functional, we use a screened version (HSE06)\textsuperscript{52} to calculate the bulk cohesive energies. The hybrid PBE0 functional generally predicts smaller formation energies than PBE, with the notable exception of $MS_3$ complexes. In contrast, the meta-GGA SCAN and the optB88-vdW functionals generally predict larger formation energies than PBE. This is mostly due to the larger cohesive energy $E_c^M = E[M$(gas$)] – E[M$(bulk$)]$ for metals predicted by the latter two functionals, especially for Au.

Although positive values of the gas-phase formation energy do not imply stability in the context of the formation process considered here (i.e., gas phase complexes are always unstable against incorporation of metal atoms into the bulk and of the S atoms into $S_2$), lower positive values might be taken as an indicator of stability in other contexts. In this respect, we find that $Cu_3S_3$, $Cu_4S_4$, and $Au_4S_4$ have a particularly strong propensity for stability, with $E_f$(gas) less than 1 eV at least with some functionals. The $MS_2$ and $M_2S_3$ complexes, which have been argued to exist at least on Cu surfaces, do not stand out as particularly stable in this analysis.
Table 3: The formation energy $E_f$(gas) (in eV) of the gas-phase $M_mS_n$ complex, using the VASP code. Note that for $M$, $E_f$(gas) is the same as the cohesive energy of the metal. Missing values correspond to unstable complexes.

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>PBE0</th>
<th>SCAN</th>
<th>optB88-vdW</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>$MS$</td>
<td>$MS_2$</td>
<td>$M_2S_2$</td>
<td>$MS_3$</td>
</tr>
<tr>
<td>Cu</td>
<td>3.47</td>
<td>2.73</td>
<td>2.63</td>
<td>1.91</td>
</tr>
<tr>
<td>Ag</td>
<td>2.52</td>
<td>2.55</td>
<td>2.99</td>
<td>2.59</td>
</tr>
<tr>
<td>Au</td>
<td>3.04</td>
<td>2.59</td>
<td>2.10</td>
<td>2.58</td>
</tr>
<tr>
<td>Cu</td>
<td>2.83</td>
<td>2.25</td>
<td>2.32</td>
<td>1.36</td>
</tr>
<tr>
<td>Ag</td>
<td>2.15</td>
<td>2.20</td>
<td>2.93</td>
<td>2.27</td>
</tr>
<tr>
<td>Au</td>
<td>2.68</td>
<td>2.39</td>
<td>2.17</td>
<td>2.35</td>
</tr>
<tr>
<td>Cu</td>
<td>3.88</td>
<td>3.02</td>
<td>3.13</td>
<td>2.40</td>
</tr>
<tr>
<td>Ag</td>
<td>2.90</td>
<td>2.84</td>
<td>3.08</td>
<td>3.21</td>
</tr>
<tr>
<td>Au</td>
<td>3.56</td>
<td>2.81</td>
<td>2.13</td>
<td>3.04</td>
</tr>
<tr>
<td>Cu</td>
<td>3.53</td>
<td>2.80</td>
<td>2.66</td>
<td>2.13</td>
</tr>
<tr>
<td>Ag</td>
<td>2.81</td>
<td>2.82</td>
<td>3.24</td>
<td>3.06</td>
</tr>
<tr>
<td>Au</td>
<td>3.41</td>
<td>2.93</td>
<td>2.41</td>
<td>3.20</td>
</tr>
</tbody>
</table>

3.2 Further analysis of energetics and geometries

To gain more insight into the interactions within the complexes, we also decompose the total interaction energy of the complex into metal-S and metal-metal components, where we focus on the former. Here, we do not explicitly account for any direct sulfur-sulfur interactions as these should be weak, but these are implicitly incorporated into what we identify as M-S interactions. To this end, we define the metal-S binding energy per sulfur atom $E^{\text{MS}}_b$(gas) as

$$E^{\text{MS}}_b(\text{gas}) = -\left\{ E[M_mS_n(\text{gas})] - E[M_m(\text{gas})] - nE[S(\text{gas})] \right\} / n$$

(3)

where $M_m$(gas) is the gas phase metal cluster obtained by removing all S atoms from the complex. The energy of this metal cluster could be evaluated either with metal atoms frozen in their positions within the equilibrated gas-phase $M_mS_n$ complex (the so-called frozen metal core approach$^{53}$), or with the metal cluster equilibrated. Given $E_a(M_mS_n)(\text{gas})$ and $E^{\text{MS}}_b$(gas), the $M-M$ interaction per $M$ atom within the complex follows from $E^{\text{MS}}_b$(gas) via $E^{\text{MM}}_b(\text{gas}) = E[M(\text{gas})] - E[M_m(\text{gas})] / m =$
\[ \left[ E_a(M_mS_n)_{\text{gas}} - nE_{MS}^{\text{gas}} \right]/m. \]

Results are presented in the Supporting Information for \( E_{b}^{MS} \) (gas) for selected complexes for the frozen core approach, although the basic trends should also be retained for an equilibrated metal cluster. The key observations are: (1) \( E_{b}^{MS} \) (gas) is systematically larger (for all metals) for higher numbers of \( M \) per S (i.e., for higher \( m/n \)); (2) \( E_{b}^{MS} \) (gas) for \( m = n \) increases as \( n \) increases; (3) \( E_{b}^{MS} \) (gas) is typically the largest for Cu, intermediate for Au, and smallest for Ag.

Finally, we comment in more detail on the special case of gas-phase \( MS_2 \) complexes, noting that this motif appears to be a common component of stable complexes observed on surfaces. We consider geometry as well as energetics. Figure 2 shows the energy variation for a bent S-M-S complex as a function of angle \( \alpha = \angle SMS \). For all \( M \), the energy initially increases as the angle \( \alpha \) deviates from 180° (i.e., as the complex deviates from linear), with Au having the largest energy penalty for bending. Thus, the complex incurs an energy penalty upon bending with S-Au-S being stiffer than S-Cu-S and S-Ag-S. For Cu and Ag, as the angle decreases from 180° to around 120°, the energy starts to drop, and eventually the bent S-M-S complex becomes even more stable than the linear form due to the development of strong S-S bonding. For \( M = \text{Au} \), however, this decrease is significantly delayed. As an aside, we remark that while the strongly bent complex has the minimum energy in the gas phase, interaction with the substrate for adsorbed complexes ensures the linear configuration is the energy minimum.

The propensity for atomic Au to form linear metal-ligand complex has generally been explained by \( s-d \) hybridization,\(^{54,55}\) while that for atomic Cu has been explained by \( p-d \) hybridization.\(^1\) This feature is particular to the late transition metals, with filled \( d \) shells, while earlier transition metals generally do not possess the propensity for forming the linear S-M-S complexes.\(^ {55} \) From a different perspective, it has long been recognized that chalcogenides of Cu, Ag, and Au generally adopt structures with low metal coordination numbers. This is exemplified by the Cu\(_2\)O cuprite (Pn\( \bar{3} \)m) structure\(^ {56} \) where Cu atoms are linearly coordinated with two oxygen atoms. In contrast, Na\(_2\)O (antiflurite, Fm\( \bar{3} \)m) has Na atoms tetrahedrally coordinated with four O atoms.\(^ {57} \)
Figure 2: Energy of a bent S-M-S complex in the gas phase as a function of angle $\alpha = \angle SMS$, where $\alpha = 180^\circ$ for a linear complex. All results are in the same state ($A_2$) with $C_{2v}$ symmetry and doublet spin multiplicity, using the PBE functional, DZ/TZ basis sets and the NWChem code.

4 Energetics of adsorbed complexes

In this section, we explore the energetics of various $M_mS_n$ complexes adsorbed on $M$(111) surfaces. Calculations are performed with a $(4 \times 4)$ supercell which is large enough so that complexes are well separated and do not form direct interconnections. However, for $M = Au$, analysis with this supercell size does not incorporate the herringbone reconstruction of extended Au(111) surfaces. This is not regarded as a shortcoming since generally exposure of the clean Au(111) surface to S, with possible subsequent formation of complexes, lifts this reconstruction. In general, it is expected that there can be a number of locally stable (or metastable) configurations for adsorbed complexes. While an exhaustive search of the most stable adsorbed structure is complicated, especially for larger $m$ and $n$, we have reasonable confidence that the lowest energy configurations have been identified.
Figure 3 shows the top views of various $M$-S complexes determined to be the most stable configuration using DFT-PBE. No stable $Au_2S_2$ and $AuS_3$ complexes are found on the $Au(111)$ surface. However, for completeness, we have included dissociated adsorbed structures which result from energy minimization starting with the corresponding gas-phase complexes placed about 0.3 nm above the substrate.

4.1 Surface atomization energy of adsorbed complexes

Here we consider the energy to separate adsorbed complexes $M_mS_n$ into isolated $M$ adatoms and chemisorbed S atoms on the surface,

$$E_{a}(M_mS_n)(ads) = mE[M(ads)] + nE[S(ads)] - E[M_mS_n(ads)],$$

where $E[X(ads)] = E[X(ads + slab)] - E(\text{slab})$ is the energy of a system with a $X$ adsorbed on the substrate minus the energy of the substrate, with both the clean and adsorbed system optimized independently. We describe this quantity $E_{a}(M_mS_n)(ads)$ as the surface atomization energy since it is the surface analogue of the corresponding gas phase quantity. A positive value of $E_{a}(M_mS_n)(ads)$ means that the complex is stable against complete fragmentation into separated atomic constituents also residing on a terrace on the surface. To elucidate the relationship between these surface and gas phase quantities, it is useful to introduce the adsorption energy, $E_{ad}(X)$, of a general species.
$X(\text{ads})$ through

$$
E_{\text{ad}}(X) = E[X(\text{ads})] - E[X(\text{gas})].
$$

(5)

Then comparing Eq. (1) and Eq. (4), one can derive a relation for the difference between gas-phase and surface atomization energies of the form

$$
E_a(M_m S_n)(\text{ads}) - E_a(M_m S_n)(\text{gas}) = m E_{\text{ad}}(M) + n E_{\text{ad}}(S) - E_{\text{ad}}(M_m S_n)
$$

(6)

Ideally, we should obtain the surface atomization energy $E_a(\text{ads})$ in the regime where adsorbed complexes and their dissociated adsorbed constituents sufficiently are far-separated so as to be non-interacting. However, unlike the gas-phase counterpart, there are some complications that make this difficult to do in practice. First, there can be long-ranged interactions between adsorbates mediated by the surface. Elimination of these requires very large supercells in DFT calculations. Second, in the case of Au, isolated adatoms on an extended unreconstructed surface are not stable since Au(111) surface can spontaneously reconstruct to configurations with a denser first layer. However, we have noted above that exposure to S lifts this reconstruction. Thus, our analysis will correspond to finite coverage, and results will depend slightly on this coverage. Specifically, we evaluate $E_a(\text{ads})$ in Eq. (4) at a particular coverage of $M_m S_n$ coverage, and use $E[M(\text{ads})]$ and $E[S(\text{ads})]$ at the corresponding $M$ and $S$ coverage. For example, using a $(4 \times 4)$ supercell, the coverage of the complex is $1/16$ ML, the coverage of $M$ is $\theta_M = m/16$ ML, and the coverage of $S$ is $\theta_S = n/16$ ML. We obtain the values at a particular coverage by interpolating results using various supercells.

Table 4: Surface atomization energy, $E_a(\text{ads})$, for various $M_m S_n$ complexes adsorbed on (111) surfaces, obtained from VASP using the PBE functional. Missing values correspond to unstable complexes.

<table>
<thead>
<tr>
<th></th>
<th>$MS$</th>
<th>$MS_2$</th>
<th>$M_2S_2$</th>
<th>$MS_3$</th>
<th>$M_2S_3$</th>
<th>$M_3S_3$</th>
<th>$M_3S_4$</th>
<th>$M_4S_4$</th>
<th>$M_4S_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111)</td>
<td>0.11</td>
<td>0.68</td>
<td>0.66</td>
<td>0.66</td>
<td>1.66</td>
<td>2.36</td>
<td>2.48</td>
<td>3.12</td>
<td>3.28</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>0.00</td>
<td>0.58</td>
<td>0.36</td>
<td>0.46</td>
<td>1.41</td>
<td>1.97</td>
<td>2.16</td>
<td>2.82</td>
<td>2.96</td>
</tr>
<tr>
<td>Au(111)</td>
<td>-0.27</td>
<td>0.12</td>
<td>0.75</td>
<td>1.68</td>
<td>1.83</td>
<td>2.94</td>
<td>2.26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4 lists the surface atomization energies for the adsorbed complexes shown in Fig 3. Note that for $M_3S_3$ on $M(111)$, the binding energies for the complexes, which equal $-E_{a}(ads)$, were reported in Ref. 26. There are some small discrepancies with the current results, the main reason being that the coverage dependence of $E[S(ads)]$ was not considered in Ref. 26 (specifically, $E[S(ads)]$ was estimated in the limit of zero S coverage).

It is immediately apparent that the atomization energies for adsorbed complexes are much smaller than the corresponding energies for their gas-phase counterparts listed in Tables 1 and 2. This indicates that the intra-complex interactions are much weaker when the complex is adsorbed on the surface, no doubt due to interaction with the metal substrate. Furthermore, while all gas-phase atomization energies are positive, the surface adsorption energy for AuS is negative indicating that this species is thermodynamically unstable against dissociation into Au and S adatoms adsorbed on the terrace.

In addition, analogous to our discussion of the stability of gas-phase complexes based on atomization energies, one should consider the stability of adsorbed complexes against fragmentation into a small number, e.g., two, fragments components. A positive $E_{a}(ads)$, which exceeds the sum of surface atomization energies for various possible fragmentation products, is naturally a prerequisite for stability of the complex on the surface against this incomplete fragmentation process. It is clear that $M_4S_5$ is always stable against dissociation into $M_4S_4$ and an adsorbed S, contrary to the analogous gas-phase detachment process. It is also natural to check the stability of $M_4S_5$ against dissociation into two adsorbed components, $MS_2$ and $M_3S_3$, each of which was previously proposed to be a stable surface complex. One finds that $M_4S_5$ is also stable against such fragmentation (and also against other fragmentation processes). Various incomplete fragmentation pathways for other adsorbed complexes also are unfavorable. A complete accounting of energy changes for the various fragmentation process is provided in the Supporting Information.

However, the above analysis of stability is incomplete as it does not account for the possibility of fragmentation of the complex into chemisorbed S atoms and metal atoms which are incorporated into the substrate at step edges (rather than remaining on terraces on the surface as isolated
adatoms). This incorporation process dramatically lowers the system energy, so many complexes
with positive $E_a^{(ads)}$ are not stable against this process. A corresponding analysis of stability
taking into account the energy cost of extracting adatom from step edges in presented in the next
subsection. (Interestingly, this does not require calculating the energies of metal adatoms.)

4.2 Formation energy of adsorbed complexes

We envision the typical pathway for formation of a $M_mS_n$ complex on the surface to involve the
following reaction

$$mM^{(sub)} + nS^{(ads)} \rightarrow M_mS_n^{(ads)}.$$  \hspace{1cm} (7)

This reaction mechanism reflects the feature that the source of the metal atoms which form the
complex is generally expected to be from the substrate, e.g., from atoms that are extracted at kink
sites along step edges, as clarified further below. On the other hand, the source of S is expected
to be from adsorbed atoms on the substrate terraces as also discussed further below. For Ag(111)
and Cu(111), step edges are preferred by S over terrace sites, so the above prescription assumes
that the S coverage is sufficiently high that step edges are saturated providing excess S atoms on
terraces which can participate in complex formation.

Here, we first discuss the above reaction for general finite temperatures, although our ultimate
focus will be on behavior at low $T$ (noting that experiments were performed at 5 K). We describe
the change in free energy associated with this reaction as the formation energy, $E_f(M_mS_n^{(ads)})$, of
the adsorbed complex. This quantity is obtained from

$$E_f(M_mS_n^{(ads)}) = F(M_mS_n + \text{slab}) - F(\text{slab}) - m\mu_M - n\mu_S,$$  \hspace{1cm} (8)

indicating that the substrate is represented as a slab in our DFT analysis, and where $F$ denotes the
free energy, and $\mu_M$ and $\mu_S$ are the chemical potentials of $M$ and S that are the components of the
complex. Negative values of $E_f(M_mS_n^{(ads)})$ imply that the complex is stable against decomposi-
tion where S atoms remain on terraces on the surface and metal atoms are reincorporated into the
bulk. An advantage in using the free energy in Eq. (8), rather than just the energy which would generally suffice for low $T$ analysis, is that in this definition there is no ambiguity regarding the choice of the reference energy. Here, we implicitly assume that diffusion of both $M$ and S adatoms is facile, so that $M$ adatoms are in equilibrium with the bulk substrate, and sulfur atoms form an equilibrated chemisorbed layer. $M$-S surface complexes can form naturally through reaction of S and metal atoms at any of terrace, kink, or step sites. The progressively stronger binding to other metal atoms of metal adatoms which are isolated on terraces, at kink sites along steps, and at straight close-packed steps, respectively, means that it is increasingly more energetically expensive to form complexes from such adatoms. This feature is compensated for by the increasing populations of metal atoms at these distinct sites. Thus, the free energy of complex formation is the same no matter where the reaction takes place, again assuming each reactant is in equilibrium and has a well-defined chemical potential.

As indicated above, our focus is on behavior at very low $T$. As a result, one can clearly ignore vibrational contributions to free energies and chemical potentials. However, it is also necessary to consider the configurational contribution to the free energy of adsorbed layers. In fact, as the coverage of a species approaches zero, this configurational component diverges logarithmically. Thus, even at 5 K, the configurational contribution to the free energy will dominate the energetic component for sufficiently low coverage, thereby destabilizing any complex (even if that complex is stable based on just energetic considerations). Said differently, at sufficiently low coverage, there is a substantial entropic gain from dissociation of the complex. However, as a practical matter, the logarithmic divergence is very slow, and for experimentally relevant coverages, the configurational contribution to the free energy is negligible at 5 K. A quantitative discussion of this issue is provided in the Supporting Information.

For evaluation of $\mu_M$ at $T = 0$, it is most straightforward to perform conventional bulk calculations using a unit cell with a single metal atom and periodic boundary conditions. This allows
determination of the energy per $M$ atom for an infinite system, so that

$$
\mu_M = E[M(\text{bulk})] = -E_c^M + E[M(\text{gas})],
$$

where $E[M(\text{bulk})]$ is the energy per $M$ atom in the bulk, and $E[M(\text{gas})]$ is the energy of an isolated $M$ atom in the gas phase. In practice, since the first two terms in Eq. (8) are obtained from slab calculations, it is often more accurate to use slab calculations for $\mu_M$ to consistently compensate for quantum size effects in the thin slabs.\textsuperscript{8,59} We adopt this approach utilizing the same lateral unit cell and $M$ coverage as for the evaluation of surface atomization energy (but where we note that $\mu_M$ has a negligible dependence on low coverage).

In typical experiments, both the complexation process and the imaging of adsorbed complexes occurs post-deposition rather than under flow conditions. Thus, the relevant parameter controlling the chemical potential, $\mu_S$, of $S$ is the coverage of $S$ on the surface, $\theta_S$. However, the calculation of $\mu_S$ is non-trivial. As mentioned earlier, we assume that chemisorbed $S$ adatoms form an equilibrated adlayer. Due to interactions between $S$ adatoms, $\mu_S$ is a nontrivial function of the $S$ coverage, even at low temperature. These interactions tend to be repulsive, so that there is no clustering of $S$ at low coverages, and $\mu_S$ increases with $S$ coverage. To determine the coverage, $\theta_S$, dependence of $\mu_S$, we first calculate the energy of chemisorbed $S$ using various supercells, and determine the energy hull by plotting $\mu_S$ as a function of $1/\theta_S$.\textsuperscript{60} Results for S/Au(111) were given in Ref. 61, and those for S/Cu(111) and S/Ag(111) were given in Ref. 62. In evaluating $E_f(\text{ads})$, we utilize interpolated values for $\mu_S$ corresponding to the same $S$ coverage as used for the evaluation of surface atomization energy.

Formation energies for the adsorbed complexes in Fig. 3 are summarized in Table 5. We will discuss these results in detail in the following paragraphs. Here we just note that for (substantial) positive formation energies, the (low) population of such complexes on the surface is given by the corresponding Boltzmann factor. For negative formation energies, all $S$ adsorbed on terraces should be incorporated into such complexes. Note that $E_f(\text{ads})$ reported in Table 5 for Cu-S com-
plexes are slightly lower than the ones cited in Ref. 1. This is largely due to the lower $\mu_S$ value used in Ref. 1 which is an extrapolation to zero S coverage. As indicated above, here, interpolated values of $\mu_S$ at finite S coverages are used. Note that one can readily obtain refined $E_f(\text{ads})$ for any change $\delta \mu_S$ in the chemical potential of S as $E_f(\text{ads})$ just changes by $n\delta \mu_S$.

Table 5: Formation energy $E_f(\text{ads})$ (in eV) of various $M_mS_n$ complexes on (111) surfaces, obtained from VASP using the PBE functional.

<table>
<thead>
<tr>
<th>$M$</th>
<th>$MS$</th>
<th>$MS_2$</th>
<th>$M_2S_2$</th>
<th>$MS_3$</th>
<th>$M_2S_3$</th>
<th>$M_3S_3$</th>
<th>$M_3S_4$</th>
<th>$M_4S_4$</th>
<th>$M_4S_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111)</td>
<td>0.82</td>
<td>0.66</td>
<td>0.10</td>
<td>0.94</td>
<td>-0.06</td>
<td>0.11</td>
<td>0.00</td>
<td>0.23</td>
<td>0.08</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>0.62</td>
<td>0.59</td>
<td>0.01</td>
<td>0.86</td>
<td>-0.19</td>
<td>-0.12</td>
<td>-0.31</td>
<td>-0.32</td>
<td>-0.47</td>
</tr>
<tr>
<td>Au(111)</td>
<td>0.65</td>
<td>0.81</td>
<td>0.46</td>
<td>0.51</td>
<td>0.29</td>
<td>0.14</td>
<td>-0.24</td>
<td>0.44</td>
<td></td>
</tr>
</tbody>
</table>

For $S/Cu(111)$, most adsorbed complexes have small but positive formation energies. However, $Cu_2S_3$ is stable with a slightly negative formation energy, and other larger complexes such as $Cu_3S_4$ are marginally stable. This implies that any S on the surface at low temperature would form $Cu_2S_3$ complexes and/or other larger complexes with negative formation energies. Indeed, STM experiments by Walen et al.\textsuperscript{1} at 5 K and very low coverages revealed a heart-shaped complex, which was interpreted as the $Cu_2S_3$ complex. Chain-like concatenations of this complex with stoichiometry $Cu_nS_{n+1}$, which we denote by $(CuS)_nS$, were observed to develop at least near step edges with increasing S coverage and DFT calculations with PBE functional find that these have stabilities close to that of $Cu_2S_3 = (CuS)_2S$, with $E_f((CuS)_3S) = 0.02$ eV and $E_f((CuS)_4S) = 0.01$ eV. Other complexes were not seen in experiments.

For $S/Ag(111)$, many complexes have negative formation energies, indicating an enhanced propensity for complexation in this system. Note the general trend of increasingly negative $E_f(\text{ads})$ for larger complexes. Indeed, while earlier STM experiments\textsuperscript{63} using liquid nitrogen cooling revealed a dot-row structure with each dot interpreted as a $Ag_3S_3$ complex, later STM measurements using liquid helium cooling\textsuperscript{7} showed more intricate and larger structures, which were interpreted as $Ag_{16}S_{13}$ monomers, and $Ag_{13n+3}S_{9n+4}$ chains.

For $S/Au(111)$, the propensity for complexation is limited. Only a ring-like $Au_4S_4$ complex has a negative $E_f(\text{ads})$ in Table 5. Additional DFT analysis reveals that a similar ring-like $Au_6S_6$
complex has an even lower $E_f(\text{ads}) = -0.59$ eV. As far as we know, there is no evidence of complexation for S/Au(111) at low coverage. Instead, S adatoms were observed to organize into rows separated from each other by $\sqrt{3}a$ at low S coverage where $a$ denotes the surface lattice constant.\textsuperscript{61} Thus, there seems to be a contradiction between experiments and DFT (at least at the GGA level). However, we recall that clean Au(111) undergoes herringbone reconstruction which, even though lifted by S adsorption, could make theoretical prediction less reliable.

We close this section with some additional comments on complex stability. Certainly, any complex with a negative value of $E_f(\text{ads})$ is stable against dissociation and reincorporation of the metal atoms into the substrate. However, this does not necessarily imply absolute stability. If we define the chemical potential of a S atom in a complex through

$$\mu_S(M_nS_n) = \left[F(M_mS_n + \text{slab}) - F(\text{slab}) - m\mu_M\right]/n,$$

then the complex with the lowest $\mu_S(M_nS_n)$ would be thermodynamically preferred. Note that from Eq. (8), the difference in chemical potentials of S in a metal-sulfur complex $M_mS_n$ and in an S adlayer can be obtained from the formation energy through

$$\Delta \mu_S(M_mS_n) = \mu_S(M_mS_n) - \mu_S = E_f(M_mS_n)(\text{ads})/n.$$ 

Thus, the formation energy (after dividing by $n$) provides direct information on the relative and absolute stability of various complexes. For S/Cu(111), the most stable complex is Cu$_2$S$_3$, while for S/Ag(111), the larger complexes tend to be more stable, consistent with experimental results.

Finally, it is appropriate to comment briefly on situations where the complex has a substantial positive formation energy, and where the surface atomization energy is also positive. This applies, e.g., for Au$_3$S$_3$ with substantial $E_f(\text{ads}) = 0.29$ eV, and very high $E_a(\text{ads}) = 1.68$ eV. Thus, while complexes are very stable against fragmentation into atomic constituents, their population on the surface, which is given by $\exp[-E_f(\text{ads})/(k_BT)]$, should actually be low. Thermodynamically, it is preferred for such complexes to dissociate with the Au atoms being incorporated into the Au(111) substrate. However, as noted in the introduction, one STM study at liquid nitrogen temperatures purported to observe absorbed Au$_3$S$_3$ complexes.\textsuperscript{4} Recall that S adsorption on Au(111) lifts the herringbone reconstruction thereby releasing Au atoms onto the terrace. We have argued that such metastable complexes can potentially form due to a supersaturation of Au adatoms associated with
5 Connecting Gas Phase and Surface Calculations

Figure 4: Illustration of the selected pathway and associated energy changes for our analysis of complex formation on surfaces based upon Hess’s law. The figure illustrates the specific case of $M_2S_3$ formation.

An overall reaction can generally be decomposed into several more elemental steps in multiple ways reflecting multiple distinct pathways. According to Hess’s law in thermochemistry, the overall enthalpy change obtained by summing enthalpy changes for the individual steps is independent
of the pathway. A standard choice which is convenient for analysis via quantum chemistry calculations is to select isolated gas-phase atoms as the reactants/products for one of the elemental steps. Applying this choice for complex formation on surfaces, one can regard the overall complex formation process as a combination of: desorption of atoms from the surface; complex formation in the gas phase; and adsorption of the complex onto the surface. See Fig. 4. Then, schematically, the complex formation process involves the following three steps:

\[
mM(\text{bulk}) + nS(\text{ads}) \xrightarrow{\Delta E_1} mM(\text{gas}) + nS(\text{gas}) \xrightarrow{\Delta E_2} M_mS_n(\text{gas}) \xrightarrow{\Delta E_3} M_mS_n(\text{ads}).
\]  

(10)

where the energy changes in the different steps are \(\Delta E_1 = -nE_{ad}(S) + mE_c(M)\), \(\Delta E_2 = -E_a(M_mS_n)(\text{gas})\), and \(\Delta E_3 = E_{ad}(M_mS_n)\). Here, \(E_{ad}(S)\) and \(E_{ad}(M_mS_n)\) are the adsorption energies of the S atom and the \(M_mS_n\) complex, respectively. The adsorption process is generally exothermic so that \(E_{ad}\) has a negative sign. \(E_c(M)\) is the cohesive energy of bulk \(M\), and \(E_a(M_mS_n)(\text{gas})\) is the atomization energy of the gas-phase \(M_mS_n\) complex, the values of which are given in Table 1. The values of \(E_{ad}\) for S and various \(M-S\) complexes are given in Table 6.

Table 6: Adsorption energy of S and \(M_mS_n\) complex on various coinage metal surfaces, obtained using the PBE functional and the VASP code. Missing values are unstable complexes.

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>MS</th>
<th>MS₂</th>
<th>M₂S₂</th>
<th>MS₃</th>
<th>M₂S₃</th>
<th>M₃S₃</th>
<th>M₃S₄</th>
<th>M₄S₄</th>
<th>M₄S₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111)</td>
<td>-4.40</td>
<td>-3.98</td>
<td>-6.31</td>
<td>-4.74</td>
<td>-8.70</td>
<td>-8.23</td>
<td>-6.77</td>
<td>-10.47</td>
<td>-7.98</td>
<td>-12.82</td>
</tr>
<tr>
<td>Ag(111)</td>
<td>-3.64</td>
<td>-3.14</td>
<td>-5.26</td>
<td>-4.01</td>
<td>-7.47</td>
<td>-7.03</td>
<td>-5.85</td>
<td>-8.96</td>
<td>-7.33</td>
<td>-11.17</td>
</tr>
<tr>
<td>Au(111)</td>
<td>-3.69</td>
<td>-2.98</td>
<td>-3.92</td>
<td>-4.81</td>
<td>-4.65</td>
<td>-6.74</td>
<td>-4.97</td>
<td>-8.26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Hess’s law one has \(E_f = \Delta E_1 + \Delta E_2 + \Delta E_3\). We then tabulate the \(\Delta E_j\) and \(E_f\) for each \(M-S\) complex in Table 7 to facilitate analysis. It should be noted that \(\Delta E_3\) are the only surface energetics that need to be calculated using DFT separately for each complex. \(\Delta E_1\)’s use the adsorption energy of S which is the same for all complexes on the same surface, and \(\Delta E_2\) is associated with gas-phase processes only. Thus Table 7 provides a conceptually easy way to connect the adsorption energy and the formation energy of a \(M-S\) complex.

As is shown in Table 7, step 1 is destabilizing while steps 2 and 3 are stabilizing. While systematic trends can be established for each quantity, there seems to be a general compensation
Table 7: Decomposition of the formation energy of metal-sulfur complex on surfaces into three elementary steps. Missing values are unstable complexes. The formation energy $E_f$ can be obtained from $E_f = \Delta E_1 + \Delta E_2 + \Delta E_3$.

<table>
<thead>
<tr>
<th>complex</th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\Delta E_3$</th>
<th>$E_f$(ads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>7.88</td>
<td>-3.23</td>
<td>-3.98</td>
<td>0.66</td>
</tr>
<tr>
<td>CuS$_2$</td>
<td>12.23</td>
<td>-5.82</td>
<td>-6.31</td>
<td>0.10</td>
</tr>
<tr>
<td>CuS$_2$</td>
<td>15.70</td>
<td>-10.02</td>
<td>-4.74</td>
<td>0.94</td>
</tr>
<tr>
<td>CuS$_3$</td>
<td>16.57</td>
<td>-7.75</td>
<td>-8.70</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu$_2$S$_3$</td>
<td>20.04</td>
<td>-11.87</td>
<td>-8.23</td>
<td>-0.06</td>
</tr>
<tr>
<td>Cu$_3$S$_3$</td>
<td>23.51</td>
<td>-16.63</td>
<td>-6.77</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu$_3$S$_4$</td>
<td>27.81</td>
<td>-17.34</td>
<td>-10.47</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu$_4$S$_4$</td>
<td>31.28</td>
<td>-23.06</td>
<td>-7.98</td>
<td>0.23</td>
</tr>
<tr>
<td>Cu$_4$S$_5$</td>
<td>35.32</td>
<td>-22.41</td>
<td>-12.82</td>
<td>0.08</td>
</tr>
<tr>
<td>AgS</td>
<td>6.19</td>
<td>-2.46</td>
<td>-3.14</td>
<td>0.59</td>
</tr>
<tr>
<td>AgS$_2$</td>
<td>9.79</td>
<td>-4.52</td>
<td>-5.26</td>
<td>0.01</td>
</tr>
<tr>
<td>AgS$_2$</td>
<td>12.32</td>
<td>-7.44</td>
<td>-4.01</td>
<td>0.86</td>
</tr>
<tr>
<td>AgS$_3$</td>
<td>13.38</td>
<td>-5.78</td>
<td>-7.47</td>
<td>0.13</td>
</tr>
<tr>
<td>Ag$_2$S$_3$</td>
<td>15.90</td>
<td>-9.06</td>
<td>-7.03</td>
<td>-0.19</td>
</tr>
<tr>
<td>Ag$_3$S$_3$</td>
<td>18.43</td>
<td>-12.69</td>
<td>-5.85</td>
<td>-0.12</td>
</tr>
<tr>
<td>Ag$_3$S$_4$</td>
<td>21.98</td>
<td>-13.32</td>
<td>-8.96</td>
<td>-0.31</td>
</tr>
<tr>
<td>Ag$_4$S$_4$</td>
<td>24.50</td>
<td>-17.49</td>
<td>-7.33</td>
<td>-0.32</td>
</tr>
<tr>
<td>Ag$_4$S$_5$</td>
<td>27.81</td>
<td>-17.34</td>
<td>-10.94</td>
<td>-0.47</td>
</tr>
<tr>
<td>AuS</td>
<td>6.77</td>
<td>-2.94</td>
<td>-2.98</td>
<td>0.85</td>
</tr>
<tr>
<td>AuS$_2$</td>
<td>10.30</td>
<td>-5.92</td>
<td>-3.92</td>
<td>0.46</td>
</tr>
<tr>
<td>AuS$_2$</td>
<td>13.34</td>
<td>-8.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AuS$_3$</td>
<td>13.79</td>
<td>-7.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au$_2$S$_3$</td>
<td>16.82</td>
<td>-11.51</td>
<td>-4.81</td>
<td>0.50</td>
</tr>
<tr>
<td>Au$_3$S$_3$</td>
<td>19.86</td>
<td>-14.92</td>
<td>-4.65</td>
<td>0.29</td>
</tr>
<tr>
<td>Au$_3$S$_4$</td>
<td>23.29</td>
<td>-16.41</td>
<td>-6.74</td>
<td>0.14</td>
</tr>
<tr>
<td>Au$_4$S$_4$</td>
<td>26.33</td>
<td>-21.60</td>
<td>-4.97</td>
<td>-0.23</td>
</tr>
<tr>
<td>Au$_4$S$_5$</td>
<td>29.57</td>
<td>-20.87</td>
<td>-8.26</td>
<td>0.44</td>
</tr>
</tbody>
</table>
effect at work that prevents an easy prediction of $E_f(\text{ads})$. This is not too surprising, since a stronger $M$-$S$ interaction will cause both desorption of individual $S$ atoms and of $M$-$S$ complexes to become more difficult. Also the atomization energy of $M$-$S$ in the gas-phase is not a reliable indicator. For example, Cu$_3$S$_3$ is much more stable in the gas phase than Cu$_2$S$_3$, as measured by $E_a$ or $\Delta E_2$. However, adsorbed Cu$_3$S$_3$ is less stable than Cu$_2$S$_3$, although only by a small amount. This is due to the significantly smaller $-\Delta E_3$ (i.e., a lower adsorption energy for the complex), and higher $-\Delta E_1$ (associated with a larger cost to extract from the substrate and desorb three versus two Cu atoms) for Cu$_3$S$_3$.

The results in Table 7 can be used to provide other insights into complex stability. For example, $MS_2$ is least stable in the gas phase for $M = \text{Ag}$, but most stable as an adsorbed species. This in part reflects the feature that $S$ adsorption on $M$(111) is weakest for Ag, and that extraction of $M$ from the substrate is easiest for Ag. The weak adsorption of AuS$_2$ also contributes to the low stability of this adsorbed species. Similarly, Ag$_2$S$_3$ and Ag$_3$S$_3$ are least stable in the gas phase, but most stable as adsorbed species. The same factors as above, weak adsorption of S and facile extraction of Ag on Ag(111), contribute to this trend.

### 6 Conclusion

We have shown that DFT at the GGA level is quite successful in predicting stability of adsorbed complexes. For S/Ag(111), Ag$_2$S$_3$, Ag$_3$S$_3$, Ag$_3$S$_4$, Ag$_4$S$_4$, Ag$_4$S$_5$, and larger complexes are all strongly stable with the S chemical potential generally decreasing for increasing size. For S/Cu(111), Cu$_2$S$_3$ is stable, and also the 3-fold symmetric Cu$_3$S$_4$ complex is marginally stable. We have shown that the linear (CuS)$_3$S, (CuS)$_4$S, ... , complexes, which are concatenations of Cu$_2$S$_3$, or equivalently of (CuS)$_2$S, have stabilities that are close that of Cu$_2$S$_3$. These results are consistent with STM observations. For S/Au(111), we find that only the ring-like Au$_4$S$_4$ is stable. This complex has not been observed in experiment, but the reliability of the analysis here may be affected by the presence of a surface reconstruction for clean Au(111). Thus, overall, our analysis
can be considered quite successful.

This success is perhaps surprising since it is known that DFT prediction of the cohesive energies and atomization energies can suffer from errors as large as 0.5 eV. However, comparison with extensive STM experiments leads us to believe DFT prediction of the formation energy is accurate to at least 0.2 eV. The success relies on error cancellations, as indicated by the compensation effects shown in Table 7. All adsorbed $M$-$S$ complexes with small or negative formation energy incorporate a linear $S$-$M$-$S$ motif, with the exception of CuS$_3$ and AgS$_3$. This seems to be a feature mainly associated with the $d_{10}$ transition metals, while the nature of ligand (S in this case) has only a secondary effect.55

With regard to our analysis of gas phase complexes, the Hess’s law framework provides a systematic way to relate the results to the stability of adsorbed complexes. In fact, we find that some trends in stability in the gas phase are preserved for adsorbed complexes, while others are not. This reflects the feature that stability on the surface can be regarded within the Hess’s law framework as resulting from a somewhat delicate balance between larger energies associated with gas phase binding within the complex and with adsorption onto the surface.

As noted previously, on both Cu(111) and Ag(111) surfaces, the presence of even trace amounts of S is responsible for a dramatic additive-enhanced acceleration of mass transport. Small two-dimensional homoepitaxial metal islands decay at a rate two orders of magnitude higher than on the pristine surface.9,10 The effective activation barrier for the mass transport pathway associated with a specific mass carrier is given by the sum of the diffusion barrier and the formation energy for the mass carrier (or just the diffusion barrier if the complex formation energy is negative).8,9,11 This applies irrespective of whether the carrier is a metal adatom or a complex (although for some complexes it is conceivable that there is an additional attachment barrier which must be included). Since the formation energies of metal adatoms are high as indicated in Table 6, even complexes with small positive formation energies (rather than just negative formation energies) can dominate mass transport provided that their diffusion barriers (which are invariably higher than for metal adatoms) are not too high. For development of a detailed kinetic theory for such phenomena, the
type of careful and comprehensive assessment of the stability of multiple metal-S complexes on metal(111) surfaces performed in this paper is essential.

Acknowledgment

JL, TLW, JWE and D-JL performed the theoretical analysis and computations in this work, and were supported by the U.S. Department of Energy (USDOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through the Ames Laboratory Chemical Physics program. We acknowledge use of resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. DOE under Contract No. DE-AC02-05CH11231. PAT contributed to the formulation of this project and provided experimental insights, and was supported for this work by NSF Grant No. CHE-1507223. The work was performed at Ames Laboratory which is operated for the USDOE by Iowa State University under Contract No. DE-AC02-07CH11358.

Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs/jpcc.xxxxxxx.

Coordinates, energies, spin states, and vibrational energies of the gas-phase complexes; spin states for gas phase complexes; formation energies for gas phase complexes using octasulfur as a reference; coordinates of the adsorbed complexes with averaging over slab thickness; energy changes for various complex fragmentation processes; assessment of the adlayer configurational contribution to free energy; select molecular orbitals for $MS_2$; assessment of M-S interaction strength for gas phase complexes (PDF).
References


(19) Stranick, S. J.; Parikh, A. N.; Allara, D. L.; Weiss, P. S. A New Mechanism for Surface


Stable adsorbed $M$-S complexes predicted by DFT

- $\text{Cu}_2\text{S}_3$ \hspace{1cm} $E_f = -0.06$ eV
- $\text{Ag}_4\text{S}_5$ \hspace{1cm} $E_f = -0.47$ eV
- $\text{Au}_4\text{S}_4$ \hspace{1cm} $E_f = -0.24$ eV