MODELING OF SYNGAS REACTIONS AND HYDROGEN GENERATION OVER SULFIDES

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**ABSTRACT**

The objective of the research is to analyze pathways of reactions of hydrogen with oxides of carbon over sulfides, and to predict which characteristics of the sulfide catalyst (nature of metal, defect structure) give rise to the lowest barriers toward oxygenated hydrocarbon product. Reversal of these pathways entails the generation of hydrogen, which is also proposed for study.

During this study, adsorption reactions of H atoms and H₂ molecules with MoS₂, both in molecular and solid form, have been modeled using high-level density functional theory. The relative stabilities of pure MoS₂ edges were calculated and small clusters exhibiting properties of the edges were modeled. The results were finalized and published in the journal *Surface Science* [1]. Hydrogen adsorption energies on both the edges and the clusters were calculated, and the thermodynamics of hydrogen adsorption on both systems were evaluated. The adsorption locations and vibrational frequencies were also determined. These additional results were published in a second paper in *Surface Science* [2].

Most recently, the bonding and effect of alkali and transition metal ions was investigated on the MoS₂ clusters. Potassium atoms bind to the clusters and increase the binding of hydrogen to the clusters while reducing the activation barriers for hydrogen adsorption. Silver attaches to the Mo7S14 cluster and donates its odd electron to the nearby Mo atoms and should have a similar effect to hydrogen as potassium does.
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Executive Summary

Modeling of hydrogen activation and bonding on molybdenum disulfide was carried out using computational approaches ranging from semi-empirical to high-level all-electron periodic density functional theory (DFT) methods. Because the structure of the trigonal prismatic MoS$_2$ is highly anisotropic, a large number of surface orientations, features, and structural motifs were examined for hydrogen site preferences. The studied MoS$_2$ systems included small clusters, from Mo$_2$S$_{14}$ down to the single MoS$_2$ monomer, and periodic supercells representing the edge structures.

Four edge structures, “vertically-cut” (10$ar{T}$0) and (1$ar{2}$10) planes, and “inclined” (10$ar{T}$x) and (1$ar{2}$1x) were examined by partial optimization which involved relaxation of the edge surface S and Mo atoms. These structures show distinct differences in surface energies. Stability of the periodic MoS$_2$ edges was found to be in the order (10$ar{T}$x)(most stable) > (1$ar{2}$1x) > (1$ar{2}$10) > (10$ar{T}$0), where the inclination index x = 3 or 4. A large relaxation energy was associated with the reconstruction of the edge from ideal geometry of a cut through the 2H-MoS$_2$ crystal: for the (10$ar{T}$x) edge, energy of 0.63 eV per MoS$_2$ molecular formula was released upon a concerted movement of exposed S atoms that increased the coordination of the edge Mo atoms from 4 to 5. The electronic band structure calculation identified surface states, which had a metallic character for the (10$ar{T}$x) edge and a narrow gap semiconducting character for the (1$ar{2}$1x) edge. For reference purposes, periodic band structure calculation of a single 2-D sheet of MoS$_2$ by the LCAO density functional theory (DFT) method used in this work yielded results practically identical to earlier LAPW DFT calculations of Park et al. [3]. The HOMO of the (10$ar{T}$x) edge was found to be a surface state that penetrates beyond the first layer of edge Mo atoms. The effective mass of an electron in this state was calculated to be 1.9 $m_e$, compared to 4.1 $m_e$ for a hole in the HOMO of the 2-D sheet. Clusters of (MoS$_2$)$_n$ ($n = 7, 3, 2, 1$) also showed large relaxation energies from the 2H-MoS$_2$ geometry, with the main tendency to increase the coordination of the exposed Mo atoms by inward movement. The difference in energies of the spin singlet and triplet states increased from near zero for (MoS$_2$)$_7$ to 0.53 eV for the single MoS$_2$ molecule, in excellent agreement with the data for MoS$_2$ in frozen argon matrix reported by Liang and Andrews [4].

The edges of MoS$_2$ were tested for activation of hydrogen using DFT by modeling the molybdenum disulfide monomer, small clusters, and the periodic edge models. Attachment of H$_2$ to the MoS$_2$ molecule was studied in detail, and several different structures were found. A dihydride with the hydrogen atoms far apart was most stable. In this configuration, the $\sigma^*$ orbital of the H$_2$ mixed with the d orbitals of Mo to achieve the hydrogen activation. The less stable $\eta^2$ hydrogen configuration had the H$_2$ bond slightly stretched with the H atoms equidistant from the Mo center. Addition of a potassium dopant further stabilized the attachment of the H$_2$. A triangular Mo$_7$S$_{14}$ cluster provided a model with edges resembling those of the cut MoS$_2$ sheets. On this cluster, both the $\eta^2$ hydrogen and the dihydride were seen. Various positions for atomic hydrogen adsorption on the most stable periodic MoS$_2$ edges were tested and the
vibrational frequencies were calculated that predict ranges for Mo-H, S-H, Mo-H-Mo, and H-H vibrations for IR and Raman spectroscopy. In addition, some configurations with H$_2$ adsorption on the edges were modeled.

The bonding of the alkali and transition metal dopants K and Ag on the MoS$_2$ clusters were calculated with DFT. The single Ag atom binds to the Mo$_7$S$_{14}$ cluster readily and donates its odd electron to the nearby Mo atoms. The effect of potassium is to increase the binding of hydrogen and reduce the activation barriers for hydrogen adsorption.
Methodology

In this theoretical modeling effort, the results were obtained using the following DFT [5,6] methods:

A. Periodic generalized gradient approximation (GGA) LCAO method with the DNP basis set and the Perdew-Wang '91 (PW) functional [7] as embedded in the DMol³ package [8];

B. Periodic generalized gradient approximation (GGA) FP-LAPW method with a dual planewave/spherical harmonics basis set and the Perdew-Burke-Ernzerhof '96 (PBE) functional [9] as embedded in the Wien2k code [10];

C. Generalized gradient approximation (GGA) LCAO method with the DN** basis set and the Becke-Perdew functional [11,12] as embedded in the Spartan package [13];

D. Semiempirical methods for preoptimization of geometry.

Geometry optimizations used the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [14] Hessian updating scheme, starting with the ideal bulk-derived MoS₂ coordinates. At times, the initial positions of some atoms were shifted slightly to break symmetry and allow the structure to find its natural minimum.

Benchmarking and comparison of the various methods were also performed. We find the semiempirical pm3(tm) code [15] particularly deficient by arriving at totally wrong geometries, presumably due to a bad parametrization for molybdenum, a key element in our systems. All other properties obtained with this method are of course also in doubt. In contrast, our experience with methods A-C above [3,16-20] permits the conclusion that results based on these methodologies are valid and reliable, albeit always amenable to refinement.

One particular challenge is to account for weak interactions such as those between adjacent MoS₂ sheets across the Van der Waals gap. A successful calculation by the periodic full-potential linearized augmented plane wave (FP-LAPW) DFT method was reported in the first year of this project [21] to yield the weak attraction (0.028 eV/MoS₂ unit), albeit the calculated attractive energy still differs from the experimental value of 0.013 eV/MoS₂ unit and the calculated size of the Van der Waals gap was larger than the experimental value.
Results and Discussion

1. Objective and Background of the Research

Overall objective. The objective of this research is to analyze pathways of reactions of hydrogen with oxides of carbon over sulfides, and predict which characteristics of the sulfide catalyst give rise to the lowest barriers toward oxygenated hydrocarbon product. The present research aims at providing complementary and predictive theoretical background for an economical optimization of these processes.

Methodology. Molecular conversions at interfaces occur via a flow of electrons during movement of atomic nuclei from reactant to product configurations over energy barriers the magnitude of which determine the reaction rate. Reactants (R) and products (P) are at local minima of a multidimensional energy-coordinate space, and the barrier is at a saddle point of that space called the Transition State (TS). The points R, TS and P are the stationary points of the reaction pathway, and search for these points is carried out by optimization methods of quantum mechanics. Specific methods used in this work are listed as A-D in the Experimental section of this report. Development of codes for TS searches in periodic systems is also planned. An important aspect of the modeling is evaluation of reliability and accuracy of the methods used.

2. Overview of MoS\textsubscript{2}-H\textsubscript{2} Results

Specific details of the results of the present work are best presented in the text of the two articles published in the journal Surface Science [1,2], attached to this report as Appendices A and B. Regardless, a summary of the most significant findings is presented herein.

- **Small molecules** formed by units of MoS\textsubscript{2} show a change in magnetic behavior as the sizes of the molecules increase. The MoS\textsubscript{2} monomer exists in a stable triplet state, in agreement with Liang and Andrews [4]. For larger clusters of MoS\textsubscript{2}, the energy difference between the singlet and triplet states decreases, and by the time the large Mo\textsubscript{7}S\textsubscript{14} cluster is reached, the singlet is more stable. The periodic MoS\textsubscript{2} edges follow this trend and exist in the singlet state.

- The large Mo\textsubscript{7}S\textsubscript{14} cluster has edges that resemble those on the periodic MoS\textsubscript{2} edges [Appendix A, Figure 13]. Because of this, the simpler cluster calculation can be used to guide and direct the slower periodic calculations and the analysis thereof.

- Hydrogen is activated on the MoS\textsubscript{2} clusters. On the MoS\textsubscript{2} monomer, a stable singlet dihydride is formed with a Gibbs free energy change of $-18.1$ kcal/mol. On the Mo\textsubscript{7}S\textsubscript{14} cluster, hydrogen binds in both the dihydride and $\eta^2$ geometries, which were described by Kubas [22].
• The **periodic edge** system must be modeled with a grid of infinite ribbons of MoS$_2$. These ribbons can be easily spaced far enough apart that they do not interact. The other parameter defining the model is the **ribbon width**, which must be at least 4 MoS$_2$ units wide to prevent the opposing edges from interacting. The calculations were done with ribbons either 4 or 5 units wide, and 2 units along the length of the ribbon, making for 24- or 30-atom periodic systems.

• Geometric **relaxation** plays a large part in the stability of the edges. The edges relax through a movement of the S atoms to protect any partially-exposed Mo atoms, while the Mo atoms retreat away from the cut. In the case of the diagonally cut edges, one row of S atoms moves from the S plane into the Mo plane. The highest relaxation energies are on the order 1 eV per MoS$_2$ unit [1].

• The **periodic** MoS$_2$ edges examined are formed from four cuts through the MoS$_2$ basal plane. The most stable is the (10\overline{1}x), followed by the previously **unstudied** (1\overline{2}1x) edge. These two **diagonally-cut** edges are more stable than the vertically-cut but logical (10\overline{1}0) and (1\overline{2}10) edges.

• The (10\overline{1}x) edge has a **metallic** surface state, in agreement with previous reports [23,24]. The electron density in the HOMO, which crosses the Fermi level, is extended along the edge allowing for conductivity in that direction.

• On the **periodic** MoS$_2$ edges, hydrogen atoms bond homolytically to different sulfur atoms, homolytically to Mo atoms, or heterolytically to separate S and Mo atoms. Both S-H and Mo-H bonds are found. Attempts to force H$_2$ adsorption geometries similar to those on the MoS$_2$ monomer met with little success.

• **Vibrational frequencies** for motions of H atoms adsorbed on MoS$_2$ clusters and edges were calculated. These frequencies on the periodic edges range from 1223 cm$^{-1}$ for hydrogen bound between two Mo atoms, to about 1860 cm$^{-1}$ for Mo-H bonds, to about 2500 cm$^{-1}$ for S-H bonds. These vibrations should be detectable experimentally, though there is a large window of allowed energies.

• **Thermodynamic analysis** of hydrogen adsorption indicates that the **Gibbs free energy** change includes **entropy penalty** associated with the loss of rotational and translational degrees of freedom, along with a change in the **zero-point vibrational energy**. Together, these factors add about 0.5 eV to the adsorption energy calculated by DFT. This makes it more difficult to dissociatively adsorb hydrogen.
3. Overview of K-MoS$_2$-H$_2$ Results

Hydrogen activation on alkali-doped sulfides has been studied, with the main result that neutral alkali dopants will promote dissociative hydrogen bonding on the transition metal. This work has been to large extent completed but is yet to be written up for publication. The intended journal is Surface Science, in which the work summarized in section 2 above has been published. A summary of the most significant findings is presented herein.

- **Potassium site preferences** have been determined. An example is given below of potassium sitting on the Mo$_7$S$_{14}$ cluster.

  Potassium site preference (→→) for sites on the Mo$_7$S$_{14}$ cluster: (a) trigonal hollowsite-edge, (b) on (10T3) edge, (c) on (0001) basal plane, (d) on (1210) edge. Energies of K$^+$ + Mo$_7$S$_{14}$ are in kcal/mol K$^+$

  ![Diagrams](image)

  (a) $171$ kcal/mol
  (b) $161$ kcal/mol
  (c) $143$ kcal/mol
  (d) $121$ kcal/mol

- **Hydrogen is activated on the K-MoS$_2$ monomer** with lower barriers and greater exothermicity than on the potassium-free MoS$_2$ monomer. A stable doublet dihydride is formed with a Gibbs free energy change of $-45.7$ kcal/mol. The K-MoS$_2$ monomer also binds CO quite strongly, and so does both the dihydrogen and CO together. However, a direct reaction of the dihydrogen with CO in the coordination sphere of Mo is not occurring, and bypass mechanisms are necessary to execute CO conversion to methanol and other oxygenates.
H2 and CO activation on MoS2 monomer:

- CO makes readily (inert) carboxyls and hydrido-carboxyls, but does not insert into the Mo-H bond

\[ E_i (\text{kcal/mol}) \begin{array}{ccc} -45.7 & -64.4 & -77.8 \\ \end{array} \]

\[ \angle (\text{S-Mo-S}): 116^\circ \quad 114^\circ \quad 115^\circ \quad 116^\circ \]

\[ \angle (\text{H-Mo-H}): 117^\circ \quad 128^\circ \]

- On the K-Mo\textsubscript{7}S\textsubscript{14} cluster, hydrogen binds in both the dihydride and \( \eta^2 \) geometries significantly more strongly than on the potassium-free cluster.
Potassium doping of MoS$_2$ clusters favors dissociative chemisorption of H$_2$. Interatomic distances are in nm. Energy of formation (DFT/GGA/DN**) of (b) K-Mo$_7$S$_{14}$H$_{10}$ from (a) K-Mo$_7$S$_{14}$ and molecular hydrogen is -3.0 kcal/mol, in contrast to K-free system, +14.0 kcal/mol. K-Mo(4d$^0$)S$_2$ thus behaves as Mo$_x$Tc(4d$^3$)$_{1-x}$S$_2$ !!!

- The periodic edge system with potassium dopant awaits further modeling, but it is expected that the effects of the alkali dopants on hydrogen activation will be similar to those on the K-Mo$_7$S$_{14}$ cluster, which showed similar features to the edges studied with the potassium-free system reported in Section 2 above. However, the additional edge ability to bind hydrogen on the exposed sulfur atoms has yet to be examined on the potassium-doped periodic system.

- The potassium dopant is expected to be chemically unstable in the presence of water, as indicated by the reactivity of the electron donated to MoS$_2$ by the Cs dopant [3]. Therefore, we have further examined the effects of a more stable electron-donor dopant, silver, which has been reported in experimental literature as forming air-stable intercalates with TaS$_2$ [25] and MoS$_2$ [26]. The Ag-Mo$_7$S$_{14}$ cluster calculations have completed as regards the relative stability of the silver dopant in various sites, as reported in Section 4 below.
4. Silver Atoms on MoS₂ Clusters

The Mo₇S₁₄ cluster was modeled with adsorbed Ag atoms in preparation for testing the effects of transition metal atoms on the activation of hydrogen. The DFT model was changed because of changes in the available computers and software. Currently, Spartan '02 for Linux [27] is being employed with the 6-31G** Gaussian basis [28], ECP pseudopotentials [28], and the BLYP functional [28]. The Ag atom was added to the previously-optimized Mo₇S₁₄ cluster, then the position of the Ag was allowed to relax in a partial optimization. The forces were optimized to a tolerance of 4.5 × 10⁻⁴ atomic units.

Several different adsorption locations around the cluster were tried, with the results summarized in the following table. Both doublet (spin 1/2) and quartet (spin 3/2) states were calculated, because the previous results of MoS₂ clusters indicate that the spin is not automatically known for this system. The adsorption energy is calculated with the separated Mo₇S₁₄ cluster and Ag atom as the zero of energy, which is included for reference. In the separated case, the silver atom has spin 1/2, while the Mo₇S₁₄ cluster is either a singlet or a triplet. The spin density of these molecules indicates the nearly complete transfer of the spin 1/2 from the silver to the Mo₇S₁₄ cluster. This odd-electron (or electrons) on the metal sites can fill the σ orbitals of the H₂ molecule, allowing for easy activation of hydrogen on these sites.
Table 1. Models and calculated properties of the Ag-Mo$_7$S$_{14}$ clusters.

<table>
<thead>
<tr>
<th>Model</th>
<th>Spin</th>
<th>Energy (eV)</th>
<th>HOMO-LUMO Gap (eV)</th>
<th>Net Spin Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separated</td>
<td>1/2,</td>
<td>-6193.139244</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Over-Mo</td>
<td>1/2</td>
<td>6193.159849</td>
<td>0.254</td>
<td>On one edge Mo, some on second edge Mo</td>
</tr>
<tr>
<td>Over-Mo</td>
<td>3/2</td>
<td>6193.161961</td>
<td>0.151</td>
<td>Symmetric on both edge Mo</td>
</tr>
<tr>
<td>Over-</td>
<td>1/2</td>
<td>6193.172551</td>
<td>0.280</td>
<td>Most on one edge Mo, very little on second edge Mo</td>
</tr>
<tr>
<td>Over-</td>
<td>3/2</td>
<td>6193.172489</td>
<td>0.078</td>
<td>Most on one edge Mo, very little on second edge Mo</td>
</tr>
<tr>
<td>hollow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hollow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-bridge</td>
<td>1/2</td>
<td>-6193.172105</td>
<td>0.19860</td>
<td>Most on one edge Mo, very little on second edge Mo (dz2-like)</td>
</tr>
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</table>

The Over-hollow doublet (S = 1/2) is the most stable, albeit of nearly equal energy to the spin quartet (S = 3/2) at the same site and the Mo-bridge doublet (S = 1/2). For this reason, H$_2$ activation is being examined on the Over-hollow doublet first. It is noted, however, that the Ag doping from different sites creates very similar spin density distribution into surface states located primarily on the edge Mo atoms. Thus it is expected that all Ag-doped MoS$_2$ geometries will generate essentially the same H$_2$-activating sites.

Additional calculations with hydrogen adsorption are in progress under the same DFT model, with the Ag and attached H atoms allowed to relaxed. One model places 2 hydrogen molecules on the edge Mo atoms, and another attaches a single H$_2$ molecule to the Ag atom. Spin doublets are being calculated for each. Though the calculations are ongoing, the preliminary results indicate that the bonding of 2 hydrogen molecules split between the two Mo edge sites appears to be stronger than one hydrogen molecule attached to the single Ag site.
Conclusions

Activation of hydrogen on defect sites of MoS$_2$ small clusters and periodic edges has been extensively studied by high-level density-functional theory. Adsorption on the MoS$_2$ molecule causes a change in spin of the system from a triplet to a singlet state. For larger systems, the singlet state is maintained throughout the reaction. The most stable edge, the (10$ar{1}$x) edge, supports dissociative adsorption with a Gibbs free energy change of $-0.27$ eV [2]. This is a first step in reactions that use hydrogen. In addition, reversal of the pathways entails generation of hydrogen.

The MoS$_2$ system, both in cluster and periodic form, provides a rich system to explore for hydrogen activation. Already, alkali doping is showing a decreased activation barrier, while transition metal doping is shown to exist on the clusters. Ongoing calculations will help pave the way towards better hydrogenation and possibly hydrogen generation catalysts. Preliminary calculations of the Ag-MoS$_2$ clusters indicate that electron transfer from Ag$^0$ into the edge Mo$^{IV}$ orbitals will occur, similarly as over the alkali-doped MoS$_2$, where the Mo edge states have proven to be active sites for H$_2$. Both the alkali and Ag “activate” those sites by electron donation. Thus the alkali- and Ag-doped MoS2 behave as electron donor-acceptor (EDA) nano-composites with enhanced reactivity toward hydrogen.

References


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Abstract

The defect structure of 2H-MoS2 is examined by density functional methods, and the results are compared with experiment where available. The defects considered range from edge structures to clusters of decreasing size to the single MoS2 molecule. Stability of the edges is found to be in the order (10\{1\}0)(most stable) > (12\{1\}x) > (12\{1\}0) > (10\{1\}0), where the inclination index x = 3 or 4. A large relaxation energy is associated with the reconstruction of the edge from ideal geometry of a cut through the 2H-MoS2 crystal: for the (10\{1\}x) edge, energy of 0.63 eV per MoS2 molecular formula is released upon a concerted movement of exposed S atoms that increases the coordination of the edge Mo atoms from 4 to 5. The electronic band structure calculation identifies surface states, which have a metallic character for the (10\{1\}x) edge and a narrow gap semiconducting character for the (12\{1\}x) edge. For reference purposes, periodic band structure calculation of a single 2-D sheet of MoS2 by the LCAO DFT method used in this work yields practically identical results to earlier LAPW DFT calculations of Park et al. [J. Chem. Phys. 111 (1999) 1636]. The HOMO of the (10\{1\}x) edge is a surface state that penetrates beyond the first layer of edge Mo atoms. The effective mass of an electron in this state is calculated to be 1.9 \( m_e \), compared to 4.1 \( m_e \) for a hole in the HOMO of the 2-D sheet. Clusters of \((\text{MoS}_2)_n\) (\( n = 7, 3, 2, 1 \)) also show large relaxation energies from the 2H-MoS2 geometry, with the main tendency to increase the coordination of the exposed Mo atoms by inward movement. The difference in energies of the spin singlet and triplet states increases from near zero for \((\text{MoS}_2)_7\) to 0.53 eV for the single MoS2 molecule, in excellent agreement with the data for MoS2 in frozen argon matrix reported by Liang and Andrews [J. Phys. Chem. A 106 (2002) 6945].

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Introduction

Molybdenum disulfide is an anisotropic solid of a hexagonal double-sheet structure with 6 sulfur atoms coordinated around each molybdenum atom in a trigonal prismatic arrangement [1]. The sheets are terminated by edge facets, which give rise to a “pyramid-like” or “column-like” crystal habit in the naturally grown mineral molybdenite [2]. The edge facets typically appear as a hexagonal outline on larger polycrystalline specimens [3]. Even high surface area specimens (60-100 m²/g) display the dominant basal plane features broken to form smaller defect regions [4], and a large amount of experimental evidence indicates that these high surface energy defect regions, referred to as “edges” based on an analogy with the low-surface polycrystals, comprise only a small fraction of the total surface area [3].

The basal plane and the edge facets have profoundly different physical and chemical properties. The surface energy has been estimated at 250 mJ/m² for the basal plane (0001) and about 100 times greater for edges [5]. The edges have been found to be active surfaces for chemisorption of oxygen and a preferred site for transition-metal dopants such as cobalt in the Co-Mo-S catalysts [3,6,7,8]. The trigonal prismatic sheets are joined together along the 〈0001〉 direction by weak attractive interactions on the order of 13 kJ/mol MoS₂ [5] that give rise to the Van der Waals gap into which foreign atoms and molecules can be intercalated [9].

Monolayers and sub-monolayers of neutral heavy alkali atoms, notably Cs, on the MoS₂ basal plane have also been reported to give rise to charge-transfer bilayers with the Cs 6s electron completely transferred into the conduction band of MoS₂ as observed via angle-resolved valence-band X-ray photoelectron spectroscopy (AR-VB-XPS) [10]. This “chemically screened” supra-valence electron was found to react with dioxygen to form surface peroxides and superoxides but not to split the oxygen molecule into atoms, and to decompose water only at elevated pressures [11]. Thus the normally inert basal plane can be rendered reactive in a controlled fashion by properly chosen dopants.

Among the many applications of MoS₂, the most important one is its use as a basic component of heterogeneous catalysts for hydrodesulfurization (HDS) and hydrodenitrification (HDN) processes [12,13,14,15,16,17], along with a wide range of other hydrogenation reactions [18]. Recently Berhault et al. [19] and Chianelli and Berhault [20] studied the effects of carbon on the mechanisms of the HDS and HDN reactions and came to the conclusion that the presence of carbon bonded to Mo in MoS₂ catalysts plays a significant role in the chemistry of the active site. In addition, Murchison of Dow Chemical Corporation discovered in the 1980's that alkali-doping of MoS₂ will switch the selectivity of CO hydrogenation from hydrocarbons on undoped MoS₂ to alcohols [21]. Subsequently, the chemistry of this fascinating co-catalyzed set of reactions, although not resulting in a commercially viable process, has been subject of extensive studies by many industrial and academic laboratories, including the surface science center of Lehigh University [4], in the quest for controlling and improving selectivity of CO hydrogenation to alcohols. Both “chemical” [4] and “electronic” [21]
hypotheses of the catalytic function of alkali-doped molybdenum disulfide have been advanced, and are awaiting resolution by theory.

The stability of the MoS$_2$ sheet structure is very large, but very recently Liang and Andrews [22] generated and characterized individual MoS$_2$ molecules in frozen argon matrix. These authors reported an excellent agreement between observed vibrational spectra and theory, and their results will serve as a reference in the present study of MoS$_2$ clusters and periodic structures. Furthermore, MoS$_2$ nanotubes and related structures have been synthesized by Tenne [23] and subsequently a variety of solid solutions Mo$_1_x$W$_x$S$_2$ were prepared, with a promise of unprecedented variations of physical and chemical properties in the entire layered chalcogenide family [24,25,26].

The practical use and fundamental scientific interest regarding the surface structure and electronic properties of the defect MoS$_2$ has prompted active theoretical research eventually aiming at the understanding, prediction, and control of structure-function relationships in the surface reactivity of this solid, without and with dopants. With rapid advances in computational hardware and software, the theoretical activity in this area is on the rise. Among the issues addressed by theory are: the geometric structure of stable and metastable surfaces [7,17,27,28,29] and clusters [30], the mechanism and energetics of chemisorption of hydrogen [31] and sulfur-containing molecules [32], and the state of first-row transition metals bonded onto MoS$_2$ to form the active HDS catalyst [7,8,16]. It is evident that the impact of theory on the field is growing, despite a great demand on computational resources needed to tackle the complex systems under study.

In the present series of papers, we focus on (I) heretofore unresolved structural aspects and energetics of edge facets and clusters of molybdenum disulfide, as well as the companion electronic surface states revealed by theory and valence-band XPS, (II) activation of hydrogen on pure and alkali-doped TS2 chalcogenides, as predicted by theory and examined by vibrational spectroscopy, (III) chemisorption and dissociation of carbon monoxide, and (IV) hydrogenations of carbon monoxide related to the selectivity control in oxygogenate synthesis, as well as the possible role of carbon suggested by experiment [19,20]. We attempt to provide a systematic account of energetics and electronic properties while going from a single chalcogenide molecule to clusters to defect solids, and thus we aim at bridging the gap between the chemistry and physics of single-center metal complexes, nanostructures, and periodic structures.

**Calculation Methods**

All of the present calculations use Density Functional Theory (DFT) [33,34] with linear combination of atomic orbitals (LCAO) basis sets. The periodic calculations were performed with the DMol$^3$ software package [35], using the Cerius$^2$ environment for building and viewing models. The basis set is of the double-numerical type with polarization functions added to all atoms (DNP). The basis size is comparable to a Gaussian 6-31 G** basis, though it is expected to be more accurate. The effective core potential (ECP) was used on Mo atoms. The calculations used generalized gradient corrected (GGA) functional by Perdew and Wang [36], and thermal smearing was used to improve convergence.
Cluster calculations were performed within the Spartan v5.1.3 framework [37]. The LCAO basis set is formed from a double-numerical atomic basis with polarization functions added to all atoms (DN**), which is the same as the DNP basis used in the periodic calculations. The functional is the Becke-Perdew (BP) [38,39] GGA functional. These were all-electron non-relativistic calculations; no ECP was used.

Geometry optimizations used the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [40] Hessian updating scheme, starting with the ideal bulk-derived MoS$_2$ coordinates. At times, the initial positions of some atoms were shifted slightly to break symmetry and allow the structure to find its natural minimum.

All edge calculations use 1-D ribbon models with $\omega \times \ell$ rectangular supercells cut from 2-D MoS$_2$ sheets. The supercells are $\ell = 2$ MoS$_2$ units long along the edge, while the width $\omega$ of the ribbons from edge to counter-edge, is varied from $\omega = 2$ to 5 MoS$_2$ units. Tests for convergence show that $\omega = 4$ is sufficient to ensure that interactions between the edges of the same ribbon are minimized, so $4 \times 2$ unit cells are used in most calculations. The ribbons were spaced 40 Å apart in the non-repeating directions to eliminate interactions between neighboring cells.

The energy (per MoS$_2$ unit) of an edge in the atomic geometry $\mathbf{R}$ is calculated directly from the total energy $E_{\text{tot}}(\mathbf{R})$ of the 1-D ribbon unit cell:

$$E_{\text{edge}}(\mathbf{R}) = \frac{1}{2\ell} (E_{\text{tot}}(\mathbf{R}) - N\mu),$$

(1)

where $\mu$ is the energy per molecular unit of the 2-D MoS$_2$ sheet and $N = \omega\ell$ is the number of MoS$_2$ units in the ribbon unit cell. The factor of $\frac{1}{2}$ enters because both the edge and counter-edge are involved. As defined, $E_{\text{edge}}(\mathbf{R})$ is the average energy of the two edges. In the case where the edge and counter-edge are identical ($(1 \overline{2} 1 0)$), this is the absolute edge energy per MoS$_2$ unit. Energies for both the unrelaxed and relaxed configurations are calculated, and the relaxation energy is defined as the change in edge energy from the initial to the relaxed configuration:

$$\Delta E_r = E_{\text{edge}}(\text{relaxed}) - E_{\text{edge}}(\text{unrelaxed})$$

(2)

The relaxation energy $\Delta E_r$ is always negative.
Results

2. Unrelaxed Edge Structures

To date, published DFT calculations of MoS$_2$ edges have focused on the (10$\overline{1}0$) edges [7,8,16,17,27–31,41,42]. These are not, however, the only stable edge planes. Figure 1 shows the MoS$_2$ basal plane, with three possible cutting planes marked. There are two (10$\overline{1}0$) planes, and one (1$\overline{2}10$) plane. In addition, the sheet can be cut at an angle, leading to stoichiometric unit cells with partial sulfur coverage on both sides. We refer to these edges as (10$\overline{1}x$) and (1$\overline{2}1x$). There is only one (10$\overline{1}x$) cut. The unrelaxed edges are shown in Figure 2. All edges are derived from an infinite optimized 2-D MoS$_2$ sheet having a rhombohedral unit cell with the experimental lattice dimensions $a = b = 3.16$ Å. Sheets are separated by 40 Å in the 2-D model, and the distance from the Mo-plane to the S-plane is 1.587 Å. The energy of the sheet is $\mu = -23538.08$ eV per MoS$_2$ unit. For our $\omega \times 2$ cells, the cell width is 6.32 Å for the (10$\overline{1}x$) edges and 5.473 Å for the (1$\overline{2}1x$) edges.

The unrelaxed energies derived from the bulk atomic positions are listed in Table 1. The relaxation energy plays a significant role in determining the energy of the edge, so the unrelaxed energies do not determine the overall stability.

![Diagram of MoS$_2$ basal plane](image)

**Figure 1:** Picture of the MoS$_2$ basal plane, as viewed from the top. Purple atoms are Mo, and yellow atoms are the S atoms which are above and below the Mo plane. One (1$\overline{2}10$) cutting plane and the two possible (10$\overline{1}0$) cutting planes are shown with black lines. The (10$\overline{1}0$) cut is more stable than the (10$\overline{1}0$)b cut because it severs fewer bonds.
Figure 2: Side views along the unrelaxed MoS$_2$ edges. Each figure shows one or more unit cells of a 4-MoS$_2$-unit wide ribbon which repeats into and out of the page. In all figures, the edge and counter-edge are on the left and right, while the ribbon repeats into and out of the page.

Table 1: Unrelaxed energies of the various MoS$_2$ edges. All calculations were done with 4 $\times$ 2 unit cells, and the energy per unit cell of the 2-D MoS$_2$ sheet is $\mu = -23538.08$ eV. The edges are listed in the same order as Table 2.

<table>
<thead>
<tr>
<th>Edge</th>
<th>$E_{\text{tot}}$(unrelaxed) (eV)</th>
<th>$E_{\text{edge}}$(unrelaxed) (eV/MoS$_2$ unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10(\bar{1})0) $b$</td>
<td>-188287.45</td>
<td>4.30</td>
</tr>
<tr>
<td>(10(\bar{1})0) $a$</td>
<td>-188295.65</td>
<td>2.25</td>
</tr>
<tr>
<td>(1210)</td>
<td>-188296.13</td>
<td>2.13</td>
</tr>
<tr>
<td>(121x)</td>
<td>-188294.92</td>
<td>2.43</td>
</tr>
<tr>
<td>(10(\bar{1})x)</td>
<td>-188293.71</td>
<td>2.73</td>
</tr>
</tbody>
</table>
3. Relaxation of MoS$_2$ Edges

The relaxation of the MoS$_2$ edges produces the geometries shown in Figures 3 and 4. The energies $E_{\text{edge}}$(relaxed) are given in Table 2. The (10 $\overline{1}$x) edge is found to be the most stable, with the (1$\overline{2}$1x) edge being only 0.09 eV/MoS$_2$ unit higher in energy.

Upon relaxation, the edges exhibit various behaviors. In the three “vertically-cut” edges, the exposed Mo atoms relax inward, while the S atoms move out from the edge and in toward the Mo plane. The S-Mo-S bond angle is 82.05° in the optimized 2-D sheet. On the Mo-exposed side, this angle increases to 83.7°, while on the S-exposed side, it decreases to 79.7°. The relaxation in the less stable (10 $\overline{1}$0)b edge is more pronounced. The S-Mo-S bond angles on the two edges are 90.7° and 48.7°. The (1$\overline{2}$10) relaxes in a similar manner.

![Diagram of MoS$_2$ edges](image)

**Figure 3:** Side views along the relaxed MoS$_2$ edges. Each figure shows one or more unit cells of a 4-MoS$_2$-unit wide ribbon which repeats into and out of the page. The left and right sides of each view are the actual edges.

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1 Structure files are available from the authors upon request.
Figure 4: Top views of the two most stable relaxed edges. Here the coordination of the edge Mo and S atoms is easily seen. Some Mo-Mo distances and Mo-S bond lengths near the edges are shown. Those distances which are not marked are within 0.1 Å of the lengths from the optimized 2-D sheet, $d$(Mo–Mo) = 3.16 Å and $d$(Mo–S) = 2.42 Å.

Table 2: Relaxed energies of the various MoS$_2$ edges, measured per unit cell of the ribbon. All calculations were done with 4 × 2 unit cells. The large relaxation energy of the (1011x) edge is due to reconstruction of the S atoms along that edge.

<table>
<thead>
<tr>
<th>Edge</th>
<th>$E_{\text{tot}}$(relaxed) (eV)</th>
<th>$E_{\text{edge}}$(relaxed) (eV/MoS$_2$ unit)</th>
<th>$\Delta E_r$ (eV/MoS$_2$ unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10110) b</td>
<td>-188292.69</td>
<td>2.99</td>
<td>-1.31</td>
</tr>
<tr>
<td>(10110) a</td>
<td>-188295.88</td>
<td>2.19</td>
<td>-0.06</td>
</tr>
<tr>
<td>(1210)</td>
<td>-188296.81</td>
<td>1.96</td>
<td>-0.17</td>
</tr>
<tr>
<td>(1211x)</td>
<td>-188298.48</td>
<td>1.54</td>
<td>-0.89</td>
</tr>
<tr>
<td>(1011x)</td>
<td>-188298.83</td>
<td>1.45</td>
<td>-1.28</td>
</tr>
</tbody>
</table>
Figure 5: A metastable geometry for the (10\bar{1}x) edge. The local minimum is obtained from a direct optimization of the unrelaxed geometry, while the true minimum in Figure 4 derives from a slightly disordered unrelaxed geometry. When the symmetry is broken, the optimizer finds the more stable configuration, leading to an energy 0.25 eV per edge MoS$_2$ unit lower than this symmetric configuration. Note that the coordination of the Mo atoms on the right is only 5 and the S atoms on the left have not assumed their up-down configuration seen in Figure 3.

The behavior of the diagonally-cut edges is somewhat different. The (1\bar{2}1x) edge is simpler, so it is discussed first. The edge S atoms move into the Mo-plane (Figures 3 and 4), keeping the same coordination and roughly the same Mo-S bond lengths. The Mo atoms move slightly inward. The Mo-Mo distances and Mo-S bond lengths are given in Figure 4. On the right-hand edge, one Mo-Mo distance between unsaturated atoms decreases to 2.55 Å. These atoms are almost bonded.

In the (10\bar{1}x) edge, something unique happens. Direct optimization of the bulk-derived coordinates can yield a local minimum of energy at the geometry shown in Figure 5. The relaxation of the S atoms closely resembles that described below for the (MoS$_2$)$_7$ cluster. In this periodic system, however, a deeper minimum is obtained with a slight shift of the edge S atoms on both sides. These edge S atoms were initially moved 0.1 Å in random directions. This leads to the fully relaxed geometry shown in Figure 4. The Mo atoms on
the right edge change coordination from a trigonal prismatic with one S vacancy to trigonal prismatic with the axis now parallel to the edge. The Mo atoms on the left edge assume a distorted tetrahedral configuration. The Mo-Mo distances are shown in Figure 4.

![Graph](image)

**Figure 6:** Test of the convergence of $E_{\text{edge}}$ for two representative edges as the ribbon becomes wider. The $4 \times 2$ ribbon is sufficient according to this result. The energies are shown for the $(1\bar{2}10)$ (solid), and $(1\bar{2}1x)$ (dashed) edges.

In this study, we also examined various ribbon widths to determine when edge-edge interactions were minimized. For the $(1\bar{2}10)$, $(10\bar{1}x)$ (symmetric partial optimization), and $(1\bar{2}1x)$ edges, $E_{\text{edge}}$ converges to within $9 \times 10^{-3}$ eV by the $4 \times 2$ size (see Figure 6). The $3 \times 2$ ribbons are within 0.02 eV, while the energy of the $2 \times 2$ ribbons varies by up to 0.7 eV from the larger sizes. The conclusion is that the $4 \times 2$ ribbon size is large enough to minimize the undesired interactions between edges, and this size ribbon will be used for all subsequent calculations.

4. Electronic Structure of Edges

The edge defect in an MoS$_2$ sheet dramatically changes the electronic structure. The valence- and conduction-band DOS for a 2-D MoS$_2$ sheet and for the most stable edges, $(1\bar{2}1x)$ and $(10\bar{1}x)$, are depicted in Figure 7. In the 2-D sheet, five peaks are found in the valence band, as in previous valence band X-Ray photoelectron spectroscopy measurements by Park, et al. [10]. The peak positions for both the experiment and present work were determined by a fit to a series of Gaussian functions. The results are compared
in Table 3. The peak intensities do not match because the Scofield cross section [43] for Mo atoms is higher than for S atoms [44], so those peaks which are of Mo character are emphasized in the experimental DOS.

The band structure of 2-D MoS$_2$ is shown in Figure 8. In the MoS$_2$ sheet, the HOMO appears at the top of the valence band, while the LUMO is at the bottom of the conduction band. The band gap is 1.8 eV, and valence band width is calculated to be 5.8 eV. For comparison, the experimental band gap of bulk MoS$_2$ is 1.29 eV [45].

**Figure 7:** Calculated valence band and conduction band DOS of the 2-D MoS$_2$ sheet (black) and the most stable 1-D edges, (121$_x$) (blue) and (101$_x$) (red). The DOS plots have been smoothed with a Gaussian having a FWHM of 0.5 eV. The HOMO energy in each case is marked with a vertical line.

**Table 3:** Valence-band peak locations (eV) from experiment [10] and the present calculations. The peaks are labeled by binding energy from the least to the most bound. The energies of the present calculation have been shifted so that the energy of peak A matches.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Park [10] Experiment</th>
<th>Present Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-2.54</td>
<td>-2.54</td>
</tr>
<tr>
<td>B</td>
<td>-3.83</td>
<td>-3.69</td>
</tr>
<tr>
<td>C</td>
<td>-5.12</td>
<td>-4.93</td>
</tr>
<tr>
<td>D</td>
<td>-5.88</td>
<td>-5.69</td>
</tr>
<tr>
<td>E</td>
<td>-7.25</td>
<td>-6.93</td>
</tr>
</tbody>
</table>
Figure 9 shows the edge band structure. Because the model is one-dimensional, there is only one direction in $k$-space. For the $(\bar{1}21x)$ edge, this is the $\Gamma$-$M$ direction, while for the $(10\bar{1}x)$ edge, it is the $\Gamma$-$K$ direction. Figure 10 shows the part of the band structure close to the Fermi level. The $(\bar{1}21x)$ edge is calculated to be semi-conducting, with the HOMO at the top of the valence band. There is a reduced, direct band gap of only 0.52 eV at the $\Gamma$-point (Figure 9, Left).

![Figure 8](image)

**Figure 8:** Upper valence band structure of the 2-D MoS$_2$ sheet.
Figure 9: Valence band structure of the (121x) and (101x) edge models of MoS$_2$. The HOMO energies are marked with black lines. The HOMO of the (101x) edge is below the top of the valence band. Here $k_y$ is in units of $2\pi/a$, where $a = 6.32$ Å is the lattice constant for the (101x) edge and $a = 5.473$ Å for the (121x) edge.
The HOMO of the \((10\bar{1}x)\) edge, however, appears \(~0.1\) eV below the top of the valence band (Figure 9, Right), leading to a Fermi edge, indicating a metallic character, in agreement with previous work [27,46]. There is one valence state just above the Fermi level.

\[ \text{Figure 10:} \text{ Upper valence band structure of the } (1\bar{2}1x) \text{ and } (10\bar{1}x) \text{ edges of MoS}_2. \text{ The Fermi energies are marked with black lines which separate the HOMO from the LUMO. An electron in the HOMO of the } (10\bar{1}x) \text{ edge has an effective mass of } 1.9 \text{ } m_e. \text{ Here } k_y \text{ is in units of } 2\pi/a, \text{ where } a = 6.32 \text{ Å is the lattice constant for the } (10\bar{1}x) \text{ edge and } a = 5.473 \text{ Å for the } (1\bar{2}1x) \text{ edge.} \]
Figure 11: Experimentally derived band structure of MoS$_2$ as determined by Böker [45] (circles) and the present calculation of the 2-D MoS$_2$ sheet (black lines) and 3-D Bulk MoS$_2$ (green lines).
The experimentally derived band structure of Böker [45] is compared with the 2-D sheet and the 3-D bulk MoS$_2$ band structures in Figure 11. The experimental valence band width is about 6 eV, while the band gap is 1.29 eV. Our calculations of the 2-D MoS$_2$ sheet show a valence band width of 5.8 eV and a band gap of 1.8 eV. 3-D MoS$_2$ has a calculated valence band width of 6.9 eV and a band gap of 0.95 eV. The GGA functional is well-known to produce a poor band gap estimate, so this is expected.

A graphical representation of HOMO of the (10$ar{1}$x) edge, a surface state, is shown in Figure 12. This state contains components of the 3p orbitals of the edge sulfur atoms, the 4d$_{z^2}$ orbital of the Mo atoms nearest to the edge, and lesser contributions of other atoms. From the top view, we can see that this orbital is bonding both parallel and perpendicular to the edge.

The bonding nature of this state in the propagation direction is reflected by its increasing orbital energy as the value of $k_x$ increases from zero at the Γ-point to higher values (Figure 9). The positive curvature of $\epsilon_{HOMO}$ dispersion means that the effective mass of

![Top View](image)

![Side View](image)

**Figure 12:** Surface state of the Mo-exposed side of the (10$ar{1}$x) edge. This orbital is the HOMO at the Γ-point. Clearly seen are the edge sulfur p contributions, along with d orbitals of the edge Mo atoms aligned along the edge. The contributions of other atoms fall off as the distance from the edge increases. The orbital is cut off in the front and back by the walls of the repeating unit cell, leading to the white “hole” artifact seen in the ring of the Mo d orbital.
an electron in that state is positive, and therefore the \((10\bar{1}x)\) edge will have an n-
conducting character in this direction when partially occupied due to a thermal
excitation. The curvature yields an effective mass of \(1.9 m_e\), where \(m_e\) is the mass of a
free electron. This behavior is just opposite to that of the top of the 2-D valence band,
which has a negative curvature of \(\varepsilon_{\text{HOMO}}\) and a negative effective mass of an electron
giving rise to p-conductivity with an effective mass of a hole of \(4.1 m_e\). In the \((10\bar{1}x)\)
model, it is the HOMO-1 which resembles the \(\varepsilon(k)\) curve of the bulk.

Further into the Brillouin zone, the LUMO and HOMO of the \((10\bar{1}x)\) ribbon become
degenerate (or nearly degenerate) at \(k = 0.4(2\pi/a)\) and appear to switch their
occupancies at higher \(k\) values up to \(\pi/a\), the zone boundary, where the “new” HOMO
again has a positive curvature of energy in \(k\)-space.

Even in this complicated system, the surface state behavior perpendicular to the edge
follows that of surface states of a one-dimensional finite slab [47]. Specifically, the
orbital is not concentrated solely on the surface itself; it extends into the sub-surface
layers. The form of the wavefunction in the 1-D case is a decaying exponential, where the
rate of decay is determined by the perturbation of the atomic orbitals by the surface [47].
In this case, the depth of the surface state is about two layers, though different Mo d
orbitals are involved on the surface and in the bulk.

5. Cluster Models

Stoichiometric clusters of composition \((\text{MoS}_2)_n, n = 1, 2, 3\) and \(7\), were examined
theoretically in order to assess the energies of formation and relaxation, and compare
those with similar energy relationships calculated for edges in periodic systems, cf.
Section 3.2 above. The clusters were chosen to include structural motifs of a monomer
\((n = 1)\), dimer \((n = 2)\), trimer \((n = 3)\) and heptamer \((n = 7)\), with sites exposing Mo atoms
surrounded by various numbers of coordinated S atoms \((2, 3, 4, 5, 6)\) and sites
exposing \(1, 2\) and \(3\) S atoms. While several metastable geometries could be expected for
each cluster size, the optimized structures in Figure 13 represent nuclei that can grow to
the periodic layer by stepwise addition of MoS\(_2\) molecular units. The driving force for the
crystal growth is the decrease of total energy per MoS\(_2\) formula with increasing cluster
size. Furthermore, the clusters of this type are shown to have peripheral sites similar to
those appearing at the edges of the periodic structures. The formal oxidation state of
molybdenum in all clusters and periodic edge structures examined is Mo(IV), [Kr] 4d\(^2\).
This oxidation state is realized in the single MoS\(_2\) molecule [22] as well as in the perfect
MoS\(_2\) crystal. Clusters with \(n = 2, 3, 7\) and MoS\(_2\) crystals with edge defects have reactive
sites which will change the oxidation state of Mo(IV) upon adsorption of electron donor
and acceptor molecules, an issue addressed is subsequent studies, wherein the reactivity
of these sites toward hydrogen and alkali atoms (Part II), and CO (Parts III and IV) is
examined. The relative stabilities of spin singlets and triplets in the \((\text{MoS}_2)_n\) clusters were
also investigated in order to determine the role of spin multiplicity when going from
small to large clusters to solid MoS\(_2\).
The cluster structures were derived from the initial geometry of single-crystal MoS$_2$ and were subsequently optimized as follows: for $n = 1$, 2, and 3, all Mo and S atoms were allowed to move to a minimum energy configuration, i.e. the MoS$_2$, MoS$_4$, and MoS$_6$ clusters were fully optimized; for $n = 7$, only peripheral Mo and S atoms were allowed to relax. Thus the Mo$_7$S$_{14}$ cluster has an Mo$_2$S$_{10}$ kernel of the ideal crystal structure with 4 peripheral Mo and 4 peripheral S atoms relaxed, to simulate the (10$ar{1}$0) and the (10$ar{1}$x) edges examined in Section 3.2 above. The initial and the relaxed structures are shown in Figure 13. The largest, Mo$_7$S$_{14}$, cluster indeed displays relaxation of peripheral atoms, e.g. that in Figure 13(c) (left), similar to that of the edges in Figure 3 (10$ar{1}$x) (right).

These relaxed structures are in fact very similar to those labeled (10$ar{1}$0) in ref. [29]. We reserve the inclination index $x$ in (hklx) for the movement of the edge atoms from unrelaxed to relaxed structures. Furthermore, the Mo$_7$S$_{14}$ cluster is a borderline species between the high-spin smaller clusters and the zero-spin periodic MoS$_2$ crystals, as will be seen below, and has intermediate electronic properties.
**Figure 13:** Initial (top) and relaxed (bottom) structures of \((\text{MoS}_2)_n\) clusters, as viewed along the side resembling the MoS\(_2\) edges. The initial structures use the bond lengths and angles from the MoS\(_2\) crystal structure.

**Figure 14:** HOMO isosurfaces in singlet (top) and triplet (bottom) \((\text{MoS}_2)_n\) clusters.
Table 4: Energies of formation $\Delta E_f$, relaxation $\Delta E_r$, and of the triplet and singlet states in the (MoS$_2$)$_n$ clusters. All energies are expressed in eV/MoS$_2$ unit.

<table>
<thead>
<tr>
<th>Energy</th>
<th>MoS$_2$</th>
<th>Mo$_2$S$_4$</th>
<th>Mo$_3$S$_6$</th>
<th>Mo$<em>7$S$</em>{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_f$</td>
<td>0</td>
<td>-2.11</td>
<td>-1.91</td>
<td>-2.61</td>
</tr>
<tr>
<td>$\Delta E_r$</td>
<td>-1.50</td>
<td>-</td>
<td>-0.89</td>
<td>-0.20</td>
</tr>
<tr>
<td>$\Delta E_{\text{spin}}$</td>
<td>0.53</td>
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<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>$E_{\text{Triplet}}$ (relaxed)</td>
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<td>-129926.71</td>
<td>-129926.52</td>
<td>-129927.21</td>
</tr>
<tr>
<td>$E_{\text{Single}}$ (relaxed)</td>
<td>-129924.07</td>
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<td>-129926.49</td>
<td>-129927.20</td>
</tr>
<tr>
<td>$E_{\text{Triplet}}$ (unrelaxed)</td>
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<td>-</td>
<td>-129925.63</td>
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<tr>
<td>$E_{\text{Single}}$ (unrelaxed)</td>
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<td>-</td>
<td>-129925.57</td>
<td>-129927.00</td>
</tr>
</tbody>
</table>

\(^a\) The Mo7S14 cluster was partially optimized by allowing movement of only the Mo and S atoms on the (101\textbar x) and (101\textbar 0) surfaces.

\(^b\) $\Delta E_f = E(\text{Mo}_n\text{S}_{2n}) - E(\text{MoS}_2)$ both being the relaxed ground states.

\(^c\) $\Delta E_r = E_{\text{Triplet}}$ (relaxed) – $E_{\text{Triplet}}$ (unrelaxed). The unrelaxed structure is that of a mathematical cut from the MoS$_2$ crystal lattice.

\(^d\) $\Delta E_{\text{spin}} = E_{\text{Single}}$ (relaxed) – $E_{\text{Triplet}}$ (relaxed).
The structural relaxations are summarized as follows: The MoS$_2$ monomer molecule is bent in both the spin singlet and triplet states, with Mo-S bonds shorter and S-Mo-S angles wider than in the crystal structure. The (MoS$_2$)$_2$ dimer is highly asymmetric and its optimize structure shows no relation to the ideal crystal. The (MoS$_2$)$_3$ trimer is highly symmetric and the exposed Mo atoms relax inward, the Mo-S bonds are longer, the S-Mo-S angles are slightly larger, and the Mo-Mo distances are significantly shorter than those in the ideal crystal structure. This attractive interaction of Mo atoms in small clusters has also emerged from CNDO/UHF calculations of Lobos [30].

Most remarkable is the similarity between structural relaxation of the peripheral atoms in the (MoS$_2$)$_7$ heptamer and the edge relaxations presented in Section 3.2 above. On the “perpendicular cut” simulating the (10T0) edge (Fig. 13-c, right), the relaxation is relatively small, while on the 'inclined cut' that simulates the (10T1) edge (Fig. 13-c, left), the relaxation is very large primarily due to the movement of the two outer S atoms from the sulfur plane in the ideal crystal to the plane of the intra-sheet Mo atoms. This latter feature closely resembles the relaxation of the periodic (10T1) edge (Figure 5 above) and has the net effect of changing the local structure of the exposed penta-coordinated Mo atoms from a trigonal prism with one sulfur vacancy to a square pyramidal site with buried Mo.

The energy relationships in Table 4 are summarized as follows: (1) Large stabilization is gained upon the cluster growth, from -2.11 eV/MoS$_2$ unit accompanying the formation of (MoS$_2$)$_2$ from the MoS$_2$ molecule to -0.70 eV/MoS$_2$ unit going from the trimer to the heptamer, all optimized for the spin triplets; (2) The relaxation energies from the unrelaxed to the relaxed structures are also large, -0.89 eV/MoS$_2$ unit in the trimer, primarily due to the Mo-Mo interaction, and -0.20 eV/MoS$_2$ unit in the heptamer, primarily due to the reconstruction of the penta-coordinated Mo site; and (3) The spin triplet is more stable than the singlet in the monomer and trimer, and is nearly equally stable as the singlet in the heptamer. The (MoS$_2$)$_n$ crystal is diamagnetic [48] and its spin singlet is most stable, as correctly accounted for by the DFT theory in earlier studies [11] as well as in the present work.
The HOMOs and the net spin density distributions in the triplet state of the clusters are shown in Figures 14 and 15. The HOMO has an Mo 4d \(_{z^2}\) character in the singlet MoS\(_2\) molecule, a mixed Mo4d-S2p character in (MoS\(_2\))\(_3\), and again Mo4d character in the largest cluster, (MoS\(_2\))\(_7\), all antibonding or non-bonding atomic-like orbitals. These results are to be compared with the well-documented Mo 4d \(_{z^2}\) antibonding character of the top of the valence band in the MoS\(_2\) crystal [10,48]. The HOMO in the triplet clusters resembles, as expected, the LUMO in the singlets. However, the triplet spin density, which represents a combined density of the hole and the electron forming the triplet (or ‘exciton’), results from spin coupling due to exchange interaction which stabilizes the electronic high-spin state in highly correlated systems. The net effect is an increased delocalization of spin density from Mo to S with increasing cluster size and a simultaneously decreasing exchange-stabilization of the triplets. At the same time, it is predicted that very small MoS\(_2\) clusters will be paramagnetic and detectable by ESR or magnetic moment measurements.

Discussion and Conclusions

Multiple edges of MoS\(_2\) basal planes have been studied by DFT using a one-dimensional ribbon model. The (10\( \overline{1} \)x) edge is found to be the most stable, though the (1\( \overline{2} \)1x) edge is found to be only 0.09 eV per edge MoS\(_2\) unit less stable. The relaxation of the edge atoms is found to be important in a description of the geometry and stability of the edges. For reference, a 2-D single sheet of MoS\(_2\) has also been modeled. The DOS of the 2-D sheet closely matches that measured by XPS [10], and the band structure is substantially identical to that previously calculated by the LAPW DFT method [11] and measured experimentally by Böker et al. [45].

The (1\( \overline{2} \)1x) is slightly higher in energy than the most stable edge, and therefore does not occur naturally. But, this edge does provide unsaturated Mo atoms which could provide for surface reactivity. Mo atoms on one edge are only 3-coordinated, while those on the other edge are 5-coordinated. The “vertically cut” (1\( \overline{2} \)10) edge is actually more stable than the (10\( \overline{1} \)0) edge by about 0.5 eV per unit cell. Both of these are less stable than the “inclined cut” edges.

The specific values of the “inclination index” \( x \) in (10\( \overline{1} \)x) and (1\( \overline{2} \)1x) cannot be determined with certainty from a single-sheet model. However, because the double-sheet structure includes the two sheets rotated with respect to each other by 180\(^\circ\), one can make a composite double-sheet edge structure by stacking two 180\(^\circ\)-rotated single sheets as shown in Figure 16. Here the red lines yield \( x = 3 \) for (10\( \overline{1} \)x) and \( x = 4 \) for (1\( \overline{2} \)1x) for stoichiometric MoS\(_2\) obtained by cuts of the ideal structure followed by relaxation. Another possible formation mechanism for the “inclined edges” is the migration of S atoms from one edge to the other, by H\(_2\)/H\(_2\)S. It has already been shown [28,17] that the (10\( \overline{1} \)0) edge will develop different structures due to adsorption and removal of S atoms.
in an H$_2$/H$_2$S atmosphere. In a pure H$_2$ atmosphere, 50% S coverage develops on both edges, which is equivalent to our (10 $\bar{1}$x) edge.

![Diagram of possible cleavage planes](image)

**Figure 16:** Possible cleavage planes which would form “inclined edges” from a single MoS$_2$ crystal.

The analysis of the electronic structure reveals surface states associated with the edges. In particular, the HOMO of the relaxed (10 $\bar{1}$x) edge is a bonding surface state with effective mass of an electron ~1.9 times the mass of a free electron. This feature stands in contrast with the “normal” electronic structure of an infinite edge-free 2-D MoS$_2$ sheet, in which the HOMO has the characteristic effective mass of a hole ~4.1 times the mass of a free electron. Thus the edge state may be viewed as an electronic “wire,” as it has been suggested by Bollinger et al. for large MoS$_2$ clusters deposited on gold [46].

In addition, small stoichiometric MoS$_2$ cluster models have been presented. These clusters exhibit much the same relaxation behavior of the infinite edges, with the exception that the Mo atoms do not change coordination on the (10 $\bar{1}$x) edge in the Mo$_7$S$_{14}$ model as they do in the periodic (10 $\bar{1}$x) edge. The calculated properties of the MoS$_2$ monomer are in excellent agreement with experimental data and theoretical results of Liang and Andrews [22] regarding the MoS$_2$ molecule isolated in solid argon, despite the different functionals, basis sets, and core potentials used, reinforcing confidence in both approaches. In the ground state $^3$B$_1$, the experimental S-Mo-S angle 114 ± 3$^\circ$ [22] agrees well with the DFT calculations, 113.5$^\circ$ [22] and 114.44$^\circ$ (present work). The calculated Mo-S bond lengths also agree, 2.132 Å [22] and 2.148 Å (present work), as does the energy difference between the excited singlet and the ground state triplet, $\Delta E(^1A_1 - ^3B_1) = 0.61$ eV [22] and 0.56 eV (present work).
The transition from high-spin molecule to zero-spin solid MoS$_2$ is reflected in the difference between the singlet and the triplet state which is just about zero in the (MoS$_2$)$_7$ cluster. The singlet-triplet bandgaps per MoS$_2$ unit are 0.53 eV for the monomer, 0.03 eV for the trimer, 0.01 eV for the heptamer. In the bulk crystal, the singlet is more stable and the bandgap is $+1.29$ eV. The triplet spin density, which represents a combined density of the hole and the electron forming the triplet (or ‘exciton’), results from spin coupling due to exchange interaction which stabilizes the electronic high-spin state in highly correlated systems. The net effect is an increased delocalization of spin density from Mo to S with increasing cluster size, as seen in Figure 15, and correspondingly weakened exchange-stabilization of the triplets. Based on these results, it is predicted that small (MoS$_2$)$_n$ clusters ($n \leq 7$) will be paramagnetic with chemical properties appropriate to their spin state.

All of the present results indicate that the high-energy edge surfaces and peripheral groups of atoms in small clusters undergo very large structural relaxations associated with significant energy stabilization. These phenomena no doubt play an important role in accessibility of reactive sites and in chemisorption of molecules that are activated for catalytic reactions on these sites.

**Acknowledgments**

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**References**


**Appendix B: Electronic Structure and Reactivity of Defect MoS₂ II. Bonding and Activation of Hydrogen on Surface Defect Sites and Clusters**

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May 20, 2004

The defects of MoS₂ were investigated for activation of hydrogen using density functional theory by modeling the molybdenum disulfide monomer, small clusters, and edges in periodic structures. Attachment of H₂ to the MoS₂ molecule was studied in detail, and several structures were found by optimization methods. A dihydride with the hydrogen atoms far apart was determined to be most stable. In this configuration, the σ* orbital of the H₂ mixes with the 4d orbitals of Mo and 3p orbitals of S to achieve the hydrogen activation. The less stable η² hydrogen configuration has the H-H bond slightly stretched with the H atoms equidistant from the Mo center. A triangular Mo₇S₁₄ cluster provides a small model with edges resembling those of the cut MoS₂ sheets. On this cluster, both the η² hydrogen and the dihydride occur.

In the periodic system, atomic hydrogen adsorbs in stable positions on the MoS₂ edges either bridging between Mo atoms or attached to Mo or S atoms. The frequencies of H vibrations are found to be highly dependent on the atom(s) to which the hydrogen is attached, and range from 1223 cm⁻¹ for a position bridging two Mo atoms, to about 1860 cm⁻¹ for Mo–H bonds, to about 2500 cm⁻¹ for S–H bonds. In addition, some configurations with molecular H₂ adsorption on the edges were investigated, and the H–H frequency of 2999 cm⁻¹ was calculated for a dihydride configuration.

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Introduction

Hydrogen, the most plentiful element in the universe, shows great promise as a fuel because it is nontoxic, exhibits clean combustion, and provides high-energy gain per electron [1]. Since the 1970’s, study of hydrogen production and storage has mushroomed into the broad and multifaceted field it is today. A major current use of hydrogen is in the catalytic industry: in hydrogenations of unsaturated hydrocarbons, hydrogenolysis and hydrocracking in petroleum reforming, selective hydrogenations of oxygen and nitrogen-containing compounds, hydrodesulfurization and hydrodenitriﬁcation of heavy residues, and many other catalytic processes. An important class of hydrogenation catalysts are sulfides, in particular those of molybdenum, tungsten, and their composites with transition metals [2,3]. The activation of hydrogen is but a part of the above catalytic processes, and there is a general agreement that it takes place on defects such as edges and other structural features of the “shaggy rag” high surface area solids that are the reactive sites of the sulfides [3]. One of the most fascinating properties of sulfides is their ability to catalyze methanol and higher alcohol synthesis from CO and hydrogen in the presence of alkali compounds [4,5], which has been reported to run continuously without the presence of H₂S in the synthesis gas [5]. Although the defects are formed during the preparation of the entire solid catalyst, much can be learned from well-deﬁned molecular complexes such as those investigated by the methods of organo-metallic chemistry. Most importantly, evolution of the surface defects may be unraveled by studying the properties of particles ranging from single metal-center complex to clusters to periodic solids. In the present work, we have undertaken this task with the help of theory and available experimental knowledge.

Hydrogen is now known to exist on single centers in organometallic complexes as either reversibly bonded hydrogen molecules, called η²-H₂, or dihydrides as shown below:

\[
\begin{align*}
\text{L}_\text{a}M & \quad \text{H} \quad \text{L}_\text{a}M \quad \text{H} \\
\quad \text{Η}_2 \text{H}_2 \text{complex} & \quad \text{dihydride complex}
\end{align*}
\]

where L is a ligand and M is a transition metal. In 1983, metal complexes with reversibly bonded molecular hydrogen were isolated for the first time [6]. Such complexes were previously thought to be unobservable intermediates, but neutron diffraction data provided conclusive evidence for their existence on W(CO)₅(P-i-Pr)₂. Molecular orbital analysis of the activation of hydrogen on transition metal complexes suggested that activation occurs by transfer of electrons from an occupied metal d orbital to the H₂ antibonding orbital [7].

Further analysis has yielded a pathway picture whereby the hydrogen molecule initially approaches the organometallic complex end-on, but then forms an η²-H₂ complex, or non-classical hydride, as the distance between the reactants decreases
[8,9,10]. On some transition metal complexes the molecular hydrogen subsequently cleaves to form a "classical hydride" [7,9,10,11,12]. Lin and Hall [9] analyzed hydrogen bonded to various transition metal complexes with phosphine ligands for periodic trends of classical and non-classical bonding (Figure 1). They discovered that classical hydrides occur on transition metals that have more diffuse d orbitals, and are heavier. For some transition metals, both dihydrides and $\eta^2$-hydrides can occur.

In contrast to organometallic complexes, there is ample evidence that the activation and adsorption of hydrogen on metal surfaces occur by direct impact mechanism and involves several metal atoms [13]. This is supported by molecular beam experiments [14] as well as quantum dynamics modeling [15,16] that distinguished between activated “end-on” and barrier-free “parallel-to-surface” dissociation of H$_2$. While exemplified on palladium, this physical picture is applicable to many transition metals. One of the basic features of this kind of hydrogen activation is partial loss of translational and rotational entropy associated with reorientation of the H$_2$ molecule into the barrier-free dissociative path. This semiclassical aspect of the process, with addition of tunneling, was addressed by Klier [17] who was able to quantitatively account for the molecular beam observations. Tunneling was found to be significant only at high incident translational energies, and therefore the entropy penalty is the dominant factor in limiting the rate of even zero-barrier H$_2$ adsorption under normal thermal velocity distributions.

The very widely used hydrogenation catalysts based on transition metal sulfides appear to be far less understood than organometallic complexes and metals, even as regards H$_2$ activation only. Based on experimental observations and interpretation thereof, H$_2$ dissociation has been proposed to occur heterolytically over metal-sulfur neighbors [18,19], in analogy with that on ZnO based on IR observations of O=H and Zn-H frequencies [20,21], or homolytically over two sulfur neighbors [22,23], but not homolytically over exposed metal centers to form dihydrides or $\eta^2$-H$_2$ species similar to those of organometallic chemistry. There is therefore a need to abridge the mechanistic gap between the single metal-center bound dihydrogen and the solid surface-based metal and sulfur-bound hydrogen. Despite the significant effort, the large body of existing knowledge appears fragmentary, conflicting, and no guiding principles emerge from it. This can be gleaned from reviewing the literature available as of now, exemplified with dissociative H$_2$ chemisorption on MoS$_2$. Molybdenum disulfide is known to activate molecular hydrogen for hydrogenation reactions and is widely used in hydrogenation catalysis [2,24,25]. Despite reports of large amounts of hydrogen adsorbed, absorbed and chemisorbed on molybdenum disulfide [26], to this day direct spectroscopic evidence for surface species such as Mo hydrides and sulhydrials appears to be lacking. There is indirect evidence indicating the existence of surface --SH species based on neutron scattering spectroscopy in the region overlapping with lattice vibrations of MoS$_2$, but to our knowledge no reproducible stretching S--H or Mo--H vibrational modes have ever been reported using IR and Raman spectroscopy. Ratnasamy and Fripiat reported stretching vibrations for surface S--H on MoS$_2$ in 1970 [27], but the work was deemed irreplicable [18]. In contrast, there is abundant spectroscopic evidence of this type (in addition to NMR) for hydrogen bonded as hydrides and dihydrides to metal centers in organometallic complexes, as discussed previously. In a recent comprehensive study,
Bollinger, Jacobsen and Nørskov investigated the electronic structure of MoS$_2$ triangular nanoparticles deposited on Au(111) surface, both experimentally by STM and using density functional theory [28]. These authors also examined adsorption of hydrogen on the MoS$_2$ edges and relative stabilities of various edge structures as a function of H$_2$S/H$_2$ and the system’s thermodynamic potentials. We have previously reported some common features regarding the hydrogen-free MoS$_2$ edge electronic structure, in particular the metallic character of extended edge surface states [29] that agree well with the earlier results of Byskov et al. [22]. In addition to the reactivity of edges, we presently examine clusters with exposed corner atoms and the MoS$_2$ monomer, for which we reported a full agreement with the results of Liang and Andrews [30]. The most stable conformer of the monomer is a spin triplet, the intermediate cluster Mo$_7$S$_4$ has nearly equally stable triplet and singlet conformers, and bulk MoS$_2$ is a diamagnetic zero-spin entity. It is therefore of interest to examine the effect of the spin states and metallic edges on hydrogen chemisorption. We focus on stoichiometric MoS$_2$, as this has been suggested to be the active form of this solid in alcohol synthesis [5]: this reaction ran without H$_2$S, and H$_2$S was not released upon a long use of the catalyst in H$_2$/CO synthesis gas. In a subsequent paper, we will report on a dramatic promotion of hydrogen activation by alkali.

The vibrational frequencies of the $\text{–SH}$ groups in various organic compounds are also well documented by IR and Raman spectroscopies [31]. The frequency range for the S–H stretching mode is 2500–2600 cm$^{-1}$ [32,33]. The frequency range for the Mo–H modes is 1800–2000 cm$^{-1}$. In addition, adsorbed undissociated molecular species H$_2$, H$_2^\delta^+$ and H$_2^\delta^-$ should be considered, as they have been argued to exist on metals based on conductivity and work function measurements [13,34], and recently proven to exist in silicon [35]. Reasons for the lack of detection of hydrogen species on MoS$_2$ solids may be the high absorbance of this material in the region of S–H and Mo–H stretching modes as well as low concentrations, low oscillator strengths particularly for weakly adsorbed H$_2$, and homogeneous or inhomogeneous line broadening.

In the present study, we make theoretical predictions regarding the existence of stable hydrogen species on various defects on MoS$_2$ surfaces and clusters. Monohydrides and dihydrides are predicted to be formed on exposed low-coordinated Mo sites on edge facets of the periodic MoS$_2$ crystals broken along crystallographic directions shown to form edges of varying degree of stability in our preceding paper [29]. The question of heteropolar splitting of molecular hydrogen to surface Mo–H and S–H moieties and homopolar splitting into two S–H groups that has been suggested to occur on pyritic sulfides [36] is also addressed. The present study is accompanied by calculations of vibrational frequencies which allow an assessment of thermodynamic free energies of adsorption as well as a clear distinction between high-frequency local vibrational modes of S-H, Mo-H, Mo-H$_2$, and Mo-H-Mo species that are verifiable by experiment.
Computational Methods

The computational tools employed in this study have been described in detail previously [29]. Briefly, all calculations use Density Functional Theory (DFT) [37,38]. Periodic systems were modeled using the DMol³ software package in the Cerius² modeling environment [39]. The double-numerical basis set is calculated by solving the Kohn-Sham equations for the individual atoms within the same DFT model as the whole calculation [40]. An effective core potential (ECP) [41] was employed for the Mo atoms to reduce the size of the basis set. DMol³ uses the GGA functional by Perdew and Wang [42]. MoS₂ clusters were modeled within the Spartan v5.1.3 framework [43] with an all-electron double-numerical basis set (DN**) and the BP86 generalized gradient (GGA) functional [44,45].

Geometry optimizations used the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [46] Hessian updating scheme, starting with the ideal bulk-derived MoS₂ coordinates. At times, the initial positions of some atoms were shifted slightly to break the symmetry and allow the structure to find its natural minimum.

Vibrational frequencies of the H₂-MoS₂ monomer and its reactants, H₂ and MoS₂ molecules, were obtained by a full diagonalization of the Hessian matrix concurrent with geometry optimization, resulting in 9 non-degenerate modes of the stable H₂-MoS₂ spin singlet and metastable H₂-MoS₂ spin triplet, 3 modes of the stable MoS₂ spin triplet, and the stretching mode of the singlet hydrogen molecule. Frequencies in the periodic system were calculated using a partial frequency method built into DMol³. Only the hydrogen atoms were moved, giving an explicit calculation of the Hessian matrix elements for those components. The remaining elements of the Hessian matrix, corresponding to motions of the Mo and S atoms, were filled with a diagonal matrix containing estimated force constants of 0.2 a.u. This estimated Hessian matrix was then fully diagonalized. The partial frequency method was tested on the H₂–MoS₂ molecule, where the full Hessian is easily calculated. The frequencies for stretching bonds of the hydrogen atoms calculated by this method were to within 0.2 cm⁻¹ of those calculated by moving all atoms. For a pure MoS₂ system, the partial frequency method predicts vibrational frequencies of 234.7 cm⁻¹ and 406.0 cm⁻¹ for motions of the Mo and S atoms, respectively.

Results

1. Cluster Calculations of MoS₂ with Hydrogen

To begin our study, we examined bonding of hydrogen to the MoS₂ monomer. Hydrogen is bonded more weakly with increasing size of clusters, so the monomer shows the strongest hydrogen attraction. The general theory of molecular hydrogen bonding to metals was recently reviewed by Kubas [8]. In his theory, Kubas categorized the H₂–metal bond as an π⁻–H₂ complex when the H–H distance is small (< 0.9 Å), an elongated H₂ complex for intermediate H–H distances, or a true dihydride only when the H–H
distance is larger (>1.6 Å). The present DFT calculations revealed both dihydride and \( \eta^2 \)–H\(_2\) formation on the MoS\(_2\) molecule.

The reaction of H\(_2\) with the MoS\(_2\) monomer was found to be exothermic and released about 1.17 eV (Table 2). The resultant H\(_2\)–MoS\(_2\) molecule (Figure 2a) had the symmetry \( C_{2v} \) and a singlet spin state. The spin is somewhat surprising, as the H\(_2\) molecule is a singlet while the MoS\(_2\) monomer was found to be most stable in the triplet state [29,30]. The H–H distance was 3.08 Å and the Mo–H distances were 1.72 Å, consistent with a dihydride configuration. The H–Mo–H bond angle was 128°.

Two metastable configurations of H\(_2\)–MoS\(_2\) have been found. One is a “tilted” singlet state in which the \( C_{2v} \) symmetry is broken by the movement of the H atoms to one side (Figure 2b). The H and Mo atoms do lie on a mirror plane, so the overall symmetry is \( C_s \) (or \( C_{1h} \)). The energy of this state is 0.35 eV higher than the minimum, the H–H distance is 1.65 Å, and the H–Mo–H bond angle is 59°.

The other metastable geometry is the triplet configuration shown in Figure 2c. It maintains the \( C_{2v} \) symmetry, but the H–H distance is much smaller, only 0.80 Å. The triplet energy is about 0.65 eV above the singlet minimum. The Mo-H distance is 2.04 Å, while the H–Mo–H bond angle is 22.5°.

Because this configuration has the same spin state as the separated MoS\(_2\) and H\(_2\) molecules, it is likely that the combination will first form this H\(_2\)–MoS\(_2\) triplet, then later change into the ground state singlet configuration. How this occurs gives insight into the interaction between the Mo center and the H\(_2\) molecule that can help unravel the mechanism for dissociative hydrogen adsorption on the MoS\(_2\) edges found in the solid.

2. Coordinate Driving

To calculate reaction rates and activation barriers between the described H\(_2\)–MoS\(_2\) structures, a continuous path through which the molecule can travel between the triplet and singlet configurations must be found. For this goal, constrained optimizations were performed. The chosen constraint was the H–Mo–H bond angle (\( \theta_H \)), as it is the most obvious visual difference between the ground state and triplet configurations. The H\(_2\) molecule is separated from MoS\(_2\) when \( \theta_H \rightarrow 0 \). In the \( \eta^2 \)–H\(_2\) geometry, as \( \theta_H \) is varied continuously from ca. 10° through the stable triplet value of 22.5°, the molecule maintains the triplet electronic state and no activation barrier is present. For larger \( \theta_H \) the energy of the triplet state increases, but this triplet pathway is crossed by other “downhill” pathways which favor singlet states at \( \theta_H > 25° \). It is either of these singlet pathways that lead to the formation of stable dihydride with \( \theta_H = 128° \). The energies of the triplet and two singlet pathways are plotted as a function of \( \theta_H \) in Figure 3. Along one singlet path, the “tilted” configuration was an intermediate (Figure 3, red line), while the other singlet path maintained the \( C_{2v} \) symmetry (Figure 3, green line).
3. Orbital Analysis

In his discussion of dihydride formation on metal complexes, Kubas [8] stressed the importance of overlap of the antibonding H$_2$ $\sigma^*$ orbital with orbitals of the metal center. The overlap creates a molecular orbital which is a mixture of an occupied d orbital in the metal with the $\sigma^*$ orbital of the H$_2$. The resulting partial occupation of the $\sigma^*$ is termed *backdonation*. Figure 4 shows the orbitals with the strongest H $\sigma^*$ contributions for the singlet and triplet configurations. In the singlet, this molecular orbital joins the H$_2$ $\sigma^*$ with the Mo4d and S3p orbitals and is doubly occupied, as required by the zero total spin. In the triplet state, the $\sigma^*$-metal d orbital is only half occupied, while at the same time, the $\sigma$ orbital of the H$_2$ is stabilized, leading to the $\eta^2$-H$_2$ configuration of that complex.

The combination of H$_2$ with MoS$_2$ involves mainly a few “valence” orbitals. These originate from the 1s orbitals of H, the 4d and 5s orbitals of Mo ([Kr]4d$^4$5s$^2$), and the 3s and 3p orbitals of S ([Ne]3s$^2$3p$^4$). These levels are occupied by 18 electrons of MoS$_2$ and 2 electrons of H$_2$. Figure 5 shows the energies of the top valence orbitals of the separated H$_2$ and MoS$_2$ molecules, along with those of the triplet and singlet H$_2$–MoS$_2$ complexes. The deeper levels originating from S3s and below are omitted in this figure, although all orbital energies including those of all core levels were calculated. The total number of electrons is 76. The numbering of atomic or molecular orbitals follows increasing orbital energies. Thus in spin-balanced singlets there are 38 doubly occupied orbitals, and in triplets 39 orbitals occupied with spin-up and 37 with spin-down. Omitting the four 3s electrons of the two S atoms, the number of valence electrons represented in Figure 5 is (18+2) – 4 = 16. Valence orbitals from 31 up are shown along with the H$_2$ $\sigma$ and $\sigma^*$ orbitals. In the transition from separated molecules to the triplet state, the predominant change in the orbital energies was the stabilization of the H$_2$ $\sigma$ orbital. In particular, there was no change in the number of occupied orbitals of each symmetry. The singly-occupied B1 symmetry orbital number 38 of the MoS$_2$ molecule came down slightly in energy, but not enough to cause the ground electronic state to be a singlet.

In the singlet state, there are several differences compared to the triplet. With increased separation of the H atoms, the gap between the MOs originating from the H–H $\sigma$ and $\sigma^*$ orbitals was reduced. This caused the rise in the energy of the lowest valence orbital number 31. At the same time, the orbitals with $\sigma^*$ character (34 and 37 in Figure 5, right) became more stabilized.

4. Hydrogen on MoS$_2$ clusters

Calculations on larger clusters provided more information about the nature of adsorption sites and energies. As the cluster size increased, hydrogen was bonded more weakly. In our previous report [29] we presented calculations of an Mo$_7$S$_{14}$ cluster with edges similar to those found in solid MoS$_2$. The edges with exposed Mo were like the Mo-exposed (10\overline{1}0) edge of the MoS$_2$ solid, while the edge with single exposed S atoms resembled the Mo-exposed (10\overline{1}x) edge.
This Mo\textsubscript{7}S\textsubscript{14} cluster was now investigated for hydrogen adsorption in multiple locations. The \((\text{MoS}_2)_7 + 5\text{H}_2\) cluster is pictured in Figure 6, showing edge-like sites, exposed S sites, and exposed Mo sites. The purpose of examining this model was to investigate whether similarities and differences if any exist between a cluster of this intermediate size, the monomer, and extended edge structures. The overall energy for the reaction

\[
(\text{MoS}_2)_7 + 5\text{H}_2 \rightarrow \text{H}_{10}(\text{MoS}_2)_7
\]

was calculated to be +3 kcal/mol \text{H}_2, slightly endothermic. On this cluster, both \(\eta^2\)-\text{H}_2 and the dihydride form were observed, with H–H distances of 0.82 Å and 1.97 Å. While the dihydride resembled the stable spin-singlet dihydride on the MoS\textsubscript{2} monomer, the \(\eta^2\)-\text{H}_2 appeared to be similar to the metastable spin-triplet \text{H}_2-MoS\textsubscript{2} monomer. Interestingly, no S-H species was found on the monomer or the \(\text{H}_{10}(\text{MoS}_2)_7\) cluster, in difference to the stable S-H species found on periodic edges both by Bollinger et al. [28] and in the present calculations summarized in 3.5.

5. Adsorption of Hydrogen on Periodic MoS\textsubscript{2}

The basal plane (0001) of MoS\textsubscript{2} is quite stable and was found to be unreactive to hydrogen. The H atoms were adsorbed releasing at most −0.59 eV of energy per atom in positions over the sulfur atoms or in the hollow site between three sulfur atoms above the Mo-plane. The dissociation energy of the hydrogen molecule was +2.28 eV/atom using the same theoretical model, so clearly dissociative adsorption of the hydrogen molecule on the basal plane would not occur.

Figure 7 shows the \((\overline{1}2\overline{1}x)\) and \((10\overline{1}x)\) edges of solid MoS\textsubscript{2}. Several adsorption sites for hydrogen atoms on these edges were tested. Both edges have two complementary sides. These are labeled in Figure 7 as the S and Mo sides on \((10\overline{1}x)\), while they were denoted as the S and MoS sides on \((\overline{1}2\overline{1}x)\).

For each hydrogen adsorption location, the atoms in half of the unit cell were allowed to relax to a stable configuration. The edge geometries are shown in Figure 8. The calculations were performed with a 4×2 or 5×2 unit cell of MoS\textsubscript{2} and a single hydrogen atom. The cell size was chosen so that adding MoS\textsubscript{2} units to the far side of the unit cell did not affect the adsorption energies. The adsorption energies were calculated for dissociation of molecular hydrogen on identical neighboring sites. The reaction is

\[
\text{H}_2 + 2(\text{MoS}_2)_n \rightarrow 2(\text{H}(\text{MoS}_2)_n)
\]

where \(n = 8\) or 10 depending on the unit cell size. The adsorption energy is then defined as

\[
\Delta E_{\text{ads}} = 2E(\text{H}(\text{MoS}_2)_n) - [2E((\text{MoS}_2)_n) + E(\text{H}_2)]
\]
With this definition, negative energies correspond to exothermic reactions. The final adsorption energies of each configuration are given in Table 3. The table also includes thermodynamic energies calculated as described in Section 3.6.

The strongest binding of hydrogen was found on the (11̅1x) edge, S side, over the second-row S atom (“S2-top”, cf. Figure 8). With $\Delta G_{\text{ads}} = -0.70$ eV (c.f. Section 3.6), there was more than enough energy to dissociate the $\text{H}_2$ molecule and overcome the thermodynamic penalties. The interest here, in addition, is in adsorption on the metal centers. The strongest binding near Mo atoms was the Mo-bridge configuration on the S side of the (10T̅x) edge, $\Delta E_{\text{ads}} = -0.34$ eV. This configuration notably had the lowest vibrational frequency of only 1222.8 cm$^{-1}$, while non-bridge positions had frequencies of at least 1700 cm$^{-1}$ (Table 3). The Gibbs energy change of this configuration, however, is +0.13 eV, so it is thermodynamically forbidden at room temperature.

The most exposed Mo atom of all of the examined edges was the Mo atom on the MoS side of the (11̅1x) edge. It is coordinated to only three S atoms in an approximately trigonal planar configuration. The expectation that this atom is especially reactive is tempered by the positive Gibbs free energy change of +0.77 eV. The Mo atom on the opposite, S side of (11̅1x) was found to have a lower affinity for the H atom, with a Gibbs free energy change of +1.36 eV. The vibrational frequencies of the H atom at the two sites were close, 1862.8 cm$^{-1}$ on the S side and 1862.4 cm$^{-1}$ on the MoS side.

Previous work by Cristol et al.[23,47] examined hydrogen adsorption on various MoS$_2$ edges with DFT using a plane-wave pseudopotential basis set. On the (10T̅x) edge (labeled “[X-3]” for the Mo side and “[3-X]” for the S side in [47]), Cristol et al. found a minimum dissociative adsorption energy of +0.01 eV on the S side of this edge and +0.27 eV on the Mo side (both endothermic). The present calculations show binding of the H atoms on the Mo side of the (10T̅x) edge with $\Delta G_{\text{ads}} = -0.27$ eV (exothermic) and $\Delta G_{\text{ads}} = +0.13$ eV on the S side. Therefore, one side was found to be an active edge for exothermic dissociative adsorption of molecular hydrogen in the present work.

A limited number of calculations of molecular H$_2$ in $\eta^2$ and dissociative adsorption geometries on MoS$_2$ edges were performed (Figure 9 and Table 4). On the MoS side of the (11̅1x) edge, a dihydride and an $\eta^2$–H$_2$ configuration were tested. The dihydride showed a metastable configuration with $\Delta E_{\text{ads}} = +0.28$ eV. Hydrogen was adsorbed exothermally in the $\eta^2$–H$_2$ configuration with $\Delta E_{\text{ads}} = -0.52$ eV. The vibrational frequencies in this $\eta^2$–H$_2$ geometry were 2999.2 cm$^{-1}$ for H–H stretching, 1483.9 cm$^{-1}$ for the symmetric H–Mo–H stretching, and 838.4 cm$^{-1}$ for the asymmetric H–Mo–H stretching, which is more like a frustrated rotation of the hydrogen molecule in the coordination sphere of Mo. On the Mo side of the (10T̅x) edge, a configuration denoted SH–SH was examined. This consisted of one H atom in the S1-top configuration with another on the bottom of the other edge S atom. The energy for dissociative adsorption H$_2$ + (MoS$_2$)$_n \rightarrow 2\text{H}(\text{MoS}_2)_n$ here was $\Delta E_{\text{ads}} = -0.06$ eV. On the Mo side of the (10T̅x) edge, a double Mo-bridge configuration was found to have an adsorption energy
of $\Delta E_{\text{ads}} = -0.35$ eV, very close to the $-0.34$ eV predicted by using the adsorption energy of an H atom from Table 3.

6. Vibrational Frequencies and Thermodynamics of Hydrogen Adsorption

The adsorption of hydrogen onto the MoS$_2$ edges at constant pressure and temperature is governed by the change in Gibbs free energy for the reaction,

$$\Delta G_{\text{ads}} = \Delta E_{\text{ads}} + \Delta(pV) + \Delta G_{\text{translation}} + \Delta G_{\text{rotation}} + \Delta G_{\text{vibration}},$$

where $\Delta G_{\text{tr,rot,vib}} = \Delta H_{\text{tr,rot,vib}} - T \Delta S_{\text{tr,rot,vib}}$.

Electronic structure calculations provide $\Delta E_{\text{ads}}$, one important term in the sum. Because the adsorption energies are small, however, the other terms do play a part in the sorption equilibria. The $\Delta(pV)$ term is also small. Because the volume of adsorbed H is small compared to H$_2$ gas, the $\Delta(pV)$ term is equal to $- pV = -RT = -0.026$ eV at room temperature, and $-0.054$ eV at 623 K.

The free energy contributions $\Delta G_{\text{tr,rot,vib}}$ are calculated from statistical mechanics of the molecular hydrogen and vibrational modes of the reacting MoS$_2$ and its adduct with hydrogen. Of those, the largest contribution is the well-known entropy penalty associated with the loss of translational and rotational degrees of freedom of the hydrogen molecule. Its value is $+0.79$ eV at 623 K and 1 atm [23] and $+0.40$ eV at 298 K and 1 atm [48]. There are also changes in the vibrational degrees of freedom when the H-H vibration of the free molecule is traded for the Mo-H, S-H vibrations and is accompanied by frequency changes of the MoS$_2$ adsorbent itself. We present herein a complete analysis for the monomeric H$_2$-MoS$_2$ system, and an approximate analysis for the edge structures as outlined in Section 2.

The H$_2$-MoS$_2$ monomer. The DFT-calculated frequencies (cf. Section 2) of the H$_2$ and MoS$_2$ molecules, and the stable H$_2$-MoS$_2$ spin singlet and the metastable H$_2$-MoS$_2$ spin triplet are given in Table 2.

All quantities in Table 2 are the results of DFT calculations, except $\Delta(pV)$ in row 19 and the last four entries in rows 26-29, which assume ideal behavior of the gaseous H$_2$. Individual “penalties” due to loss of entropy and enthalpy are broken down into translational, rotational and vibrational contributions. The losses of Gibbs free energy associated with hydrogen gas dominate the differences between the internal energy changes and Gibbs free energy changes due to bonding of the two hydrogen atoms of H$_2$ with the MoS$_2$ molecule. These losses amount to 8.8 – 9.6 kcal/mol at 298.15 K for the formation of spin singlet H$_2$-MoS$_2$ and 8.9 – 9.7 kcal/mol at 298.15 K for the formation of spin triplet H$_2$-MoS$_2$, in agreement with Fast [46]. Extensions to higher temperatures yield nearly proportionally increasing free energy penalties, some 20 kcal/mol at 600 K.
At this temperature, the formation of the singlet H₂-MoS₂ would still be thermodynamically favored by -6 kcal/mol, but that of the triplet H₂-MoS₂ would run thermodynamically uphill by +9 kcal/mol and this positive Gibbs free energy change could be offset only at high pressures.

Because of the dominance of the free energy penalties by the losses of degrees of freedom of hydrogen gas, these losses will also be very similar in magnitude in hydrogen adsorption on clusters and solid MoS₂

The H₂–MoS₂ Edge system. The statistical mechanics of the MoS₂ edge system is very similar to that of the MoS₂ monomer. The change in the Gibbs free energy is broken down into the calculated DFT energy, the Δ(pV) term, and the rotational, translational, and vibrational energies. The DFT energy is calculated and reported in Table 3 as ΔE_ads. The Δ(pV) term, along with ΔGₜₐₚ and ΔG_rot are the same as the values for the monomer calculation (Table 2) and total to 0.331 eV.

The vibrational energy change, is somewhat more complicated. In addition to the change in the vibrational energy associated with the adsorbed hydrogen atom, the MoS₂ edge suffers a small shift in the vibrational frequencies when the adsorption takes place. This shift was estimated by observing the frequencies calculated by the partial frequency method described above. In all cases, the lattice vibrational energy was lowered by the adsorption of hydrogen, but only by about 0.01 eV. This confirms the validity of the approximation made by Bollinger, et al [28], that the change in the Gibbs free energy due to shifts of lattice vibrations is small.

The more significant vibrational Gibbs free energy change associated with hydrogen is explicitly calculated. For the high-frequency hydrogen vibrations, only the zero-point energies are significant, though the complete vibrational energy formula is used. The vibrational energy of the H₂ molecule is 0.271 eV from Table 2. It is subtracted from the total vibrational energy of the hydrogen modes of the adsorbed H-MoS₂ system to obtain the vibrational energy change. The value ranges from +0.08 eV to +0.20 eV for the various adsorption locations. The final formula for calculating the Gibbs free energy changes in Table 3 is ΔG_ads = ΔE_ads + 0.331 eV + ΔG_vib.
Discussion and Conclusions

On the monomeric MoS$_2$ molecule a stable singlet dihydride with zero spin, S=0, was found, though the bare MoS$_2$ is a triplet with S=1 and the H$_2$ molecule is a singlet. In the most stable H$_2$–MoS$_2$ configuration, the H–H separation was found to be 3.08 Å and there was little electron density seen between the H atoms while there was a strong overlap between the H1s, Mo4d and S3p orbitals. There also was a metastable $\eta^2$-H$_2$ configuration with a triplet spin and an H–H distance of only 0.8 Å, but the $\eta^2$-H$_2$ energy was 0.65 eV higher than that of the dihydride. An important finding here is that the path from separated H$_2$ and MoS$_2$ molecules to the stable dihydride involves crossing of high-spin (S=1) to low-spin (S=0) pathways (cf. Figure 3). This crossing is spin-forbidden and will lead to low rates of formation of the stable singlet H$_2$–MoS$_2$ molecule, even though the overall pathway is “downhill”. Among the mechanisms for overcoming this bottleneck, co-catalysis by paramagnetic third bodies such as neutral alkali atoms (S=1/2) may provide the necessary perturbation to enable the crossing via spin-orbit coupling. Therefore, the present results suggest that investigation of systems such as the H$_2$–MoS$_2$–K will afford clues for alkali promotion of hydrogen activation on monomers and small oligomers of MoS$_2$. As the size of the MoS$_2$ cluster was increased, the spin tended more toward the singlet state as in bulk MoS$_2$. The edges of the Mo$_7$S$_{14}$ cluster resembled some of the edges of the periodic structure, and both the dihydride and the $\eta^2$–H$_2$ configurations were found. There was no indication of binding of the adsorbed H to the S atoms.

The periodic edge calculations did show H–S bonds. Single hydrogen atoms were adsorbed on sites neighboring both the S and the Mo atoms, with the strongest binding on the (1 2 1 x) edge on the second-row S atom (cf. Figure 8, (1 2 1 x) edge, S side, S2-top). With molecular hydrogen adsorption, the only dihydride configuration examined indicated an endothermic adsorption. Strong binding in an $\eta^2$–H$_2$ configuration was found on the (1 2 1 x) edge, in contrast with previous reports of heteropolar or homopolar adsorption on S from previous studies.

The vibrational frequencies of hydrogen bound to the S and the Mo atoms were found to be quite distinct and provide a definitive way to determine the adsorption sites of the hydrogen. When hydrogen was bound to the S atoms, the vibration frequency was about 2500 cm$^{-1}$, while this same frequency was lowered to about 1800 cm$^{-1}$ when the H was bound to the heavier Mo atoms. The exception was for adsorption on the basal plane S atoms, where the H atom was found to have a vibration frequency of 2036 cm$^{-1}$. This is due to the sulfur being braced by its bonds with the molybdenum plane, giving it a slightly higher effective mass.

The Gibbs free energies that will enable dissociative hydrogen adsorption to proceed require that the internal energy change overcome the dissociation energy of H$_2$ and the entropy penalty. This gives break-even internal energy $\Delta E_{\text{ads}}$ of $-0.41$ eV at 298 K and $-0.80$ eV at 623 K. Only few defect sites afford more negative $\Delta E_{\text{ads}}$ values: these are (a) the monomeric MoS$_2$ for both the singlet dihydride and triplet $\eta^2$–H$_2$ at 298 K and only
for the singlet dihydride at 623 K; (b) none on the Mo₇S₁₄ cluster for dissociative adsorption but this cluster could bind hydrogen to form the \( \eta^2 \)-H₂ species, (c) sites S2-top and S2-out on the \((1\overline{2}1x)\) edge at 289 K and 623 K, and (d) additional site S1-top on the Mo side of the \((10\overline{1}x)\) edge. All of the edge sites yield vibrational frequencies of the S-H bonds, although the most reactive one, S2-top on \((1\overline{2}1x)\), coordinates the H atom both to the S and (weakly) to two neighboring Mo atoms.

Despite differences in detail, the overall pattern has clearly emerged: dissociative adsorption of hydrogen will be favored on the exposed Mo atoms of monomers and small clusters, while it will yield S-H species on exposed edges of periodic structures. A new metastable Mo-H-Mo species is predicted on the \((10\overline{1}x)\) edge, with very low vibrational frequency of 1223 cm⁻¹, which could be observed as a result of adsorption of atomic hydrogen or high-temperature dissociative chemisorption of H₂ followed by migration of H atoms to this site.
Figure 1: Periodic trends for neutral and cationic polyhydride complexes with phosphine ligands as dihydrides and $\eta^2$-hydrides [7]. Dihydrides exist on metals to the left of the line, $\eta^2$-hydrides to the right of the line, and metals along the diagonal may exhibit either type. Note that lines are included for both cationic and neutral complexes.

Figure 2: Stable and metastable geometries of $\text{H}_2\text{–MoS}_2$. Structure (a) is the ground state singlet dihydride, (b) is a metastable “tilted” configuration with an energy 0.3 eV above the ground state, and (c) is the lowest-energy triplet $\eta^7$ hydrogen configuration, with an energy 0.6 eV above the ground state.
Figure 3: Constrained optimization of the H$_2$MoS$_2$ molecule as a function of the H–Mo–H bond angle $\theta_{H}$. The hydrogen molecule is attracted to the exposed Mo atom in the MoS$_2$ monomer (small $\theta_{H}$) and could form a metastable $\eta^2$–H$_2$ complex in a spin triplet. Overcoming a small activation energy leads to a stable configuration as a dihydride (large $\theta_{H}$) in this coordinate-driven set of calculations. Easily seen are the metastable triplet state (blue line, $\theta_{H}$ ~ 20°) and a “tilted” singlet state (red line, $\theta_{H}$ ~ 60°), along with the ground singlet state (red and green lines, $\theta_{H}$ ~ 128°). The upper singlet path maintains the $C_{2v}$ symmetry, while the lower path has the $C_s$ ($C_{1h}$) symmetry of the “tilted” configuration until it reaches the same stable singlet geometry as the $C_{2v}$ path.
**Figure 4:** Molecular orbitals of H$_2$–MoS$_2$ that have the highest H$_2$ $\sigma^*$ character for the optimized singlet (left) and triplet (right) configurations. Both orbitals show interaction between the $\sigma^*$ and the Mo d$_{yz}$ orbital, but in the triplet case, this MO is only singly occupied. The z-axis passes from Mo to mid-points of the H-H and S-S lines and the yz plane is H-Mo-H.
Figure 5: Energy levels of separated H$_2$ and MoS$_2$ monomer (left), the metastable triplet H$_2$–MoS$_2$ (center), and the ground state singlet H$_2$–MoS$_2$ (right). All geometries have the C$_{2v}$ symmetry, and the orbitals are colored by their symmetries (black=A1; blue=A2; red=B1; green=B2). Between the triplet and singlet geometries, one A1 spin-up electron moves to the B1 spin-down orbital, a forbidden transition.
Figure 6: Geometry of hydrogen adsorption on the Mo$_7$S$_{14}$ cluster. The left side of the cluster resembles the (10 1 0) edge of the MoS$_2$ crystal and has monohydrides. The top and bottom resemble the (10 1 0) edge and show both $\eta^2$–H$_2$ and dihydride formation. Distances are in nm.
Figure 7: The two most stable relaxed edges. Here the coordination of the edge Mo and S atoms is easily seen. Some Mo-Mo distances and Mo-S bond lengths near the edges are shown. Those distances which are not marked were within 0.1 Å of the lengths from the optimized 2-D sheet, \( d(\text{Mo–Mo}) = 3.16 \) Å and \( d(\text{Mo–S}) = 2.42 \) Å. The two complementary sides of each edge are labeled.
Figure 8: Geometries of adsorption locations for hydrogen atoms on the (10\overline{1}x) and (1\overline{2}1x) edges of MoS$_2$. When two H atoms are seen, it is because of the repeating unit cell.
Figure 9: Geometries tested with two H atoms adsorbed on the MoS$_2$ edge.

Table 1: Various properties of the singlet and triplet geometries of the H$_2$–MoS$_2$ complex.

<table>
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<th>Property</th>
<th>C$_{2v}$ Singlet</th>
<th>C$_s$ Singlet</th>
<th>Triplet</th>
</tr>
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<tbody>
<tr>
<td>Geometry</td>
<td>Dihydride</td>
<td>Tilted</td>
<td>$\eta^2$–H$_2$</td>
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<td>$d$(H–H)</td>
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<td>1.65 Å</td>
<td>0.80 Å</td>
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<td>1.72 Å, 1.65 Å</td>
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$\Delta E_{ads} = E(H_2$–MoS$_2$) – [$E(H_2) + E$(MoS$_2$)]
Table 2: Thermodynamic functions and vibrational frequencies for the reactions of hydrogen molecule with monomeric singlet and triplet MoS$_2$. Energies are given in various units for comparison with the literature, 1eV/molecule = 23.06046845 kcal/mol = 96.4850 kJ/mol = 8065.5 cm$^{-1}$.

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(Footnotes on next page.)
a DFT energy in Hartrees
b DFT zero-point vibrational energy in kcal/mol
c DFT energies in kcal/mol
d DFT entropy in cal/deg-mol
e DFT vibrational frequencies in cm\(^{-1}\)
f DFT adsorption energy, eV
g Loss of pV upon adsorption of H\(_2\) molecule taken as ideal gas, eV
h Gibbs free energy changes upon formation of the H\(_2\)-MoS\(_2\) adducts calculated from DFT enthalpies and entropies, eV
i \(\Delta G_{ads}\) \(^h\) in kcal/mol
j \(\Delta E_{ads}\) \(^f\) in kcal/mol
m \(\Delta G_{rot-ortho-para} = -(3/2)RT - T\Delta S_{rot}\). \(T=298.15\) K and \(\Delta S_{rot}\) is negative value of rotational entropy of hydrogen molecule calculated from partition functions involving ortho-para equilibrium as in P. Atkins, Physical Chemistry, 5\(^{th}\) ed., W.H. Freeman & Co., N.Y. 1994, p. 697, in eV
n \(\Delta G_{transST} = -(3/2)RT - T\Delta S_{trans}\). \(T=298.15\) K and \(\Delta S_{trans}\) is negative value of translational entropy of hydrogen molecule calculated from partition functions involving the Sackur-Tetrode equation as in P. Atkins, Physical Chemistry, 5\(^{th}\) ed., W.H. Freeman & Co., N.Y. 1994, pp. 680 and 686, in eV
p \(\Delta G_{ads} = \Delta E_{ads} + \Delta(pV)^{g} + \Delta G_{vib}^{h} + \Delta G_{rot-ortho-para}^{m} + \Delta G_{transST}^{n}\), eV
q \(\Delta G_{ads}^{q}\) is \(\Delta G_{ads}^{p}\) in kcal/mol
Table 3: Adsorption energies and vibrational frequencies of hydrogen on MoS$_2$ (10¡x) and (1¿1x) edges. The adsorption of hydrogen on the MoS$_2$ basal plane is shown at the bottom. The labels of the edges, sides, and positions are defined in Figure 7. The DFT Energy change $\Delta E_{\text{ads}}$ is given per adsorbed hydrogen molecule (c.f. Section 3.5). The Gibbs free energy change $\Delta G_{\text{ads}}$ is defined in Section 3.6 and includes contributions from DFT, $\Delta(pV)$, vibrational, rotational, and translational energies. The $\Delta(pV)$, rotational and translational contributions to the Gibbs free energy change are the same as in Table 2 and total to 0.331 eV for all cases. The vibrational Gibbs free energy change $\Delta G_{\text{vib}}$ is listed for each case. Gibbs free energies are given for 298.15 K.

<table>
<thead>
<tr>
<th>Edge</th>
<th>Side</th>
<th>Position</th>
<th>$\Delta E_{\text{ads}}$ (eV)</th>
<th>$v_1$ (cm$^{-1}$)</th>
<th>$v_2$ (cm$^{-1}$)</th>
<th>$v_3$ (cm$^{-1}$)</th>
<th>$\Delta G_{\text{vib}}$ (eV)</th>
<th>$\Delta G_{\text{ads}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10¡x)</td>
<td>S side</td>
<td>Mo-bridge</td>
<td>-0.34</td>
<td>1222.8</td>
<td>1207.0</td>
<td>859.2</td>
<td>0.14</td>
<td>0.13</td>
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<tr>
<td></td>
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<td>S1-out</td>
<td>0.43</td>
<td>2544.4</td>
<td>620.1</td>
<td>598.6</td>
<td>0.19</td>
<td>0.95</td>
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<td></td>
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<td>S-bridge</td>
<td>1.69</td>
<td>1735.5</td>
<td>637.4</td>
<td>508.0</td>
<td>0.08</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S2-top</td>
<td>1.73</td>
<td>2455.0</td>
<td>662.5</td>
<td>567.2</td>
<td>0.18</td>
<td>2.25</td>
</tr>
<tr>
<td>Mo side</td>
<td>S1-top</td>
<td></td>
<td>-0.79</td>
<td>2588.6</td>
<td>661.1</td>
<td>576.8</td>
<td>0.20</td>
<td>-0.27</td>
</tr>
<tr>
<td></td>
<td>S2-top</td>
<td></td>
<td>1.05</td>
<td>2561.9</td>
<td>597.7</td>
<td>575.1</td>
<td>0.19</td>
<td>1.57</td>
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<tr>
<td>(1¿1x)</td>
<td>S side</td>
<td>S2-top</td>
<td>-1.24</td>
<td>2550.2</td>
<td>691.2</td>
<td>627.7</td>
<td>0.20</td>
<td>-0.70</td>
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<td>S2-out</td>
<td>-1.15</td>
<td>2491.0</td>
<td>673.4</td>
<td>490.1</td>
<td>0.18</td>
<td>-0.64</td>
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<tr>
<td></td>
<td></td>
<td>S1-out</td>
<td>-0.32</td>
<td>2570.8</td>
<td>573.5</td>
<td>414.6</td>
<td>0.16</td>
<td>0.17</td>
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<td></td>
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<td>Mo-out</td>
<td>0.92</td>
<td>1862.8</td>
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<tr>
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<td>S1-top</td>
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<td>2553.8</td>
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<td>Basal plane</td>
<td>S-top</td>
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<td>2035.5</td>
<td>447.2</td>
<td>443.2</td>
<td>0.08</td>
<td>3.80</td>
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</table>
Table 4: Adsorption energies and vibrational frequencies for selected 2H–(MoS₂)$_n$ configurations. $\Delta E_{\text{ads}} = E(2H–(MoS₂)_n) – [E((MoS₂)_n) + E(H₂)]$

<table>
<thead>
<tr>
<th>Edge</th>
<th>Side</th>
<th>Position</th>
<th>$\Delta E_{\text{ads}}$</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10 1x)</td>
<td>S side</td>
<td>Mo-bridge</td>
<td>-0.34 eV</td>
<td></td>
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<tr>
<td></td>
<td>Mo side</td>
<td>SH–SH</td>
<td>-0.06 eV</td>
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<tr>
<td>(121x)</td>
<td>MoS side</td>
<td>$\eta^2$–H₂</td>
<td>-0.52 eV</td>
<td>2999.2 cm$^{-1}$</td>
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<tr>
<td></td>
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<td>dihydride</td>
<td>+0.28 eV</td>
<td>(H-H) 1483.9 cm$^{-1}$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Mo-H₂ sym) 838.4 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Mo-H₂ asym)</td>
</tr>
</tbody>
</table>

References