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ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

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SUMMARY OF TECHNICAL PROGRESS

During this quarter, a systematic study of the preparation of MoS_3 , the subsequent decomposition treatment to form MoS_2 , and the Cs-containing reagents and techniques to achieve surface doping of the MoS_2 with Cs has been initiated. Complete characterization of the samples is being carried out at each stage, beginning with the MoS_3 samples and ending with the tested catalysts. The goal of this research is to achieve a high surface area catalyst containing lower quantities of the Cs promoter in a highly dispersed state that is stable during catalytic testing. The results of these studies, along with the catalytic testing results of selected high surface area MoS_2 and Cs/ MoS_2 catalysts, will be presented in the next quarterly progress report.

Using experimental data (high resolution electron spectroscopy for chemical analysis (HR-ESCA)) and computational data (solid state Extended Hückel (EH) theory) obtained previously, investigation and interpretation of the electronic structure of MoS_2 (hexagonal 2H form, indicating 2 MoS_2 molecules/unit cell) was carried out since the activation of hydrogen depends on the electronic properties of the catalyst. The theoretical valence band (TVB) of MoS_2 was obtained by modification of the density of states (DOS) with appropriate valence shell photoelectron cross-sections for AlK_α radiation. Qualitative agreement between theoretical and experimental MoS_2 valence bands was obtained after parametrization of the EH input ionization potentials H_{11} and Slater-type orbital (STO) double zeta coefficients c_{11} . Theoretical energy dispersion curves, not given here, of two- and three-dimensional MoS_2 model systems (referred to as 2-D and 3-D MoS_2) also compared

well with experimental energy dispersion curves available in the literature. The highest occupied band of the valence band is shown to consist of contributions not only from Mo $4d_{z^2}$ orbitals but also from Mo $4d_{xy}$ and Mo $4d_{x^2-y^2}$ orbitals. The theoretical systems 2-D MoS₂ and 3-D MoS₂, containing zero for the former and an infinite number of Van der Waals gaps for the latter, exhibit direct and indirect gaps, respectively. The nature of the 2H-MoS₂ indirect gap is found to be directly linked to the interaction of crystal orbitals across the Van der Waals gap between adjacent layers of MoS₂ in the realistic 3-D model. Thus, the electronic properties, and therefore the ability of adsorbing and activating hydrogen, of very small and thin particles of MoS₂ might be expected to be distinctly different from large bulk particles of MoS₂.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

TECHNICAL PROGRESS

A. Catalyst Preparation and Doping Procedures:

The currently utilized preparation methods for synthesizing the alkali-doped MoS₂ catalysts originate from the Dow Chemical Co. and Union Carbide Corp. patents. These methods yield MoS₂ that has a surface area generally in the 60-90 m²/g range. However, upon doping with alkali salts, the surface area decreases significantly and can be in the range of 10-20 m²/g. In addition, the amount of the alkali dopant needed to prepare an optimum catalyst by aqueous impregnation is very high, i.e. 10-20 wt% alkali salt. The alkali dopant tends to agglomerate into large particles on the surface of the MoS₂ catalyst. Last quarter, a 10 wt% Cs/MoS₂ catalyst was extensively tested. It was shown that the catalytic activity was initially lower than previously prepared and tested samples of Cs/MoS₂. Determination this quarter of the BET surface areas of the MoS₂ sample as prepared, doped under vacuum with Cs, and after testing, showed the surface areas to be 60, 13, and 6 m²/g, respectively.

This quarter, a systematic study of the preparation of MoS₃, decomposition treatment to form MoS₂, and reagents and techniques to achieve surface doping of the MoS₂ with Cs has been initiated. The goal of this research is to achieve a high surface area catalyst containing the Cs promoter in a highly dispersed state that is stable during catalytic testing. This involves decomposition/calcination of the precipitated MoS₃ precursor under N₂, He, or H₂S/H₂ environments, use of various Cs dopants (including Cs hydroxide, formate, sulfate, etc.) in air or under N₂, and doping before or after the decomposition of MoS₃ to

MoS₂. BET surface area and XRD crystallite size analyses are being carried out with each sample at each step of the procedure. The results of these studies, along with the catalytic testing results of selected high surface area MoS₂ and Cs/MoS₂ catalysts, will be presented in the next quarterly progress report.

B. Examination of the Electronic Properties of MoS₂:

1. Introduction.

We have been concerned for some time in regard to the mechanisms and kinetics of activation of dihydrogen on the surface of heterogeneous catalysts, including metal sulfides [1]. In some manner, hydrogen must be adsorbed and activated on the surface of the catalyst and then made available for hydrogenation of intermediate carbon-containing species. In the reverse water gas shift reaction, the carbon-containing moiety is CO₂. This activation of H₂ is important in hydrodesulfurization, hydrodenitrogenation, and alcohol synthesis from H₂/CO synthesis gas over promoted MoS₂ catalysts. Knowledge of the surface properties of the transition metal disulfide species is important before the mechanism of hydrogen dissociation (and optimization or retardation thereof) can be addressed. For instance, on the surface of MoS₂ the specific site at which H₂ is activated depends on the electronic properties of the sample.

It was the intent of our experimental and theoretical investigation to study in detail the bulk and surface electronic structure of the transition metal disulfide MoS₂. Experimental studies of the MoS₂ valence band were carried out earlier [2] using high resolution electron spectroscopy for chemical analysis (HR-ESCA), also referred to as high resolution X-ray photoelectron spectroscopy (HR-XPS). However, the valence band obtained *via* HR-ESCA is a combination of the atomic valence levels of sulfur and

molybdenum. The HR-ESCA experiment does not resolve the valence band into contributions due to the atomic valence levels from different atoms. Theoretically calculated valence bands were determined to interpret the HR-ESCA experimental results. A solid state adaptation of the Extended Hückel theory is a very simple method that will calculate the density of states, as well as contributions of the valence atomic orbitals to the density of states [3]. Theoretical studies of the MoS₂ valence band and energy dispersion curves for one- and two-dimensional (1-D and 2-D) models of MoS₂ were carried out earlier [4] using the Extended Hückel method applied to solid state systems. In this quarterly report, the experimental and theoretical data for the electronic properties of 2-D and 3-D models of MoS₂ are interpreted and correlations with structure are made.

Molybdenum disulfide exhibits semiconductor behavior due in part to the d² configuration of Mo⁴⁺, possesses the layer-type structure, and is the most active disulfide used for alcohol synthesis. The layer structure of MoS₂ exists in either the hexagonal modification 2H-MoS₂ or the rhombohedral modification 3R-MoS₂ [5]. The focus of this research has been on the hexagonal modification since this is the structure of the synthesized polycrystalline samples, as well as of the naturally occurring single crystals of MoS₂. In 2H-MoS₂, the molybdenum atoms are coordinated to six sulfur atoms in a trigonal prismatic environment; the sulfur atoms are each coordinated to three molybdenum atoms. 2H-MoS₂ forms a layer structure with two MoS₂ molecules per unit cell. One MoS₂ unit translated in two-dimensions within the layer by a linear integral combination of primitive translations **a** and **b** forms the infinite single sheet structure. Three-dimensional crystals are formed by stacking of the MoS₂ layers. The three-dimensional crystal is held together by weak Van der Waals forces between the sulfur atoms on adjacent MoS₂ layers. In the three-dimensional crystal the real lattice vector, **c**, is perpendicular to the real lattice vectors, **a**

and $\mathbf{b}$, and to the direction of propagation of the MoS_2 layer. The second MoS_2 molecule in 2H- MoS_2 resides in a second MoS_2 layer. This second MoS_2 layer is offset from the first such that Mo atoms in the second are beneath (or above) S atoms in the first, while S atoms in the second are beneath (or above) Mo atoms in the first layer. Positions of the atoms (in terms of real lattice vectors) in one unit cell of 2H- MoS_2 are the following: Mo, (0,0,0); S, ($\frac{1}{3}$, $-\frac{1}{3}$, $\pm u$); Mo, ($\frac{1}{3}$, $-\frac{1}{3}$, $\frac{1}{2}$); and S, (0, 0, $\frac{1}{2} \pm u$). The length of the real lattice vectors $\mathbf{a}$ and $\mathbf{b}$ is the same and equal to 3.16 Å. The length of $\mathbf{c}$ is 12.30 Å. The parameter u , equal to 0.1282, is defined as the elevation of the sulfur atoms above and below the plane of molybdenum atoms in terms of $\mathbf{c}$. Thus, the two atomic layers of sulfurs in one MoS_2 layer are located 1.578 Å and -1.578 Å above and below the atomic layer of molybdenums. The distance between the layers of sulfur belonging to two different MoS_2 layers, the Van der Waals gap, is defined as h and is equal to 0.2435 or in actual units, 2.995 Å.

The electronic properties of MoS_2 have been reported in the literature by a variety of researchers. Theoretical methods of studying the band structure of MoS_2 include the following: semiempirical tight binding method [6,7], simplified linear combination of muffin-tin orbitals method [8], first principles augmented-plane-wave theory [9], pseudopotential form of the linear combination of atomic orbitals (LCAO) neglecting three-center terms [10], augmented-spherical-wave method [11,12], and the atom superposition and electron delocalization molecular orbital method (ASED-MO) [13]. The studies mentioned above concentrated on assigning the excitons observed in optical spectroscopy to electronic transitions. Valence bands obtained from photoelectron spectroscopy were only qualitatively discussed in terms of the aforementioned electronic structure calculations. The solid state Extended Hückel electronic structure study of MoS_2 undertaken in this work was performed in order to better understand the HR-ESCA valence band and the character of the energy

dispersion curves to aid in the correct interpretation of experimental and theoretical data obtained with H-MoS₂ after H₂ adsorption and activation.

2. Experimental.

2.1. Sample Preparation. Polycrystalline MoS₂ was prepared by the thermal decomposition in flowing N₂ of precipitated and dried molybdenum trisulfide, MoS₃ [14,15]. The MoS₂ resulting from this type of preparation was highly stoichiometric and poorly crystalline with a surface area of ≈ 60 m²/gm. Since this sample was not prepared fresh, pretreatment of the sample prior to analysis was necessary. Pretreatment consisted of heating the polycrystalline MoS₂ sample in a quartz tube at 400°C for 1 hr in a 2.04% H₂/N₂ gas flow of 1 cc/sec. Exposure of the polycrystalline sample to air prior to analysis was avoided by removing the sample from the quartz tube in a N₂-filled glove box. Polycrystalline MoS₂ was mounted on an ESCA sample holder through the use of indium foil. Transfer of the sample and holder to the HR-ESCA fast entry chamber was performed under N₂ to minimize exposure of the sample to air.

2.2. HR-ESCA Analyses. The instrument used for HR-ESCA analysis of the core levels and valence bands of MoS₂ was the SCIENTA ESCA-300 that is located in the Zettlemoyer Center for Surface Studies at Lehigh University. The SCIENTA ESCA-300 is equipped with a water-cooled high intensity rotating AlK _{α} anode. The X-rays resulting from this source are monochromatized by seven quartz crystals and impinge on the sample at an angle of 45° from the detector axis. The high intensity and monochromaticity of the source make analysis of valence bands a routine procedure. The detector system consists of a large radius (60 cm) hemispherical analyzer combined with a multichannel plate detector. High sensitivity and high energy resolution are achieved with this type of detector system.

Pressure in the sample chamber during analysis remained low, in the low 10^{-9} to 10^{-10} torr range. The SCIENTA ESCA-300 is also equipped with a spatial prelens. When in place, the prelens decreases the area of the sample from which photoelectrons are detected. Essentially, the prelens magnifies the area sampled. In the spatial mode, a rectangular spot of $3.9 \text{ mm} \times 110 \mu$ can be analyzed. In this mode, optimal spatial resolution is achieved at the expense of photoelectron intensity.

The following core levels of polycrystalline MoS_2 were examined by HR-ESCA in order to determine sample uniformity and homogeneity: Mo 3d, S 2p, C 1s, and O 1s. Typical instrumental parameters used for obtaining core level scans were the following: pass energy, E_p , 75 eV; step size, 0.05 eV; time/step, 0.04 sec; slit width, 1.1 mm; number of scans, 4-5; and transmission mode. The symmetries and narrow peaks in the Mo 3d and S 2p regions indicate the presence of only one Mo and one S oxidation state. Carbon and oxygen surface contaminants were present in small amounts on the polycrystalline MoS_2 surface. Typical instrumental parameters used for obtaining the MoS_2 valence band were the following: pass energy, E_p , 75 eV; step size, 0.05 eV; time/step, 0.4 sec; slit width, 1.1 mm; and number of scans, ca. 50. Measurement times for valence band analyses using the SCIENTA ESCA-300 vary from 1-4 hr, according to the amount of detail required from the spectrum. Use of pass energies E_p of 75 eV, 150 eV, and 300 eV and a 1.1 mm slit width leads to the following values for the instrumental energy resolution: 0.30 eV, 0.39, and 0.62 eV, respectively.

Small amounts of surface contaminants such as C and O did not affect the appearance of the valence band to a great extent. Valence band electrons ejected by AlK_α radiation of energy 1486.6 eV have kinetic energies (prior to leaving the surface) extending from about 1486 eV to 1466 eV. These kinetic energies correspond to an escape depth of

≈ 14 monolayers or $38 \text{ \AA}$ for the valence band region [16,17]. Thus, valence band spectra obtained using AlK_α radiation are fairly representative of the bulk compound.

The valence band of polycrystalline MoS_2 obtained with the use of the present HR-ESCA is shown in Figure 1. The valence band of MoS_2 shows two distinct regions. The first region appears at approximately 14 eV binding energy, and this region will be referred to as the S 3s valence band region. The second region extends from approximately 0 eV (the Fermi level of the instrument) to 8 eV, and this region will be referred to as the Mo 4d-S 3p region. The Mo 4d-S 3p region consists of four distinct peaks. The valence band region of MoS_2 shown in Figure 1, does not possess significant electron density above 0 eV binding energy, confirming the semiconducting nature of this sample.

2.3. Solid State Extended Hückel Computations. The theoretical method used for obtaining MoS_2 valence bands and energy dispersion curves was a solid state adaptation of the extended Hückel method. A computer program entitled Extended Hückel Molecular, Crystal and Properties Package (EHMCAPP) was obtained from the Quantum Chemistry Program Exchange (QCPE) and was used for calculation of the electronic structure [3]. Calculations were carried out on the Lehigh University VAX 8530 system. Some features of the program are the ability to calculate the density of states, energy dispersion curves, orbital character of energy bands, total energy, and electron population for a variety of systems, all to the same level of approximation. This theory is essentially an empirical one-electron theory in which correlation effects (due to electron-electron repulsion) are not taken into account. The empirical nature of extended Hückel theory means that the results depend on the input parameters. Specifically, the results depend to a large degree on the atomic ionization potentials H_{ii} and Slater-type atomic orbital radial exponents ζ_i and orbital coefficients c_i . Agreement with experiment can be improved by adjustment of the

Figure 1. Valence band spectrum of polycrystalline MoS₂ obtained by HR-ESCA. This spectrum was obtained using a pass energy of 75 eV and slit width of 1.1 mm resulting in an instrumental energy resolution of 0.30 eV.

input parameters, H_{ii} , ζ_i , and c_i of the atomic orbitals used as the basis.

The approach of solid state extended Hückel theory is to define a set of local molecular orbitals, $\psi_i(\mathbf{r} - \mathbf{R}_p)$, that consist of contributions from the valence atomic orbitals, χ_μ , of the atoms in the primitive cell of the solid under study. Background information on solid state extended Hückel theory was obtained from References [18-20], and will be discussed in greater detail elsewhere [21].

In order to carry out the theoretical calculations, the bulk structure of 2H-MoS₂ was modelled by two different systems: 2-D MoS₂ and 3-D MoS₂. A two-dimensional infinite sheet of MoS₂, 2-D MoS₂, was used to model one layer of a 2H-MoS₂ single crystal. This structure excluded effects due to interactions of crystal orbitals across the Van der Waals gap. The 2-D MoS₂ system was generated by translating one unit of MoS₂ (Mo, (0,0,0); S, ($\frac{1}{3}$, $-\frac{1}{3}$, $\pm u$)) in two dimensions within a single layer by linear integral combinations of the primitive translation vectors **a** and **b**. A three-dimensional MoS₂ structure, 3-D MoS₂, was used to model the bulk structure of 2H-MoS₂. This structure included effects due to interactions of crystal orbitals across the Van der Waals gap. The 3-D MoS₂ structure was generated by translating two units of MoS₂ (Mo, (0,0,0); S, ($\frac{1}{3}$, $-\frac{1}{3}$, $\pm u$); Mo, ($\frac{1}{3}$, $-\frac{1}{3}$, $\frac{1}{2}$); and S, (0, 0, $\frac{1}{2}\pm u$)) in three-dimensions by linear integral combinations of the primitive translation vectors, **a**, **b**, and **c**.

Basis orbitals used for calculating the electronic structure of MoS₂ were the Mo 5s, Mo 5p, Mo 4d, S 3s, and S 3p valence orbitals. After much preliminary work on the MoS₂ system, EH input parameters obtained from the SCF computed, tabulated list of Slater-type orbital double zeta coefficients, exponents and valence shell ionization potentials of Clementi and Roetti (C&R) were used as initial EH input parameters prior to parametrization [22]. The unparametrized C&R double zeta functions reproduced the shape

of the S 3s band and the four-peaked nature of the Mo 4d-S 3p portion of the experimental valence band. However, these theoretical bands were not positioned at energies corresponding to the location of the experimental bands. For instance, the S3s band was separated from the bottom of the Mo 4d-S 3p valence band by about 9 eV. Experimentally, the S 3s band is separated from the bottom of the Mo 4d-S 3p valence band by about 6 eV. By parametrizing the C&R radial functions according to the HR-ESCA valence band experiment, a good description of the experimental valence band was obtained. The ionization potentials $H_{\underline{11}}$, specifically for the Mo 4d, S 3s, and S 3p orbitals, were varied to match the position of the valence levels in the HR-ESCA experiment. Slater-type orbital coefficients $c_{\underline{1}}$ were subsequently adjusted to achieve the best overlap by varying the radius of the valence shell. The original HR-ESCA valence band spectrum of MoS₂ was shifted to higher binding energies by the work function of the sample. Work function measurements obtained from the literature vary from 4.1 eV [23] through 4.55 ± 0.1 eV [24] to 4.8 ± 0.05 eV [25]. The HR-ESCA valence band spectrum was corrected by the most recently obtained value of the work function 4.1 eV in order to obtain accurate values for the valence state ionization potentials $H_{\underline{11}}$ as measured from the vacuum level E_v instead of from the Fermi level E_F .

The EHMCAAPP program package output provides the MoS₂ density of states. A theoretical valence band is desired for comparison with the HR-ESCA experimental valence band. An experimental valence band is actually a density of states modified by the sensitivity of the photoelectrons to detection and convoluted with the final states. For ESCA, final states are known to vary smoothly with energy, and hence their effect on the structure of the valence band is small. Sensitivity of the photoelectrons to detection depends on a number of parameters such as the energy of the incident X-rays and the atom type and

orbital from which the photoelectrons originate. This sensitivity is quantified and referred to as the photoelectron cross-section, σ . Values of the photoelectron cross-section have been theoretically calculated for AlK_{α} radiation and are tabulated in Reference [26]. Photoelectron cross-sections for the valence orbitals of MoS_2 are the following: Mo 4d, 0.3162; Mo 5s, 0.0157; S 3s, 0.1465; and S 3p 0.0774.

The theoretical density of states can be partitioned into atomic orbital populations (AOPOP's), which are defined as contributions to the density of states due to the valence atomic levels in the basis. The resulting sum of the AOPOP's is the density of states. Modification of the individual AOPOP's by the appropriate photoelectron cross-section with subsequent summation of the modified AOPOP's (MAOPOP's) will result in a calculation of the theoretical valence band. The theoretical valence band can then be compared with greater accuracy to the experimental valence band. This method of modifying the density of states is based on an approach, developed by U. Gelius, that is used for the molecular orbitals of molecules [27]. In this study, the major contributions to the density of states are due to the S 3s, S 3p, and Mo 4d valence levels. The Mo 5s and Mo 5p levels contribute a small amount to the density of states with an even smaller contribution to the valence band due to the small photoelectron cross-sections involved. For this reason, the Mo 5s and Mo 5p levels have been neglected in calculations of the theoretical valence band. The Mo 4d to S 3p cross-section ratio is 4.09. Thus, the Mo 4d AOPOP is effectively multiplied by 4.09 relative to the S 3p AOPOP.

3. Results and Discussion.

3.1. Valence Bands. Results for the theoretical system 2-D MoS_2 will be discussed first. The theoretical valence band of 2-D MoS_2 obtained after parametrization of the C&R

input parameters [22] is shown in Figure 2. The Mo 4d, S 3s, and S 3p radial parameters used in this set of calculations are given in Table 1. The radial parameters of Table 1 were obtained by parametrization of the C&R ionization potentials and coefficients as discussed in the preceding section. Modified atomic orbital populations (MAOPOP's) for the S 3s, S 3p and Mo 4d orbitals are shown in Figure 3. Figure 4 shows both the theoretical and experimental valence bands plotted to the same energy scale for better comparison. The upper Mo 4d-S 3p theoretical valence band consists of four distinct peaks, similar to the experimental valence band. The total width of the Mo 4d-S 3p theoretical valence band region is about 6 eV, the experimental width is also about 6 eV. Experimentally and theoretically, the S 3s band is separated from the upper Mo 4d-S 3p valence band by about 6 eV. Thus, the theoretical valence band obtained after parametrization of the C&R input parameters qualitatively reproduces the experimental valence band as shown in Figure 4.

As shown in Figure 3, S 3p orbitals contribute primarily to the lower and center portions of the Mo 4d-S 3p valence band. Double zeta S 3p radial functions lead to a three-peaked S 3p MAOPOP that overlaps with the Mo4d MAOPOP to produce a four-peaked theoretical valence band. The highest occupied band has almost no contribution from S3p or S 3s orbitals. During the course of the parametrization, it was found that diffuse S3p double zeta functions are needed to produce a theoretical valence band that is in qualitative agreement with the experimental valence band. Diffuse double zeta S 3p functions lead to a theoretical valence band that reproduces the four-peaked Mo 4d-S 3p region; however, diffuse single zeta S 3p functions (such as those used by Hughbanks and Hoffmann in Reference [28]) lead to a theoretical valence band displaying a three-peaked Mo 4d-S 3p region. The nature of the radial part of the S 3p atomic functions has the greatest effect on the appearance of the Mo 4d-S 3p region.

TABLE 1.

Radial parameters, H_{11} , ζ_1 , and c_1 , for the Mo4d, S3s, and S3p atomic orbitals used as the basis set for 2H-MoS₂. Parametrization of the C&R double zeta radial parameters (Reference 22) via comparison of the theoretical valence band to the experimental valence band shown in Figure 1 led to the parameters listed in this table.

<u>Atom</u>	<u>Orbital</u>	<u>H_{11}(eV)</u>	<u>ζ_1(a.u.⁻¹)</u>	<u>c_1</u>
Mo	4d	-6.00	3.81446 (1)	0.38841 (1)
			1.86369 (2)	0.72684 (2)
S	3s	-17.80	2.66221 (1)	0.43538 (1)
			1.68771 (2)	0.60731 (2)
S	3p	-8.84	2.33793 (1)	0.35338 (1)
			1.33331 (2)	0.70431 (2)

Figure 2. Theoretical valence band of the model system 2-D MoS₂ obtained using the parameters given in Table 1 and solid state Extended Hückel theory.

Figure 3. Theoretical modified atomic orbital populations (MAOPOP's) for the S 3s, S 3p, and Mo 4d orbitals.

Figure 4. Theoretical valence band of 2-D MoS₂ (solid line) and experimental valence band of polycrystalline MoS₂ (crosses +) plotted to the same energy scale.

The individual Mo 4d MAOPOP's for 2-D MoS₂ are shown in Figure 5. The highest occupied band (at the top of the valence band) consists of primarily Mo 4d character such that the contribution of $d_{z^2} > d_{xy} \geq d_{x^2-y^2}$. Two intense bands form the lowest unoccupied portion of the conduction band. The lowest unoccupied band (at the bottom of the conduction band) also consists of primarily Mo 4d character such that the contribution of $d_{x^2-y^2} > d_{xy} \approx d_{z^2}$. The next lowest unoccupied band consists of Mo 4d character such that the contribution of $d_{yz} > d_{zx}$. Crystal field splitting of the 4d orbitals of Mo coordinated by six sulfur ligands in a trigonal prismatic environment was studied by R. Huisman et al. [29]. Splitting of the Mo4d orbitals was found to occur such that d_{z^2} is lowest in energy followed by degenerate d_{xy} and $d_{x^2-y^2}$ orbitals and the highest energy degenerate d_{yz} and d_{zx} orbitals. The Mo 4d orbital contributions in 2-D MoS₂ follow the crystal field splitting to a limited extent. However, the d_{xy} and $d_{x^2-y^2}$ orbitals mix with the d_{z^2} orbitals to a large degree in the valence band. At the top of the valence band and at the bottom of the conduction band, mixing of the d_{yz} and d_{zx} orbitals with the d_{z^2} , d_{xy} , and $d_{x^2-y^2}$ orbitals does not occur.

In 1988, Sancrotti et al. experimentally studied the empty conduction bands of a natural single crystal of 2H-MoS₂ by inverse photoemission spectroscopy [30]. The conduction band spectra obtained with this method were said to be representative of the entire MoS₂ Brillouin zone. Two structures of Mo 4d character close to the Fermi level were resolved in the conduction band of 2H-MoS₂. The first structure denoted A₁ was located 1.2 eV above the Fermi level; the second structure denoted A₂ was located 2.4 eV above the Fermi level. Thus, the separation between A₁ and A₂ was ≈ 1.2 eV. As shown in Figures 2 and 3, the theoretical conduction bands of 2-D MoS₂ show two distinct bands residing above the Fermi level. The first band is located 1.1 eV above the Fermi level (at -

Figure 5. Theoretical modified atomic orbital populations (MAOPOP's) for individual Mo 4d orbitals of 2-D MoS_2 .

3.8 eV) and can be considered to correspond to the A_1 band observed by Sancrotti et al. [30]. The second band is located 3.4 eV above the Fermi level (at -1.4 eV) and can be considered to correspond to the A_2 band found in the experiment. Separation between the two theoretical conduction bands is ≈ 2.4 eV, as compared to the separation of 1.2 eV in the inverse photoemission experiment. However, the two-peaked nature of the experimental conduction band close to the Fermi level is reproduced by solid state Extended Hückel theory using the parameters of Table 1.

4.2. Theoretical Energy Dispersion Curves. Theoretical energy dispersion curves for the 2-D MoS_2 system using the parameters of Table 1 were calculated, but these results will not be described here. A full description of these calculations will be presented elsewhere [21].

4.3. Origin of the Indirect Gap. The theoretical energy dispersion curves indicated correctly that 2-D MoS_2 is a small band gap semiconductor. Using the parameters of Table 1, a *direct* gap of 1.08 eV was calculated for 2-D MoS_2 . Optical experiments indicate that the band gap of 2H- MoS_2 is actually *indirect* with a gap of ≈ 1.25 eV [31]. Scanning tunneling microscopy (STM) experiments also show the presence of a 1.35 eV indirect gap in 2H- MoS_2 [32]. During the course of this study, it was found possible to increase the size of the theoretical band gap by increasing the contribution c_2 of the more diffuse Mo 4d double zeta STO. Increasing the Mo 4d radial diffusivity increases the splitting between the valence and conduction bands by destabilizing the conduction band relative to the valence band.

The theoretical valence band of 3-D MoS_2 was calculated using the parameters of Table 1. Because large differences between the theoretical valence bands of 2-D and 3-D MoS_2 were not found, this valence band is not shown. Energy dispersion curves for 3-D

MoS₂ were calculated, and one immediately obvious feature was that the number of bands in the 3-D case was twice that of the 2-D case. However, the 2-D case involved only one MoS₂ per unit cell, while the 3-D case involves two MoS₂ molecules per unit cell.

Addition of interactions across the Van der Waals gap in 3-D MoS₂ dramatically affects the band gap of the theoretically calculated system. It was found that on proceeding from the 2-D to the 3-D system, the band gap changes from *direct* to *indirect* and narrows from 1.08 eV to 0.35 eV.

Addition of the third dimension adds MoS₂ layers in the *c* direction. Adjacent MoS₂ layers result in attractive Van der Waals forces between the layers as well as interactions between the crystal orbitals of each MoS₂ layer. Because of the one-electron nature of the Extended Hückel method, correlation between electrons is not treated. Attractive Van der Waals forces are the result of electron correlations. Thus, the absence of correlation also leads to absence and improper treatment of Van der Waals forces. However, interaction of the crystal orbitals on adjacent MoS₂ layers is treated in the 3-D MoS₂ system. If the atomic orbitals involved in a particular band (or crystal orbital) do not possess a significant component in the *c* direction, for instance *p_x*, *p_y*, *d_{xy}*, or *d_{x²-y²}*, then these orbitals will not interact across the wide Van der Waals gap to a significant extent. If the atomic orbitals involved in a particular band do possess a component in the *c* direction, for instance *p_z*, *d_{z²}*, *d_{zx}*, and *d_{yz}*, then these orbitals will interact across the Van der Waals gap.

The change from a direct gap to an indirect gap on proceeding from 2-D to 3-D MoS₂ is a result of the interaction of crystal orbitals across the Van der Waals gap. Energy destabilization due to antibonding interactions of crystal orbitals across the Van der Waals is greater than energy stabilization due to bonding interactions. Thus, theoretical energies of formation of 3-D MoS₂ systems with an infinite number of Van der Waals gaps are less

stable than 2-D MoS₂ systems with no Van der Waals gaps. For 2-D MoS₂, the highest occupied crystal band consists primarily of Mo 4d_{z²} and S 3p_z character. These atomic orbitals each possess a component in the c direction and are expected to interact across the Van der Waals gap when adjacent MoS₂ layers are added as in 3-D MoS₂. However, the S 3p_z orbitals are affected to a greater extent than the Mo 4d_{z²} orbitals by introduction of the Van der Waals gap. For 3-D MoS₂, the highest occupied crystal band consists primarily of Mo 4d_{x²-y²}, Mo 4d_{xy}, S 3p_x, and S 3p_y character. These atomic orbitals do not possess a component in the c direction and are not expected to interact significantly across the Van der Waals gap when adjacent MoS₂ layers are added. In 2-D MoS₂, the highest occupied crystal band possessed an energy of -5.36 eV. The highest occupied crystal band in 3-D MoS₂ had an energy of -5.42 eV and was slightly stabilized by 0.06 eV.

4. Conclusions

Comparison of 2-D MoS₂ theoretical valence bands with the experimental HR-ESCA valence band of polycrystalline MoS₂ led to parametrization of the S 3s, S 3p, and Mo 4d atomic ionization potentials, $H_{\perp\perp}$, Slater-type coefficients, $c_{\perp}$, and exponents, $\zeta_{\perp}$. Theoretical valence bands were obtained by summation of modified atomic orbital populations, MAOPOP's. MAOPOP's were obtained by multiplication of individual atomic populations by the appropriate photoelectron cross-sections. The theoretical valence band of 2-D MoS₂ calculated using Extended Hückel theory and the atomic parameters of Table 1 qualitatively reproduces the experimental HR-ESCA valence band of polycrystalline MoS₂. The theoretical conduction band of 2-D MoS₂ also qualitatively reproduces the experimental inverse photoemission spectroscopy conduction band of single crystal MoS₂.

Individual Mo 4d MAOPOP's were also calculated for the theoretical 2-D MoS₂ system. The highest occupied band consists of Mo 4d character such that $d_{z^2} > d_{xy} \geq d_{x^2-y^2}$. The lowest conduction band also consists of Mo 4d character such that $d_{x^2-y^2} > d_{xy} \approx d_{z^2}$. The second conduction band consists of Mo 4d character such that $d_{yz} > d_{zx}$.

Theoretical energy dispersion curves of 2-D and 3-D MoS₂, not presented here, qualitatively reproduced the experimental energy dispersion curves of Mamy et al. [23]. A direct gap of 1.08 eV was calculated for 2-D MoS₂, while an indirect gap of 0.35 eV was calculated for the 3-D MoS₂ system. Electronic structure calculations of 3-D MoS₂ involved interactions of crystal orbitals across the Van der Waals gap resulting in splitting of the highest occupied band. Because of this splitting, an indirect gap in agreement with experiments was calculated for the 3-D MoS₂ system.

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