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Molybdenum–Sulfur Bond: Electronic Structure of Low-Lying States of MoS

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ABSTRACT: The molybdenum–sulfur bond plays an important role in many processes such as nitrogen-fixation, and it is found as a building block in layered materials such as MoS_2 , known for its various shapes and morphologies. Here, we present an accurate theoretical and experimental investigation of the chemical bonding and the electronic structure of 20 low-lying states of the MoS molecule. Multireference and coupled cluster methodologies, namely, MRCISD, MRCISD + Q, RCCSD(T), and RCCSD[T], were employed in conjunction with basis sets up to aug-cc-pwCVSZ-PP/aug-cc-pwCVSZ for the study of these states. We note the significance of including the inner $4s^24p^6$ electrons of Mo and $2s^22p^6$ of S in the correlated space to obtain accurate results. Experimentally, the



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predissociation threshold of MoS was measured using resonant two-photon ionization spectroscopy, allowing for a precise measurement of the bond dissociation energy. Our extrapolated computational D_0 value for the ground state is 3.936 eV, in excellent agreement with our experimental measurement of 3.932 ± 0.004 eV. The largest calculated adiabatic D_0 (5.74 eV) and the largest dipole moment (6.50 D) were found for the ${}^{5}\Sigma^{+}$ state, where a triple bond is formed. Finally, the connection of the chemical bonding of the isolated MoS species to the relevant solid, MoS₂, is emphasized. The low-lying septet states of the diatomic molecule are involved in the material as a building block, explaining the stability and the variety of the shapes and morphologies of the material.

1. INTRODUCTION

Transition-metal sulfides attract considerable attention because of their widely recognized importance in many biological and industrial processes.^{1,2} The molybdenum–sulfur bond plays an important role in the process of nitrogen-fixation,³ in the formation of molybdenum–sulfur clusters,⁴ in 2D materials,⁵ and in many other areas. For instance, MoS₂ forms twodimensional layers with remarkable mechanical and photoelectric properties,⁶ with applications in catalysis, energy conversion and storage, sensing, photonics, nanocomposites, and membranes.^{6–10} Diatomic metal sulfides are the simplest systems to understand the metal–sulfur bonding. A thorough understanding of how these species interact is an essential step to increase our knowledge of more complicated systems.

The electronic structure of MoS was calculated in 1989 for the first time by two theoretical groups, by Ma and Dai¹¹ at the configuration interaction single and double excitation (CISD) level of theory, and by Langhoff *et al.*¹² *via* the modified coupled pair functional method (MCPF) and the multireference-based state-averaged complete active space selfconsistent field (CASSCF)/multireference configuration interaction (MRCI) methodologies. Both groups used the LANL2DZ basis set for Mo, which includes a relativistic effective core potential for the 28 inner electrons and a [3s,3p,2d] basis set for the 14 outer electrons,¹³ and a double¹¹ or triple¹² zeta quality basis set for S. Ma and Dai calculated four electronic states, ${}^{1}\Sigma^{+}$, ${}^{5}\Sigma$, ${}^{5}\Pi$, and ${}^{1}\Sigma^{+}$; 11 they found the $^1\Sigma^{\scriptscriptstyle +}$ state to be the ground state, while the $^5\Pi$ state was an excited state. On the contrary, Langhoff et al. studied seven electronic states, ${}^{5}\Pi$, ${}^{3}\Delta$, ${}^{5}\Sigma^{+}$, ${}^{3}\Pi$, ${}^{5}\Delta$, ${}^{7}\Pi$, and ${}^{7}\Sigma^{+}$; 12 they calculated the $X^5\Pi$ state to be the ground state. The groundstate bond length was calculated as 1.710(1.726) Å at the MCPF(MRCI + Q) level, while the MCPF dissociation energy was calculated as $D_0 = 4.04$ eV. The first excited state is a ${}^3\Delta$ state found at 0.61(0.25) eV at the MCPF(MRCI + Q) level of theory.¹² In 2002 and 2009, the ground $X^5\Pi$ state was studied via DFT(B3LYP and BPW91) using (LANL2DZ and LANL2DZ_{Mo}/6-311+G_S^{*}) basis sets;^{14,15} the DFT r_e and D_e values were calculated as $r_e = 2.152 - 2.163$ Å and $D_e = 3.43 - 2.163$ 3.72 eV. Experimentally, the IR spectrum of matrix-isolated MoS was measured,¹⁴ and the dissociation energy of the cation, MoS⁺, was obtained using guided ion beam tandem mass spectrometry as 3.68 ± 0.05 eV.^{16,17} Thus, there are four theoretical studies, two of them giving DFT results on the

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ground state, and all four employed the small basis set, LANL2DZ. Very little experimental data are available. There is a serious gap in the literature for the MoS molecule. The aims of this work are (1) to fill that gap and (2) to provide useful information regarding the shapes and morphologies of the MoS_2 material adding a physical insight into the role of the molybdenum–sulfur bond.

Here, accurate data on the ground and low-lying excited states of MoS are provided. Experimentally, the bond dissociation energy (BDE) of the ground state, $X^5\Pi$, is precisely measured using resonant two-photon ionization (R2PI) spectroscopy, while theoretically, the molecule was systematically studied using coupled cluster methodologies, including the core electrons in the valence space for a series of basis sets up to an augmented quintuple weighted corevalence basis set for the calculation of the dissociation energy and bond distance extrapolated to the infinite basis set. Additionally, spectroscopic data, potential energy curves (PECs), and a bonding analysis of several excited states are provided via high-level multireference configuration interaction methodologies. All these data will be useful in technologically important materials, such as 2D MoS₂ as well as in describing molybdenum-containing enzymes.

2. METHODOLOGY

2.1. Computational Details. Twenty low-lying states of MoS are calculated by employing the correlation consistent basis sets of Dunning et al., aug-cc-pV5Z, (21s,13p,5d,4f,3g,2h) \rightarrow [8s,7p,5d,4f,3g,2h] for S,¹⁸ and of Peterson *et al.*, aug-ccpV5Z-PP, $(17s,14p,12d,5f,4g,3h,2i) \rightarrow [8s,8p,7d,5f,4g,3h,2i]$ for Mo.¹⁹ The latter basis sets employ accurate core relativistic pseudo-potentials for the 1s²2s²2p⁶3s²3p⁶ electrons and treat the $4s^24p^6(5s4d)^6$ electrons of Mo in the *ab initio* calculation. The multireference configuration interaction + single + double excitations (MRCISD), 20° MRCISD + Q 21 where the Davidson correction (+Q) was included in MRCISD, methodology is applied for all states. Additionally, the ground state is also calculated via the restricted coupled cluster + singles + doubles + perturbative triples (RCCSD(T) and RCCSD[T]) methodology.²² These methods differ in their treatment of the perturbative inclusion of triple excitations. The perturbative triple corrections are computed without contributions of single excitations in the RCCSD[T] method.

Specifically, the ground state, $X^5\Pi$, is systematically studied by employing the C-RCCSD(T) and C-RCCSD[T] methods, in conjunction with a systematic sequence of weighted core correlation consistent Gaussian basis sets ranging from augmented double to augmented quintuple zeta quality, that is, aug-cc-pwCVxZ-PP_{Mo}/aug-cc-pwCVxZ_S, x = D, T, Q, and 5.^{19,23} These basis sets are designed for the accurate calculation of the correlation of the semi-valence electrons $4s^24p^6$ electrons of Mo and $2s^22p^6$ of S, which are also included in the valence space of the C-RCCSD(T) method. The size of the basis set ranges from aug-cc-pwCVDZ-PP $_{Mo}$ /aug-cc $pwCVDZ_s: (10s,9p,8d,3f) \rightarrow [6s,6p,5d,3f]/(14s,10p,3d) \rightarrow$ [6s,5p,3d] to aug-cc-pwCV5Z-PP_{Mo}/aug-cc-pwCV5Z_S: $(19s, 16p, 14d, 6f, 5g, 4h, 3i) \rightarrow [10s, 10p, 9d, 6f, 5g, 4h, 3i]/$ $(21s,13p,9d,7f,5g,3h) \rightarrow [12s,11p,9d,7f,5g,3h]$. The complete basis set (CBS) limit of bond distances, dissociation energies, and other spectroscopic constants are obtained.

Generally, for the evaluation of the CBS limit of the energetics, bond distances, spectroscopic values, and so forth, there are two approaches. Approach (I):^{24,25} All parameters are

calculated in a series of basis sets, and then these obtained values are extrapolated using the exponential formula $1,^{24,25}$ the mixed Gaussian/exponential form $2,^{24}$ or the polynomial forms $3.^{26,27}$

$$y_x = y_{\text{CBS}} + Ae^{-Bx} \tag{1}$$

$$y_x = y_{\text{CBS}} + Ae^{-(x-1)} + Be^{-(x-1)^2}$$
 (2)

$$y_x = y_{\text{CBS}} + \sum_{k=3}^{K} a_k (x + b_k)^{-k}$$
 (3)

Approach (II): 27,28 the total energies are extrapolated to the CBS limit by 1, 2 or a simplified form of 3, for example 27,28

$$y_x = y_{\text{CBS}} + Ax^{-b} \tag{4}$$

and then the spectroscopic constants would be defined by the extrapolated CBS PECs.

In the present study, we use both approaches. First, the CBS limits of bond distances, dissociation energies, and other spectroscopic parameters are calculated employing the exponential form 1 *via* the first approach. Note that this approach has been successfully used as an extrapolation scheme.^{25,26} However, additionally, we use the second approach using 1, 2, and 4, for the dissociation energy.

For the CASSCF calculations, 10 valence electrons are allotted to 9 valence orbitals, that is, six (5s4d) of Mo + three (3p) orbitals of S. We must keep the $3s^2$ electrons doubledoccupied in the CASSCF, because if not, there is a wrong ordering of the orbitals; that is, the $4p_z^2$ electrons of Mo are incorporated in the active space instead of 3s² of S. The mutual rotation of the orbitals does not alter the ordering. Thus, the 3s² electrons are doubled-occupied in the CASSCF, but in the following MRCISD calculations, there are also excitations from these orbitals/electrons, that is, from the 10 valence orbitals. Thus, excitations from the 3s² orbital are also included. The size of the MRCISD spaces is up to 1.1×10^9 , and it is reduced to about 5×10^6 CSFs after applying the internal contraction approximation (icMRCISD).²⁰ At the RCCSD(T) level of calculations, 12 electrons $(3s^23p^4 \text{ of S and } 4d^55s^1 \text{ of Mo})$ are correlated, and the RCCSD(T) space consists of up to $1.2 \times$ 10^6 CSFs, while at the C-RCCSD(T) level, 28 electrons $(2s^22p^63s^23p^4 \text{ of } S \text{ and } 4s^24p^64d^55s^1 \text{ of } Mo)$ are correlated, and the C-RCCSD(T) space consists of up to 5×10^6 CSFs. Note that in C-RCCSD(T), all electrons are correlated except for $1s^2$ of S and the inner electrons of $Mo(1s^22s^22p^63s^23p^6)$, which are treated via accurate core relativistic pseudo-potentials. To evaluate our RCCSD(T), which is a single-reference method, the single (t_1) and the double (t_2) amplitudes and the T_1 diagnostic are checked. It is found that in all calculations, the t_1 and t_2 amplitudes were very small. In most cases, they are smaller than 0.05. Moreover, the T_1 diagnostic is about 0.04 or less in all calculations. These small values of t_1 and t_2 amplitudes and of the T_1 diagnostic indicate that the single reference RCCSD(T) and C-RCCSD(T) methods are appropriate for the calculated states of the species. All calculations were done under $C_{2\nu}$ symmetry constraints; however, the CASSCF wave functions possess correct angular momentum symmetry, that is, $|\Lambda| = 0$ ($\Sigma^{+/-}$), 1 (Π), and 2 (Δ). Thus, Σ^+ corresponds to the A₁ symmetry, $\Sigma^$ corresponds to A_{2} , Π is a linear combination of B_1 and B_2 , whereas Δ is a linear combination of A₁ and A₂ symmetries. Of

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course, MRCISD and RCCSD(T) wavefunctions do not display in general a pure spatial angular momentum symmetry, but A_1 for Σ^+ , A_2 for Σ^- , B_1 or B_2 for Π , and A_1 or A_2 for Δ states.

PECs up to R = 15 Å have been plotted at the MRCISD and MRCISD + Q levels of theory for all states. Bond distances, dissociation energies $(D_e;$ adiabatic D_e^a and diabatic $D_e^d)$, relative energy ordering (T_e) , and other spectroscopic constants are computed at all of the employed levels of theory. It should be noted that spin-orbit effects are not considered here; hence, the calculated states correspond to the Ω -averaged values (*J*-averaged values for the atomic limits). The scalar relativistic effects are implicitly parametrized in the accurate core relativistic pseudo-potentials that are used here.^{23,29} Moreover, the bonding of the states is analyzed; it is depicted pictorially via a valence bond Lewis (vbL) icons and via 3D contour plots of the valence molecular orbitals (MOs).³⁰ Note that the bond order is the number of chemical bonds between the atoms; that is, a whole bond corresponds to a pair of electrons, while a half bond corresponds to a bond with one electron. All CASSCF, MRCISD, and RCCSD(T)calculations were carried out with the MOLPRO suite of codes.³¹

2.2. Experimental Details. The measurement of the BDE of MoS was conducted using R2PI spectroscopy on the same instrument that was recently used to measure the BDEs of the diatomic lanthanide sulfides and selenides.³² The spectrometer used in these studies comprises two different chambers, both evacuated to low pressures $(10^{-5} \text{ to } 10^{-6} \text{ Torr})$ and connected by a pneumatic gate valve. The first chamber houses the molecular source. Here, the MoS molecules were produced by pulsed laser ablation (Nd:YAG, 532 nm, 5 ns) of a V/Mo (4:1) alloy disk over which a flow of 40 psig of 0.7% H_2S in helium was pulsed. Collisions between the ablated metal atoms and the H₂S molecules led to the production of the desired MoS molecules. The V/Mo alloy was already available in the laboratory and was the most convenient source of Mo atoms at the time. A pure Mo disk would probably have produced the MoS molecules even more effectively. After the MoS molecules were produced, they continued colliding with the background helium gas, cooling the molecules close to ambient thermal temperatures. Following production and cooling in the reaction channel, the MoS and other molecules exited the terminal orifice of the reaction block and underwent supersonic expansion into the low-pressure region of the source chamber. In the process, we estimate that the rotational temperature was cooled to below 30 K.³

After the molecules exit the terminal orifice, they continue expanding outwardly until they are loosely collimated into a molecular beam by a 1 cm diameter conical skimmer. Upon passage through the skimmer, the molecular beam enters the differentially pumped second chamber, which houses a Wiley-McLaren time-of-flight ion source assembly.³⁴ Inside the ion source, a pulse of light from an optical parametric oscillator (OPO) laser irradiates the molecular beam. If the wavenumber of the OPO laser matches an optical transition in the molecule, the molecule can be promoted to the excited electronic state. Before the molecule can lose its energy by fluorescence, however, it is irradiated again 25 ns later by a pulse of light from an excimer laser operating on KrF gas (248 nm/5.00 eV). The total energy imparted by the two-photon excitation is sufficient to ionize the molecule. Once the molecules are ionized, they are accelerated up the electrode assembly into a

time-of-flight mass spectrometer and through a reflectron,³⁵ spatially separating the ions by mass. At the end of the time-offlight path, the molecules impact a dual microchannel plate (MCP) detector at different times according to their mass (all are singly charged). The temporal resolution of the MCP and the spatial resolution of the Wiley–McLaren electrode assembly allow for mass-resolved optical spectra to be collected as a function of the OPO laser wavelength.

An experimental cycle in our spectrometer begins with the production of the molecule of interest and ends with the digitization of the ion signal as the ions impact the MCP. Experimental cycles repeat at a rate of 10 Hz, allowing 10 mass spectra to be collected per second. In these experiments, 30 experimental cycles are averaged at each OPO laser wavelength as the OPO laser scans through a predefined wavelength range in 0.05 nm increments. Mass-specific optical spectra are collected by monitoring the signal in a given mass peak as a function of the laser wavelength. Further, because of the 25 ns delay between the OPO laser and the KrF laser, all of the peaks in the mass spectrum are doubled, with one peak consisting of ions produced by the absorption of two OPO photons and a second, delayed peak consisting of ions produced by an OPO + KrF process. The ion signal in the latter peak then displays the spectrum where the upper state survives long enough to be ionized by the KrF laser, 25 ns after the OPO laser is fired. Multiple scans are collected in the energetic vicinity of the predissociation threshold and averaged for the final spectrum. All spectra are calibrated to atomic transitions based on the well-known tabulated atomic energy levels.³

In a molecule such as MoS, the electronic states at low energies are well-described by the individual potential curves, as calculated in this report. As the ground separated atom limit is approached, however, nonadiabatic and spin-orbit couplings among the multitude of states accessible make the Born-Oppenheimer approximation invalid. As a result, it becomes fundamentally incorrect to think of the molecule as moving on a single PEC. Couplings among the myriad of states in this high-energy region allow the molecule to hop from curve to curve, eventually finding its way to dissociation if the total energy exceeds the energy of the ground state of the separated atoms. When the dissociation rate is sufficiently fast, the molecule will dissociate before it can be ionized. The purpose of the 25 ns delay between OPO excitation and KrF ionization is to allow sufficient time for molecules excited above the ground separated atom limit to dissociate. Although the predissociation threshold that is observed represents an upper limit to the BDE of the molecule, there is good reason to believe that in systems with a high density of electronic states, efficient predissociation occurs as soon as the BDE is exceeded in energy.³⁷⁻³⁹ Thus, the observed predissociation threshold provides a good estimate of the true thermochemical BDE.

3. RESULTS AND DISCUSSION

3.1. Experimental Section. The R2PI spectrum of MoS in the vicinity of its predissociation threshold is shown in Figure 1. Here, the predissociation threshold is given as the point at which the complicated quasicontinuous spectrum of vibronic transitions falls to baseline. In Figure 1, the top blue trace is the $9^{8}Mo^{32}S^{+}$ ion signal, with an arrow pointing to where the predissociation threshold in MoS is assigned, at 31,715(30) cm⁻¹ (3.932(4) eV). At the top of the arrow is an overhanging bar, which visually defines the 30 cm⁻¹ error limit assigned to the BDE of MoS. This error limit was assigned to account for



Figure 1. R2PI spectrum of MoS (upper blue trace) in the energetic vicinity of its predissociation threshold located at 31715(30) cm⁻¹. Mo atomic transitions (lower red trace) were used to calibrate the spectrum.

various experimental uncertainties: the rotational temperature of the molecules ($\sim 20 \text{ cm}^{-1}$), the linewidth of the OPO laser in this energy range (<10 $\,\mathrm{cm^{-1}})\!,$ and a subjective assessment of the sharpness of the predissociation threshold. The red trace at the bottom of the figure displays the Mo atomic transitions that were recorded simultaneously with the MoS molecular signal. These were used to calibrate the wavenumber axis of the MoS spectrum. The MoS spectrum also displays a few sharp decreases in intensity that fall at the same wavenumbers as the strong Mo atomic lines (near 31,300 and 31,533 cm⁻¹). These are artifacts resulting from the huge number of Mo⁺ atomic ions produced at these wavenumbers. The large number of Mo⁺ atomic ions produced on resonance causes the entire ion cloud to expand as it traverses the time-of-flight drift tube so that only a small fraction of the ions reach the detector. The number of atomic ions produced is so large that a strong atomic signal is still observed at these wavenumbers, but all other ionic species, including MoS⁺, are depleted due to this effect.

3.2. Theoretical Section. The PECs of the 20 calculated states of MoS are depicted in Figures 2 and 1S of the Supporting Information (SI). The bond distances, dissociation energies, spectroscopic parameters, and dipole moments calculated as expectation values $(\langle \mu \rangle)$ and by the finite-field method $(\mu_{FF})^{40,41}$ and relative energy differences of the calculated states are given in Table 1. The leading configurations, the formed bonds, the atomic products at the equilibrium position, the asymptotic atomic products, and the avoided crossings that occur are given in Table 2. Below, the states are categorized according to their correlated atomic states.

3.2.1. States Correlated to $Mo(^7S) + S(^3P)$. The atomic ground-state products of $Mo(^7S, 5s^14d^5)$ and $S(^3P, 3s^23p^4)$ give rise to six molecular states: ${}^{5}\Pi, {}^{7}\Pi, {}^{9}\Pi, {}^{5}\Sigma^{-}, {}^{7}\Sigma^{-}$, and ${}^{9}\Sigma^{-}$. Their PECs are plotted in Figures 3 and 2S of the SI. All six states retain the $Mo(^{7}S)$ and $S(^{3}P)$ characteristics in their PECs. The quintets and the septets are bound, while the nonets are repulsive. This happens because in both nonet



Figure 2. PECs of the 20 calculated states of MoS at the MRCISD + Q/aug-cc-pV5Z(-PP_{Mo}) level of theory.

states, the atoms have their valence electrons, $5s^{1}4d^{5}$ (Mo) and $3s^{2}3p^{4}$ (S), with a parallel spin; no bonds are formed.

The $X^{5}\Pi$ state is the ground state, while the $A^{5}\Sigma^{-}$, ${}^{7}\Pi$, and ${}^{7}\Sigma^{-}$ states lie 1.07, 1.31, and 2.60 eV above the $X^{5}\Pi$ state. The $X^{5}\Pi$ and the ${}^{5}\Sigma^{-}$ states have a double bond, $\sigma^{2}\pi^{2}$ and $\pi^{2}\pi^{2}$, respectively, and their calculated MRCISD + Q/aug-cc-pV5Z(-PP)_{Mo} bond distances are 2.148 and 2.161 Å, respectively. The septets, ${}^{7}\Pi$ and ${}^{7}\Sigma^{-}$, have a single bond, that is, σ^{2} and π^{2} , respectively, and, as a result, their bond distances are elongated by about 0.3 Å. Finally, the vibrational frequencies ω_{e} are 479($X^{5}\Pi$), 466(${}^{5}\Sigma^{-}$), 337(${}^{7}\Pi$), and 386 cm⁻¹ (${}^{7}\Sigma^{-}$).

3.2.2. States Correlated to $Mo(^7S) + S(^1D)$. The $Mo(^7S, Ss^14d^5) + S(^1D, 3s^23p^4)$ separated atom limit gives rise to three molecular states: $^7\Delta$, $^7\Pi(2)$, and $^7\Sigma^+$. Their PECs are plotted in Figures 4 and 3S of the SI. All are bound states. The $^7\Sigma^+$ and $^7\Delta$ states have a half bond, σ^1 and π^1 , respectively, and they retain the character $Mo(^7S) + S(^1D)$ in their PEC. The $^7\Pi(2)$ state presents an avoided crossing with the $^7\Pi(3)$ state that correlates to the excited $Mo(^5S) + S(^3P)$ limit; thus, at r_e the *in situ* atoms, that is, the atomic states in the minimum, are $Mo(^5S) + S(^3P)$, and a σ^2 bond is formed. The MRCISD + Q r_e and D_e values for dissociation to the $^7S + ^1D$ limit are 2.376 Å, 2.50 eV $(^7\Sigma^+)$, 2.451 Å, 1.94 eV $(^7\Delta)$, and 2.538 Å and 1.83 eV $(^7\Pi(2))$. The diabatic D_e value for the $^7\Pi(2)$ state with respect to the *in situ* atoms $(^7S + ^1D)$ is 2.04 eV.

3.2.3. States Correlated to $Mo({}^{5}S) + S({}^{3}P)$. Totally, six states result from the $Mo({}^{5}S, 5s^{1}4d^{5}) + S({}^{3}P, 3s^{2}3p^{4})$ separated atom limit: $a^{3}\Sigma^{-}$, ${}^{3}\Pi$, ${}^{5}\Pi(2)$, ${}^{5}\Sigma^{-}(2)$, ${}^{7}\Pi(3)$, and ${}^{7}\Sigma^{-}(2)$, see Figures 5 and 4S of the SI. The Mo atom is excited; the $Mo({}^{5}S, 5s^{1}4d^{5}) \leftarrow Mo({}^{7}S, 5s^{1}4d^{5})$ energy difference is calculated as 1.354(1.271) eV at the MRCISD(MRCISD + Q)/aug-cc-pV5Z level, in excellent agreement with the experimental value of $1.335 \text{ eV}.^{36}$ Five of these states are bound, while the ${}^{7}\Sigma^{-}(2)$ state is repulsive. Finally, the $a^{3}\Sigma^{-}$, ${}^{5}\Sigma^{-}(2)$, and ${}^{7}\Pi(3)$ states present the avoided crossings with the ${}^{3}\Sigma^{-}(2)$, ${}^{5}\Sigma^{-}(3)$, and ${}^{7}\Pi(2)$ states, respectively, see Table 3.

The first excited state of MoS is the $a^3\Sigma^-$ state, which is located 0.59 eV above the $X^5\Pi$ state. It is of interest that the first excited state $a^3\Sigma^-$ presents an avoided crossing at 3.2 Å with another ${}^3\Sigma^-(2)$ state, and as a result, the $a^3\Sigma^-$ state changes its character to Mo(5D) + S(3P). The diabatic and adiabatic curves of the $a^3\Sigma^-$ state are shown in Figure 5. This state has a triple bond, $\sigma^2 \pi^2 \pi^2$, and the shortest bond distance $r_e = 2.070$ Å at the MRCISD + Q/aug-cc-pV5Z(-PP)_{Mo} level of theory. Its corresponding adiabatic D_e value (dissociation to 5S + 3P) is 4.375 eV, while the diabatic D_e (dissociation to 5D + Table 1. Bond Lengths $r_{\rm e}$ (Å), Dissociation Energies $D_{\rm e}$ (eV), Harmonic Frequencies and Anharmonic Corrections $\omega_{e'}$, $\omega_{e'\chi_{e'}}$ (cm⁻¹), Rotational Vibrational Couplings $\alpha_{\rm e}$ (cm⁻¹), Centrifugal Distortions $\overline{D}_{\rm e}$ (cm⁻¹), Dipole Moments Calculated as Expectation Values $\langle \mu \rangle$ (Debye) and by the Finite-Field Method $\mu_{\rm FF}$ (Debye) and Energy Differences $T_{\rm e}$ (eV) of 20 Calculated States of MoS at the MRCISD, MRCISD + Q/aug-cc-pV5Z(-PP)_{Mo} Level of Theory

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state	method ^a	r _e	$D_{\rm e}$	$D_{\rm e}^{{\rm d}a}$	$\omega_{\rm e}$	$\omega_{e\chi_{e}}$	$a_{\rm e}~(10^{-4})$	$\overline{D}_{\rm e}~(10^{-8})$	$\langle \mu \rangle$	$\mu_{ m FF}$	$T_{\rm e}$
$X^{5}\Pi$	MRCISD	2.1571	3.371		467.0	2.32	7.663	6.138	4.479	4.710	0.000
	MRCISD + Q	2.1479	3.646		479.0	2.18	7.285	5.986		4.561	0.000
$^{3}\Sigma^{-}$	MRCISD	2.0740	4.085	4.486	549.2	1.84	6.396	5.618	2.469	2.697	0.702
	MRCISD + Q	2.0704	4.375	4.740	554.7	1.78	6.285	5.565		2.348	0.594
$5\Sigma^{-}$	MRCISD	2.1635	2.393		465.0	1.92	7.094	6.083	0.117	0.234	0.978
	MRCISD + Q	2.1614	2.580		465.8	1.97	7.183	6.095		0.205	1.066
$5\Sigma^+$	MRCISD	2.1953	4.137	5.292	473.7	1.50	5.484	5.37	7.018	6.829	1.052
	MRCISD + Q	2.1912	4.307	5.422	476.3	1.36	5.299	5.371		6.501	1.027
$^{3}\Delta$	MRCISD	2.0913	4.079	4.338	537.6	1.78	6.343	5.579	3.877	3.965	1.110
	MRCISD + Q	2.0876	4.266	4.654	540.8	1.74	6.264	5.572			1.068
7Π	MRCISD	2.4320	2.162		333.6	1.28	5.859	5.857	4.862	4.938	1.209
	MRCISD + Q	2.4239	2.334		337.1	1.26	5.804	5.852		4.896	1.312
$^{3}\Pi$	MRCISD	2.1300	3.559		509.1	1.67	6.08	5.572	4.342	4.436	1.228
	MRCISD + Q	2.1238	3.819		514.5	1.65	6.011	5.551		4.412	1.150
${}^{5}\Delta$	MRCISD	2.1692	3.606	4.762	486.0	1.57	5.882	5.479	4.542	5.040	1.583
	MRCISD + Q	2.1642	3.850	4.965	492.4	1.53	5.705	5.413		4.852	1.484
$^{7}\Sigma^{+}$	MRCISD	2.3945	2.326		304.2	1.30	6.971	7.733	5.591	5.445	2.201
	MRCISD + Q	2.3759	2.500		313.5	1.35	6.963	7.632		5.059	2.260
⁵ Π(2)	MRCISD	2.3644	2.415		414.2	1.15	3.903	4.498	5.154	4.891	2.372
	MRCISD + Q	2.3427	2.696		406.8	1.73	3.231	4.929		4.667	2.273
$^{3}\Sigma^{+}$	MRCISD	2.1917	2.733	3.888	437.9	2.79	8.211	6.347	4.857	5.088	2.456
	MRCISD + Q	2.1797	2.973	4.087	457.0	2.48	7.283	6.023		4.789	2.362
$^{3}\Delta(2)$	MRCISD	2.2158	2.682	3.838	443.8	2.22	5.808	5.786	5.454	6.504	2.506
	MRCISD + Q	2.1954	3.017	4.132	468.7	1.80	4.904	5.481		6.191	2.317
$^{7}\Sigma^{-}$	MRCISD	2.3824	0.812		384.0	2.26	5.066	5.002	0.184	0.015	2.559
	MRCISD + Q	2.3944	1.043		386.0	1.02	3.38	4.805		0.232	2.603
$^{7}\Delta$	MRCISD	2.4578	1.791		326.8	0.92	4.969	5.728	1.45	1.267	2.736
	MRCISD + Q	2.4511	1.935		328.3	0.95	5.084	5.769		1.007	2.825
${}^{5}\Sigma^{-}(2)$	MRCISD	2.3185	1.957	2.358	384.4	0.97	5.43	5.876	0.252	1.521	2.831
	MRCISD + Q	2.3065	2.254	2.620	387.5	1.04	5.704	5.967		1.871	2.714
$^{7}\Pi(2)$	MRCISD	2.5487	1.684	1.945	310.8	0.88	4.303	5.093	3.008	2.501	2.843
	MRCISD + Q	2.5380	1.833	2.042	308.6	0.93	4.528	5.297		2.146	2.927
$^{7}\Pi(3)$	MRCISD	2.5328	1.428		307.2	0.95	4.936	5.413	2.509	2.442	3.382
	MRCISD + Q	2.5232	1.501		308.9	0.98	5.092	5.476		2.098	3.474
⁹ Σ ⁻	MRCISD		repulsive							3.361	
	MRCISD + Q		repulsive							3.647	
9П	MRCISD		repulsive							3.371	
	MRCISD + Q		repulsive							3.646	
$^{7}\Sigma^{-}(2)$	MRCISD		repulsive							4.788	
	MRCISD + Q		repulsive							4.969	
^{<i>i</i>} D ^d _o : diabati	ic dissociation ener	gy.									

 ^{3}P) is 4.740 eV. Finally, its vibrational frequency is 555 cm⁻¹; this state has the largest harmonic frequency among all of the calculated states.

The ${}^{5}\Sigma^{-}(2)$ state also presents an avoided crossing at ~3 Å with a ${}^{5}\Sigma^{-}(3)$, which correlates to the Mo(${}^{5}D$) + S(${}^{3}P$) separated atom limit. The ${}^{3}\Pi$ and ${}^{5}\Sigma^{-}(2)$ states have a double bond, $\sigma^{2}\pi^{2}$, their bond distances are 2.124 and 2.306 Å, and their $D_{\rm e}$ values (dissociation to ${}^{5}S + {}^{3}P$) are 3.819 and 2.254 eV, respectively, at the MRCISD + Q/aug-cc-pV5Z(-PP)_{Mo} level of theory. The corresponding diabatic $D_{\rm e}$ (dissociation to ${}^{5}D + {}^{3}P$) of ${}^{5}\Sigma^{-}(2)$ is 2.620 eV. The ${}^{5}\Sigma^{-}(2)$ presents more elongated $r_{\rm e}$ and smaller $D_{\rm e}$ values than ${}^{3}\Pi$, even though they both form a double bond. These differences result from the fact that the π^{2} bond in ${}^{5}\Sigma^{-}(2)$ is dative ($d_{xz}^{0} \leftarrow 3p_{x}^{2}$) and its

σ² bond is covalent, while in the ³Π state, both of its σ² π²bonds are covalent. Finally, both ⁵Π(2) and ⁷Π(2) states have a single σ² bond, and their MRCISD + Q bond distances and D_e values (dissociation to ⁵S + ³P) are 2.343 Å, 2.696 eV and 2.538 Å, 1.833 eV, respectively.

3.2.4. States Correlated to $Mo({}^{5}D) + S({}^{3}P)$. Five states have been calculated that correlate to $Mo({}^{5}D, 5s^{2}4d^{4}) + S({}^{3}P, 3s^{2}3p^{4})$: ${}^{5}\Sigma^{+}, {}^{3}\Delta, {}^{5}\Delta, {}^{3}\Sigma^{+}$, and ${}^{3}\Delta(2)$, see Figures 6 and 5S of the SI. All are bound states, and all present avoided crossings with higher excited states. The ${}^{3}\Delta$ state has an avoided crossing with a state that correlates to $Mo({}^{5}G) + S({}^{3}P)$; the other states have avoided crossings with states that correlate to $Mo({}^{5}D) + S({}^{1}D)$, see Table 2. All states have a triple $\sigma^{2}\pi^{2}\pi^{2}$ bond. The MRCISD + Q bond distances and the adiabatic(diabatic)

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Table 2. Leading Configurations, Bonding, Atomic Products at r_e ,^{*a*} Bond Distances (Å) Where Avoided Crossings Occur, and Asymptotic Atomic Products^{*a*} (15 Å) at the MRCISD/aug-cc-pV5Z(-PP)_{Mo} Level of Theory

state	leading configuration (valence electrons)	bonds	atomic products at $r_{\rm e}$	avoid. cross.	asymptotic atomic products
Х ⁵ Π	$\frac{0.89}{\sqrt{2}} 1\sigma^2 2\sigma^2 3\sigma^1 (1\pi_x^2 \pi_y^2 2\pi_y^1 + 1\pi_x^2 2\pi_x^1 1\pi_y^2) 1\delta_+^1 1\delta^1\rangle)$	$\sigma^2 \pi^2$	$Mo(^{7}S) + S(^{3}P)$		$Mo(^{7}S) + S(^{3}P)$
${}^{3}\Sigma^{-}$ ${}^{5}\Sigma^{-}$	$0.89 1\sigma^{2}2\sigma^{2}3\sigma^{2}1\pi_{x}^{2}1\pi_{y}^{2}1\delta_{+}^{1}1\delta_{-}^{1}\rangle$ $0.88 1\sigma^{2}2\sigma^{2}3\sigma^{4}4\sigma^{1}1\pi_{*}^{2}1\pi_{*}^{2}1\delta_{+}^{1}1\delta_{-}^{1}\rangle$	$\sigma^2 \pi^2 \pi^2 \pi^2 \pi^2 \pi^2 \pi^2$	$Mo({}^{5}D) + S({}^{3}P)$ $Mo({}^{7}S) + S({}^{3}P)$	3.2	$Mo({}^{5}S) + S({}^{3}P)$ $Mo({}^{7}S) + S({}^{3}P)$
${}^5\Sigma^+$	$0.96 1\sigma^2 2\sigma^2 1\pi_x^2 2\pi_x^{-1} 1\pi_y^2 2\pi_y^{-1} 1\delta_+^{-1} 1\delta^{-1}\rangle$	$\sigma^2 \pi^2 \pi^2$	$Mo(^{5}D) + S(^{1}D)$	3.0	$Mo(^{5}D) + S(^{3}P)$
$^{3}\Delta$	$0.91 1\sigma^{2}\sigma^{2}3\sigma^{1}1\pi_{x}^{2}1\pi_{y}^{2}(1\delta_{+}^{1}1\delta_{-}^{2}+1\delta_{+}^{2}1\delta_{-}^{1})\rangle$	$\sigma^2 \pi^2 \pi^2$	$Mo({}^{5}G) + S({}^{3}P)$	2.7	$Mo(^{5}D) + S(^{3}P)$
$^{7}\Pi$	$\frac{0.99}{\sqrt{2}} 1\sigma^2 2\sigma^2 3\sigma^1 (1\pi_x^{-1} 2\pi_x^{-1} 1\pi_y^{-2} 2\pi_y^{-1} + 1\pi_x^{-2} 2\pi_x^{-1} 1\pi_y^{-1} 2\pi_y^{-1}) 1\delta_+^{-1} 2\delta^{-1}\rangle$	σ^2	$Mo(^{7}S) + S(^{3}P)$		$Mo(^{7}S) + S(^{3}P)$
$^{3}\Pi$	$\frac{0.84}{\sqrt{2}} 1\sigma^2 2\sigma^2 3\sigma^1 (1\pi_x^{\ 2} 1\pi_y^{\ 2} 2\overline{\pi}_y^{\ 1} + 1\pi_x^{\ 2} 22\overline{\pi}_x^{\ 1} 1\pi_y^{\ 2}) 1\delta_+^{\ 1} 2\delta^{\ 1}\rangle$	$\sigma^2 \pi^2$	$Mo(^{5}S) + S(^{3}P)$		$Mo(^{5}S) + S(^{3}P)$
$^{5}\Delta$	$\frac{0.90}{\sqrt{2}} 1\sigma^2 2\sigma^2 1\pi_x^2 2\pi_x^{-1} 1\pi_y^2 2\pi_x^{-1} (1\delta_+^{-1} + 1\delta^{-1})\rangle$	$\sigma^2 \pi^2 \pi^2$	$Mo(^{5}D) + S(^{1}D)$	2.7	$Mo(^{5}D) + S(^{3}P)$
$^{7}\Sigma^{+}$	$0.99 1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^{\ 2} 2\pi_x^{\ 1} 1\pi_y^{\ 2} 2\pi_y^{\ 1} 1\delta_+^{\ 1} 1\delta^{\ 1}\rangle)$	σ^1	$Mo(^{7}S) + S(^{1}D)$		$Mo(^{7}S) + S(^{1}D)$
⁵ Π(2)	$\frac{0.75}{\sqrt{2}} 1\sigma^2 2\sigma^2 3\sigma^1 (1\pi_x^{-1} 2\bar{\pi}_x^{-1} 1\pi_y^{-1} 2\pi_y^{-1} + 1\pi_x^{-1} 2\pi_x^{-1} 1\pi_y^{-1} 22\bar{\pi}_y^{-1}) 1\delta_+^{-1} 1\delta^{-1} \rangle)$	σ^2	$Mo(^{5}S) + S(^{3}P)$		$Mo(^{5}S) + S(^{3}P)$
$^{3}\Sigma^{+}$	$0.44 1\sigma^2 \sigma^2 (1\pi_x^2 2\pi_x^{-1} 1\pi_y^2 2\pi_y^{-1} + 1\pi_x^2 2\overline{\pi}_x 11\pi_y^2 2\pi y^{-1}) (1\delta_+^{-1} 1\overline{\delta}^{-1} + 1\overline{\delta}_+^{-1} 1\delta^{-1})\rangle$	$\sigma^2 \pi^2 \pi^2$	$Mo(^{5}D) + S(^{1}D)$	3.0	$Mo(^{5}D) + S(^{3}P)$
$^{3}\Delta(2)$	$0.49 1\sigma^2 2\sigma^2 (1\pi_x^2 2\pi_x 11\pi_y^2 2\overline{\pi}_y^1 - 1\pi_x^2 2\overline{\pi}_x 11\pi_y^2 2\pi_y 1) (1\delta_+^{-1} 1\overline{\delta}^{-1} + 1\overline{\delta}_+^{-1} 1\delta^{-1})\rangle$	$\sigma^2 \pi^2 \pi^2$	$Mo(^{5}D) + S(^{1}D)$	2.6	$Mo(^{5}D) + S(^{3}P)$
$^{7}\Sigma^{-}$	$0.63 1\sigma^{2}\sigma^{2}3\sigma^{1}4\sigma^{1}(1\pi_{x}^{1}2\pi_{x}^{1}1\pi_{y}^{2}+1\pi_{x}^{2}1\pi_{y}^{1}2\pi_{y}^{1})1\delta_{+}^{1}1\delta_{-}^{1}\rangle$	π^2	$Mo(^{7}S) + S(^{3}P)$		$Mo(^{7}S) + S(^{3}P)$
$^7\Delta$	$\frac{0.70}{\sqrt{2}} 1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 (1\pi_x^{-1} 1\pi_y^{-2} 2\pi_y^{-1} - 1\pi_x^{-2} 2\pi_x^{-1} 1\pi_y^{-1} + 1\pi_x^{-1} 2\pi_x^{-1} 1\pi_y^{-1} - 1\pi_x^{-2} 1\pi_y^{-2} 2\pi_y^{-1})1\delta_+^{-1} 1\delta^{-1} \rangle)$	π^1	$Mo(^{7}S) + S(^{1}D)$		$Mo(^{7}S) + S(^{1}D)$
${}^{5}\Sigma^{-}(2)$	$0.54 1\sigma^2 2\sigma^2 3\sigma^2 (1\pi x^1 2\pi_x^{-1} 1\pi_y^{-2} + 1\pi_x^{-2} 1\pi_y^{-1} 2\pi_y^{-1}) 1\delta_+^{-1} 1\delta^{-1} \rangle$	$\sigma^2 \pi^2$	$Mo(^{5}D) + S(^{3}P)$	3.0	$Mo(^{5}S) + S(^{3}P)$
⁷ Π(2)	$\frac{0.90}{\sqrt{2}} 1\sigma^2 2\sigma^2 3\sigma^1 (1\pi_x^{-1} 2\pi_x^{-1} 1\pi_y^{-2} 2\pi_y^{-1} + 1\pi_x^{-2} 2\pi_x^{-1} 1\pi_y^{-1} 2\pi_y^{-1}) 1\delta_+^{-1} 1\delta^{-1}\rangle)$	σ^2	$Mo(^{5}S) + S(^{3}P)$	2.9	$Mo(^{7}S) + S(^{1}D)$
⁷ Π(3)	$\frac{0.70}{\sqrt{2}} 1\sigma^2 2\sigma^2 3\sigma^1 (1\pi_x^2 2\pi_x^{-1} 1\pi_y^{-1} 2\pi_y^{-1} - 1\pi_x^{-1} 2\pi_x^{-1} 1\pi_y^{-2} 2\pi_y^{-1})(1\delta_+^{-1} + 1\delta^{-1})\rangle)$	σ^2	$Mo(^{7}S) + S(^{1}D)$	2.9	$Mo({}^{5}S) + S({}^{3}P)$
$9\Sigma^{-}$	$0.99 1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi_x^{-1} 2\pi_x^{-1} 1\pi_y^{-1} 2\pi_y^{-1} 1\delta_+^{-1} 1\delta^{-1}\rangle$				$Mo(^{7}S) + S(^{3}P)$
9П	$\frac{0.99}{\sqrt{2}} 1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 (1\pi_x^{\ 1} 2\pi_x^{\ 1} 1\pi_y^{\ 1} 2\pi_y^{\ 1} + 1\pi_x^{\ 1} 2\pi_x^{\ 1} 1\pi_y^{\ 1} 2\pi_y^{\ 1}) 1\delta_+^{\ 1} 1\delta^{\ 1}\rangle)$				$Mo(^{7}S) + S(^{3}P)$
$^{7}\Sigma^{-}(2)$	$0.99 1\sigma^2 2\sigma^2 3\sigma^1 4\overline{\sigma}^1 1\pi_x^{\ 1} 2\pi_x^{\ 1} 1\pi_y^{\ 1} 2\pi_y^{\ 1} 1\delta_+^{\ 1} 1\delta^{\ 1}\rangle$				$Mo({}^{5}S) + S({}^{3}P)$
^{<i>a</i>} Mo(⁷ S,	5s ¹ 4d ⁵); Mo(⁵ S, 5s ¹ 4d ⁵); Mo(⁵ D, 5s ² 4d ⁴); Mo(5G, 5s ² 4d ⁴); S (³ P,	3s ² 3p ⁴); §	$S(^{1}D, 3s^{2}3p^{4}).$		



Figure 3. PECs of the six states of MoS, which correlate to the atomic ground-state products at the MRCISD + $Q/aug-cc-pVSZ(-PP_{Mo})$ level of theory.

dissociation energies are 2.191 Å, 4.31(5.42) eV for ${}^{5}\Sigma^{+}$; 2.088 Å, 4.27(4.65) eV for ${}^{3}\Delta$; 2.164 Å, 3.85(4.96) eV for ${}^{5}\Delta$; 2.180 Å, 2.97(4.09) eV for ${}^{3}\Sigma^{+}$; and 2.195 Å, 3.02(4.13) eV for ${}^{3}\Delta$ (2). We observe that the ${}^{3}\Delta$ has a shorter bond distance by about 0.1 Å than the remaining four calculated states because its triple bond is formed by a double covalent bond and a



Figure 4. PECs of the three states of MoS, which correlate to the $Mo(^7S) + S(^1D)$ atomic state products and of $^7\Pi(3)$, which present avoided crossing with $^7\Pi(2)$ at MRCISD + Q/aug-cc-pVSZ(-PP_{Mo}). The dotted line corresponds to the diabatic PEC of $^7\Pi(2)$.

single dative bond; the other four states have a single σ^2 covalent and two $\pi^2 \pi^2$ dative bonds, see below. The formation of triple bonds results in strong bonds with diabatic dissociation energies up to 5.42 eV (${}^{5}\Sigma^{+}$).





Internuclear Distance (Angstrom)

Figure 5. PECs of the calculated states of MoS, which correlate to the $Mo(^{5}S) + S(^{3}P)$ atomic state products at MRCISD + Q/aug-ccpVSZ(-PP_{Mo}). The dotted line corresponds to a diabatic PEC.

Table 3. Bond Distances r_e (Å), Dissociation Energies D_e (eV), and Corrected Values for Zero-Point Energy D_0 (eV), and Harmonic Frequencies ω_e (cm⁻¹), of the $X^{S}\Pi$ State at RCCSD(T), RCCSD[T]/aug-cc-CV5Z-PP_{Mo}/aug-cc-CV5Z_S, and C-RCCSD(T), RCCSD[T]/aug-cc-pwCV5Z-PP_{Mo}/aug-cc-pwCV5Z_S

	aug-cc-pV	5Z(-PP _{Mo})	aug-cc-pwCV5Z(-PP _{Mo})			
	RCCSD(T)	RCCSD[T]	C-RCCSD(T)	C-RCCSD[T]		
r _e	2.1313	2.1461	2.1161	2.1337		
$D_{\rm e}$	3.705	3.863	3.757	3.937		
D_0	3.674	3.834	3.725	3.907		
$\omega_{\rm e}$	508.7	480.9	513.0	490.8		



Figure 6. PECs of the calculated states of MoS, which correlate to the $Mo(^{5}D) + S(^{3}P)$ atomic state products at MRCISD + Q/aug-ccpVSZ(-PP_{Mo}).

3.2.5. Bonding Analysis. The leading configurations, the bonding, the avoided crossings that occur, and the asymptotic and the *in situ* atomic products of the 20 calculated states are given in Table 2. The vbL bonding icons and the electron density of selected states are given in Scheme 1 and shown in Figure 7. These two pictures correspond to the description of the chemical bonding *via* the two basic theories, that is, valence bond (VB) theory and MO theory. To compare the two theories, the atomic orbitals with the main contribution are noted for each MO, shown in Figure 7, while the existent hybridization is discussed below. The vbL icons focus on how the atomic orbitals of the equilibrium atoms are combined to

give individual chemical bonds when a molecule is formed, while some of the valence electrons are represented as not shared and not involved in the formation of the molecule. On the contrary, in the MO theory, all the electrons of the valence shell are represented as having taken part in the bonding. VB theory is simpler and more convenient than MO for the calculation of the bond order of the diatomics. In MO theory, the bond order is half the difference between the number of bonding electrons minus the number of antibonding electrons; however, careful attention must be paid to characterize the orbitals as bonding, antibonding, or non-bonding. In the vbL icons, the bond order is the number of chemical bonds between the atoms, that is, a whole bond corresponds to a pair of electrons, while a half bond corresponds to a bond with one electron. Both theories predict the same bond order after careful examination of the MOs for the MO theory.

For the bound calculated states of MoS, the bond order ranges from a half bond (σ^1 or π^1) to a triple bond, $\sigma^2 \pi^2 \pi^2$. The electronic configuration of the ground $X^5\Pi$ state is $1/\sqrt{2}\{|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^1 1\delta_+^{-1} 1\delta_-^{-1}\rangle + 1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^{-2}$ $2\pi_y^{-1}1\delta_+^{-1}1\delta_-^{-1}$. According to the vbL icon, this has a double covalent bond σ^2 : $4d_{z2}^{-1} - 3p_z^{-1}$ and π_x^2 : $4d_{xz}^{-1} - 3p_x^{-1}$ (or π_y^2 : $4d_{yz}^{1}-3p_{y}^{1}$), see Scheme 1. The $1\pi_{y}^{2}$ and $2\pi_{x}^{1}$ orbitals in the B₁ symmetry (or $1\pi_x^2$ and $2\pi_y^1$ in B₂ symmetry) are located mainly on the S and Mo atoms, respectively, resulting in a double bond of $\sigma^2 \pi^2$. Theoretically, according to the MO theory, there are four fully occupied bonding valence orbitals, $1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^2$, two half-occupied antibonding orbitals $3\sigma^{1}2\pi_{x}^{1}$, and two half-occupied non-bonding orbitals $1\delta_{+}^{1}1\delta_{-}^{1}$. Thus, the bond could be characterized as a triple bond. However, through examination of the calculated MOs, we observe that $1\sigma^2$ is mainly on S and $3\sigma^1$ is on Mo and are therefore nonbonding orbitals. Additionally, the $1\pi_x^2$ and $1\pi_y^2$ orbitals shown in Figure 6 are an average of the B_1 and \dot{B}_2 symmetry orbitals. If the calculation is conducted using only one symmetry, B₁ or B₂, then the $1\pi_x^2 2\pi_x^1$ (B₁) or $1\pi_y^2 2\pi_y^2$ (B₂) orbitals are mainly localized on $S(1\pi_x^2)$ and $Mo(2\pi_x^1)$ in B_1 or on $S(1\pi_v^2)$ and $Mo(2\pi_v^1)$ in B_2 . Thus, they can also be classified as non-bonding orbitals, again giving a bond order of 2. In our discussion below, we calculate the bond order using the vbL picture because it is more convenient than the MO picture. The second excited state, ${}^5\Sigma^-$ (| $1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 1\pi_x^2 1\pi_y^2 1\delta_+^{-1} 1\delta_-^{-1})$, also has a double $\pi^2 \pi^2$ covalent bond, as do the ${}^{3}\Pi$ and ${}^{5}\Sigma^{-}(2)$ states. It may be noted that the bond distance of the calculated states with double bonds ranges from 2.12 to 2.30 Å.

The first excited state, $a^3\Sigma^-$, which presents an avoided crossing at 3.2 Å with another ${}^3\Sigma^-(2)$ state, has a triple $\sigma^2 \pi^2 \pi^2$ bond, and the *in situ* atoms are Mo(5D) + S(3P). The two π^2 bonds are covalent, while the σ^2 bond is dative, that is, $4d_{z2}^0 \leftarrow$ $3p_z^2$. It should be noted that there is a quite strong hybridization of $3s3p_z$ in the MOs of S; however, the main participant in bonding seems to be $3p_z^2$. Apart from the $a^3\Sigma^$ state, triple bonds are formed in the ${}^5\Sigma^+$, ${}^3\Delta$, ${}^3\Sigma^+$, and ${}^3\Delta(2)$ states. The ${}^3\Delta$ state also has two π^2 covalent bonds and a σ^2 dative bond, as in the $a^3\Sigma^-$ state; however, the *in situ* atoms are Mo(5G) + S(3P) and the main participant in σ^2 bonding seems to be $3s^2$. The remaining ${}^5\Sigma^+$, ${}^5\Delta$, ${}^3\Sigma^+$, and ${}^3\Delta(2)$ states form triple bonds with a σ^2 covalent and two $\pi^2\pi^2$ dative bonds, that is, $5p_x^0 \leftarrow 3p_x^2$ and $5p_y^0 \leftarrow 3p_y^2$. It is of interest that the Mo Sp orbitals are involved in the bonding; the atomic orbital occupation analysis shows an electron charge of about 0.1 e⁻. Bond distances of these states range

Scheme 1. vbL Bonding Icons of the $X^{\delta}\Pi$, $a^{3}\Sigma^{-}$, $A^{\delta}\Sigma^{-}$, ${}^{3}\Delta$, ${}^{7}\Pi$, and ${}^{5}\Sigma^{+}$ States



Figure 7. MOs of the $X^{3}\Pi$, $\alpha^{3}\Sigma^{-}$, $^{3}\Delta$, and $^{7}\Pi$ states. The atomic orbitals with the main contribution are given for each MO.

from 2.07 to 2.20, and the diabatic dissociation energies range from 4.13 to 5.42 eV at the MRCISD + Q/aug-cc-pV5Z(-PP) level. Finally, the ⁷Π, ⁷Σ⁺, ⁵Π(2), ⁷Σ⁻, ⁷Δ, and ⁷Π(2) form a single σ or π bond or a half single bond, their bond distances range from 2.34 to 2.54 Å, and their diabatic dissociation energies are 1.04–2.70 eV. The lowest energy state forming a single bond is the ⁷Π state, which has a σ^2 covalent bond, that is, σ^2 : $4d_{z2}^{-1}-3p_z^{-1}$, see Table 2. Again, there is a quite strong hybridization of 3s–3p_z in MOs of S; however, the main participant in bonding seems to be $3p_z$. Finally, it should be noted that in all states, there is a $5s4d_{z2}$ or $5s5p_z4d_{z2}$ hybridization in the MOs for Mo, which is clearly depicted in MO plots, see Figure 7.

Comparing the MoS with MoO,^{38,42} both have a $X^{5}\Pi$ ground state, forming double bonds. However, MoO has a BDE that is larger by 1.5 eV and a bond distance that is shorter by 0.42 Å than MoS. Specifically, for MoO: expt: $D_0 = 5.414(19)$ eV³⁸ and calc: $D_0 = 5.515 \pm 0.007$ and $r_e = 1.7131$



Figure 8. C-RCCSD[T] bond distances R_{e_r} dissociation energies D_{e_r} dissociation energies corrected for zero-point energy D_{0r} and harmonic frequencies ω_{e_r} with respect to the basis set size, aug-cc-pwCVxZ-PP_{Mo}/aug-cc-pwCVxZ₅, x = D(2), T(3), Q(4), 5.

 \pm 0.0008 at C-RCCSD[T] CBS-limit.⁴³ This is because S is larger than O and thus the bond distance is increased, resulting in a smaller dissociation energy. Finally, it should be noted that MoS cannot form low-lying states having quadruple bonds as do the neutral and anionic diatomic molecules of Tc, Ru, Rh, and Pd, that is, TcN^{0/-}, RuC^{0/-}, RhB^{0/-}, and PdBe^{44,45} because the Mo(c5D; 4d⁶) state is located about 3.156 eV above the Mo(⁷S) ground state.³⁶ Thus, no low-lying states of MoS exist with unoccupied orbitals (5s) that can receive electrons from S, resulting in an additional bond beyond the triple bond $\sigma^2 \pi^2 \pi^2$.

3.2.6. Dipole Moments. Dipole moments have been calculated as expectation values $(\langle \mu \rangle)$ and by the finite-field method ($\mu_{\rm FF}$), see Table 1. Both procedures predict similar values. The difference in the values obtained in the two procedures is less than 0.2 Debye with the exception of the ${}^{5}\Delta$, ${}^{\overline{5}}\Pi(2)$, and ${}^{3}\Delta(2)$ states. The largest difference is observed for the ${}^{3}\Delta(2)$ state, about 1 Debye. It has been reported that the finite-field method is more accurate than the expectation values due to fact that the MRCISD methodology is truncated.⁴⁴ The ground state $X^5\Pi$ has a dipole moment of 4.71(4.56) Debye at the MRCISD(+Q) level of theory. The largest values are found for the ${}^{5}\Sigma^{+}$ state [6.83(6.50) Debye] and the ${}^{3}\Delta(2)$ state [6.50(6.19) Debye], where a single bond, that is, σ^2 bond, is formed. The smallest ones are found for the ${}^{5}\Sigma^{-}[0.23(0.21)]$ Debye] and $^{7}\Sigma^{-}[0.02(0.23) \text{ Debye}]$ states, where $\pi^{2}\pi^{2}$ and π^{2} bonds are formed, respectively. Generally, we observe that the existence of a σ bond results in large values of the dipole moment, while the existence of doubly π^2 occupied bonds, without any σ bond, results in small values of dipole moments, cf. Tables 1 and 2. This occurs because charge is more easily

transferred through the σ framework (σ bonds) than through the π framework (π bonds).

Additionally, the occupancy (or not) of the 5s-like 3σ orbital has a major influence on the dipole moment. A major contributing factor to the dipole moment of these sorts of molecules centers on whether the metallic ns-based orbital is occupied (5s for Mo). This orbital is fairly diffuse and polarizable and projects out on the side of the molecule opposite to the S atom. When it is occupied, it can cancel out some of the polarization due to the negatively charged S atom. Thus, it would be expected for the largest dipole moments to occur when this orbital is unoccupied, as in the ${}^5\Sigma^+$ (6.83(6.50) Debye), the ${}^{5}\Delta$ (5.040(4.852) Debye), the ${}^{3}\Sigma^{+}$ (5.088(4.789) Debye), and the ${}^{3}\Delta(2)$ (6.504(6.191) Debye) states. When this orbital is doubly occupied, it would be expected to give much smaller dipole moments, with examples of ${}^{3}\Sigma^{-}$ (2.697(2.348) Debye) and ${}^{5}\Sigma^{-}(2)$ (1.521(1.871) Debye). When it is singly occupied, intermediate values might be expected. This is observed for most of the other states, whose dipole moments fall in the range of 2.442(2.098)-4.938(4.896) Debye, with the exception of the $^7\Sigma^+$ state. However, the $^7\Sigma^+$ state is unique, in that the 2σ orbital is singly occupied. Finally, it can also be noted that when the 4σ orbital is occupied, the dipole moments are tiny, as in the ${}^{5}\Sigma^{-}$ (0.234(0.205) Debye), ${}^{7}\Sigma^{-}$ (0.015(0.232) Debye), and $^{7}\Delta$ (1.267(1.007) Debye) states.

3.2.7. Benchmark Calculations for the $X^5\Pi$ State. The importance of the inclusion of the semi-valence electrons $4s^24p^6$ electrons of Mo and $2s^22p^6$ of S in the correlated valence space has been checked. We observe that this inclusion leads to a decrease of about 0.015(0.012) Å in the bond length

and an increase in the dissociation energy of about 0.16(0.18) eV at RCCSD(T) (RCCSD[T]) using an augmented quintuple zeta quality basis set, see Table 3.

Moreover, benchmark calculations are carried out for the ground state, $X^{5}\Pi$. The X state is systematically studied by employing the C-RCCSD(T) and C-RCCSD[T] methods, in conjunction with a series of weighted core correlation consistent basis sets, that is, aug-cc-pwCVxZ-PP_{Mo}/aug-cc-pwCVxZ_S, x = D, T, Q, and 5. The semi-valence electrons $4s^{2}4p^{6}$ electrons of Mo and $2s^{2}2p^{6}$ of S are also included in the correlated valence space. The extrapolation to the CBS limit of the calculated bond length, dissociation energies (D_{e} and D_{0}), and other spectroscopic parameters are depicted in Figures 8, 6S and 7S of the Supporting Information; all calculated values are given in Tables 4 and 2S of the Supporting Information.

The CCSD(T) and CCSD[T] methods differ in their treatment of the perturbative inclusion of triple excitations. They differ in one-fifth-order term of the perturbation contribution to the energy, which CCSD(T) includes and CCSD[T] does not.^{46–48} However, the CCSD(T) method has been shown to be especially successful for ground-state energies, and for the calculation of the properties of systems with single-reference character, it has been reported that CCSD[T] can describe noncovalent interactions better than the CCSD(T), CCSD(TQ), and CCSDT methods compared to CCSDTQ.⁴⁸ Here, we employ both CCSD(T) and CCSD[T], and we compare their results with experimental values.

Two approaches are used for the calculation of the CBS limits. At first, they are obtained using the exponential formula 1 on the calculated $R_{\rm e}$, $D_{\rm e}$, $D_{\rm 0}$, and $\omega_{\rm e}$ values for the basis sets n= 2-5 (approach I). The CBS limit of the bond distance (R_e) of the $X^{5}\Pi$ state is calculated as 2.114 ± 0.0005 Å (C-RCCSD(T) and 2.131 \pm 0.001 Å at (C-RCCSD[T]). The CBS limit of the dissociation energy corrected for the zeropoint energy is $D_0 = 3.78 \pm 0.01$ eV (C-RCCSD(T)) and 3.956 ± 0.009 eV at (C-RCCSD[T]). We observe that the C-RCCSD(T) methodology predicts a shorter bond length by 0.02 Å, a smaller dissociation energy by 0.18 eV, and smaller harmonic frequency by about 20 cm^{-1} than C-RCCSD[T]; these differences are almost the same at all basis sets. Our experimental dissociation energy is $D_0 = 3.932 \pm 0.004$ eV, in excellent agreement with our C-RCCSD[T] value. Thus, the C-RCCSD[T] methodology predicts the dissociation energy of the Mo–S diatomic molecule better than C-RCCSD(T). Our best D_e value is 3.99 \pm 0.01 (CBS-limit via C-RCCSD[T]), see Table 4. Thus, for a benchmark study of MoS, an augmented weighted core valence quintuple zeta quality basis set is needed where the semi-valence $4s^24p^6$ electrons of Mo and $2s^22p^6$ of S have been included.

Additionally, another extrapolation strategy (approach II) was applied for the dissociation energy. The CBS limits of D_0 and D_e are obtained using the exponential eq 1, the mixed Gaussian/exponential eq 2, and polynomial eq 4 on the extrapolated total energies, see Table 5 (approach II). We observe that all three extrapolated formulas predict similar dissociation energies. The gap of their values is less than 0.03 eV. Moreover, the CBS limits obtained using the exponential formula 1 on the calculated D_e and D_0 values for each basis set (Table 5; approach I) are in excellent agreement with the values obtain with approach II. Thus, both approaches and all three extrapolated forms are very good choices in excellent agreement with the experimental values. From Table 5, it is

	C-RCCSD[T]/aug-cc-pw	-CVxZ(-PP _{Mo})		
x = D $x =$	T = T = C	x = 5	CBS-limit ^a	expt
is 2.1673 2.	1461 2.1365	2.1337	2.131 ± 0.001	
3.498 3.	759 3.886	3.937	3.99 ± 0.01	
3.469 3.	730 3.856	3.907	3.956 ± 0.009	3.932 ± 0.004
465.6 479.	7 487.6	490.8	494.8 ± 1.2	

Table 4. Bond Distances $r_{
m e}$ (Å), Dissociation Energies $D_{
m e}$ (eV), Dissociation Energies Corrected for Zero-Point Energy D_0 (eV), and Harmonic Frequencies $\omega_{
m e}$ (cm⁻¹), of the

Table 5. CBS Limits of Dissociation Energies D_e (eV) and Dissociation Energies Corrected for Zero-Point Energy D_0 (eV) of the $X^5\Pi$ State at C-RCCSD(T) and C-RCCSD[T]

		C-RCCSD(T)		C-RC	CSD[T]
		$D_{\rm e}$	D_0	$D_{\rm e}$	D_0
$y_x = y_{\rm CBS} + A e^{-Bx}$	\mathbf{I}^{a}	3.81 ± 0.01	3.78 ± 0.01	3.99 ± 0.01	3.956 ± 0.009
$y_x = y_{\rm CBS} + A e^{-Bx}$	II^{b}	3.788	3.756	3.971	3.940
$y_x = y_{\text{CBS}} + Ae^{-(x-1)} + Be^{-(x-1)^2}$	II^{b}	3.786	3.755	3.967	3.936
$y_x = y_{\rm CBS} + Ax^{-b}$	II^{b}	3.812	3.780	3.998	3.967
expt			3.932 ± 0.004		3.932 ± 0.004

^{*a*}Approach I: the dissociation energies are calculated in a series of basis sets, and then these obtained values are extrapolated using exponential formula. ^{*b*}Approach II: total energies, for n = T, Q, 5, are extrapolated to the CBS limit, and then the dissociation energies are calculated for the extrapolated CBS PEC.

found that the best choice that exactly predicts our experimental value is the mixed Gaussian/exponential eq 2.

It is interesting to note that the bond length, 2.1313 Å at RCCSD(T)/aug-cc-pV5Z(-PP_{Mo}), is almost the same as our best CBS-limit, 2.131 \pm 0.001 at C-RCCSD[T]/aug-cc-pwCV5Z(-PP_{Mo}), due to cancelation of errors. This means that the elongation of the RCCSD(T) bond distance, since the correlation of the semi-valence Mo and S electrons has not been included, is compensated by the reduction due to the extrapolation to the CBS limit. However, the corresponding $D_{\rm e}$ or D_0 values are about 0.28 eV smaller than our best CBS-limit, showing the importance of the calculation of the semi-valence correlation.

Comparing the bond length and the dissociation energy of the $X^5\Pi$ state obtained at the MRCISD + Q/aug-cc-pV5Z(-PP)_{Mo} level of theory and the CBS limits of the C-RCCSD[T] methodology, we observe that the CBS limits of C-RCCSD[T] predict a shorter bond distance by 0.017 Å and a larger dissociation energy by 0.34 eV. Making these corrections to the results of Table 1, we present in Table 6 our final predicted R_e , D_e , and D_0 values for all 20 calculated states.

3.2.8. Mo–S Bonding in Materials and Enzymes. The molybdenum–sulfur bond is found as a building block in layered materials such as MoS_2 known for its various shapes

Table 6. Final Bond Lengths r_e (Å), Dissociation Energies D_e (eV), Corrected Values with Respect to the Zero-Point Energy, D_0 (eV), and the Corresponding Diabatic Values D_e^d and D_0^d

$D_{\rm e}$	D_{e}^{d}	D_0	D_0^{d}
3.99		3.96	
4.72	5.08	4.68	5.05
2.92		2.90	
4.65	5.77	4.62	5.74
4.61	5.00	4.58	4.96
2.68		2.66	
4.16		4.13	
4.19	5.31	4.16	5.28
2.84		2.82	
3.04		3.01	
3.32	4.43	3.29	4.40
3.36	4.48	3.33	4.45
1.39		1.36	
2.28		2.26	
2.60	2.96	2.57	2.94
2.18	2.39	2.16	2.37
	$\begin{array}{c} D_{e} \\ 3.99 \\ 4.72 \\ 2.92 \\ 4.65 \\ 4.61 \\ 2.68 \\ 4.16 \\ 4.19 \\ 2.84 \\ 3.04 \\ 3.32 \\ 3.36 \\ 1.39 \\ 2.28 \\ 2.60 \\ 2.18 \end{array}$	$\begin{array}{c ccc} D_e & D_e^e \\ 3.99 \\ 4.72 & 5.08 \\ 2.92 \\ 4.65 & 5.77 \\ 4.61 & 5.00 \\ 2.68 \\ 4.16 \\ 4.19 & 5.31 \\ 2.84 \\ 3.04 \\ 3.32 & 4.43 \\ 3.36 & 4.48 \\ 1.39 \\ 2.28 \\ 2.60 & 2.96 \\ 2.18 & 2.39 \end{array}$	D_e D_e^e D_0 3.993.964.725.084.655.774.655.774.615.004.632.664.164.134.195.314.162.842.842.823.043.013.324.433.364.483.362.262.602.962.782.262.602.962.182.392.16

and morphologies.^{4,5} From a crystalline point of view, layered MoS₂ exists in three polymorphic crystalline structures: 1T (tetragonal),⁴⁹ 2H (hexagonal),⁵⁰ and 3R (rhombohedral), see Figure 9.⁵¹ In the case of mono- to few-layer structures, the 2H-MoS₂ structure is the most thermodynamically stable phase.⁵² Furthermore, MoS₂ layered materials are observed to exhibit other morphologies, such as planar⁴⁹ and vertically aligned nanosheets,⁵³ nanoflowers,⁵⁴ nanotubes,⁵⁵ nanowires,⁵⁶ and nanoplatelets.⁵⁷ Note that the layers are stacked one on top of another, but the bonds between the layers are very weak. This variety of forms could be controlled by choosing suitable synthesis routes and it is feasible to adjust the 2D-MoS₂ properties to develop high performance devices for a variety of applications. In the 1T, 2H and 3R morphologies, each Mo is surrounded by six S atoms, forming single covalent bonds with them, see Figure 9, with bond distances ranging from 2.37 to 2.41 Å⁵⁸⁻⁶⁰ depending on the conditions; while in other polymorphs, the Mo-S bonds range from 2.38 to 2.59 Å.⁶¹ It is of interest that the septet states of the diatomic MoS form a half or a single bond, and they present bond distances ranging in the same region, that is, they range from 2.36 to 2.52 Å, see Table 6. The lowest septet state, $^{7}\Pi$, is the fifth excited state of MoS, and it is lying 1.3 eV above the ground state. Additionally, the S vacancy of solid MoS₂ has a formation energy of 2.35 eV in S-rich conditions,⁶² while the dissociation of $MoS(^7\Pi)$ is 2.66 eV, only 0.3 eV larger. Thus, clearly the septet state of the diatomic molecule is involved in the material as a building block. It is also interesting that the MoS species has bound septet excited states, that is, ${}^{7}\Sigma^{+}$ and ${}^{7}\Delta$, that form a half bond with dissociation energies of 2.82 and 2.26 eV. These values are large given that the bond is formed by only one electron. This can explain the variety of stable morphologies of the material, that is, it is like carbon, which presents an sp³ hybridization and forms four bonds, while molybdenum presents an sd⁵ hybridization, and it can form six bonds.

Additionally, in 2D-MoS₂ and in Mo_xS_y nanoparticles, the Mo–S distances of the surface, when the Mo plane is on the top, are shorter at about 2.3 Å,⁶³ that is, up to 0.1 Å with respect to the solid MoS_2 , and they resemble the Mo–S bond distances of the quintet states.

Finally, in complexes and in enzymes, Mo atoms are in octahedral coordination, forming six bonds,^{64–68} with Mo–S bond distances of about 2.35 Å. For instance, in nitrogenase, which is a complex enzyme that catalyzes the formation of ammonia, it is found that the Mo–S bonds have bond distances ranging from 2.31 to 2.35 Å,⁶⁸ that is, similar to the bond distances of the septet states with the shortest bond distances. Note that in the complexes, Mo is charged, and as a result, the Mo–S bonds are shorter than in the neutral MoS. In



Figure 9. Top and side views of (a) 2H, (b) 1T and 3R, and (c) Mo_3S_4 polymorphs.

diatomic MoS, the bonds are mainly covalent because the Mo⁺ + S⁻ products are not favored energetically; the first ionization energy of Mo is 7.09243(4) eV⁶⁹ and the electron affinity of S is 2.077103(3) eV.⁷⁰ Thus, while the Mo⁺(⁶S) + S⁻(²P) asymptote can yield a ⁵Π state, that is, the same as the ground state of MoS, these asymptotic products are lying 5.015 eV higher than Mo(⁷S) + S(³P). Of course, in complexes included Mo–S bonds, as in the case of the Fe–S bonds,⁷¹ this energy difference between ionic and covalent bonds can be provided by the interactions with solvents, other ions, ligands, and so forth.

Thus, the data of the MoS diatomic molecule could be useful in understanding solid MoS_2 and molybdenum complexes. The connection of an isolated MoS species to the relevant solid MoS_2 is far from trivial. We hope that the present study and analysis can be of some help for the better understanding of this very interesting material.

4. CONCLUSIONS

In this article, we present a detailed and accurate theoretical and experimental investigation of spectroscopic data, PECs, and bonding analysis of 20 low-lying states of the MoS molecule at the highest level of currently achievable accuracy. Theoretically, the states were studied using multireference and coupled cluster methodologies, namely, MRCISD, MRCISD + Q, RCCSD(T) and RCCSD[T], employing the aug-cc-pVSZ-PP basis sets. Additionally, the ground state, $X^{S}\Pi$, was systematically studied using the C-RCCSD(T) and C-RCCSD[T] methods, in conjunction with a series of basis sets aug-cc-pwCVxZ-PP_{Mo}/aug-cc-pwCVxZ_S, x = D, T, Q, and 5. Experimentally, for the first time, the predissociation threshold of the MoS has been measured using R2PI spectroscopy, allowing for a precise assignment of the BDE.

In contrast to commonly held beliefs, we found that the C-RCCSD[T] methodology predicts the dissociation energy of MoS better than the C-CCSD(T). The C-RCCSD[T] D_0 values are larger by about 5% than the C-RCCSD(T) ones. Our extrapolated D_0 value of the ground state, $X^5\Pi$, is 3.936 eV, which is in excellent agreement with our experimental value, 3.932 \pm 0.004 eV; the corresponding extrapolated r_e value is 2.131 \pm 0.001 Å.

Additionally, we found that the inclusion of the inner $4s^24p^6$ electrons of Mo and $2s^22p^6$ of S in the correlated space is necessary for the accurate calculation of MoS. It results in a shorter bond distance of ~0.02 Å and a larger dissociation energy of up to 2%.

Regarding the bonding, the $X^5\Pi$ ground state has a double covalent bond $\sigma^2 \pi^2$, while the first excited state, $a^3\Sigma^-$, has a triple bond $\sigma^2 \pi^2 \pi^2$. The third excited state ${}^5\Sigma^+$ also has a triple bond $\sigma^2 \pi^2 \pi^2$ and presents the largest dissociation energy with respect to the equilibrium atoms, that is, a diabatic D_0 value of 5.74 eV. The dipole moment of the $X^5\Pi$ state is 4.71(4.56) Debye at the MRCISD(+Q) level of theory, while the largest values are found for the ${}^5\Sigma^+[6.83(6.50)$ Debye] and the ${}^3\Delta(2)$ states [6.50(6.19) Debye].

Finally, the connection of the chemical bonding of the isolated MoS species to the relevant solid, MoS_2 , is emphasized. The low-lying septet states of the diatomic molecule are involved in the material as building blocks. MoS species present a variety of bound septet excited states with significant dissociation energies up to 2.82 eV, even though only a single or a half bond is formed. Similar to carbon, which presents an sp³ hybridization forming four bonds, molybde-num presents an sd⁵ hybridization forming six bonds involving MoS septet states. The variety of the bound septet states of MoS diatomic explains the variety of the stable morphologies of the material.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.1c10672.

Spectra shown in Figure 1 and computational results at the CASSCF, MRCISD(+Q), RCCSD(T), and RCCSD[T] levels of theory (PDF)

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Notes

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