Pressure-Dependent Optical and Vibrational Properties of Monolayer Molybdenum Disulfide

Avinash P. Nayak,†,▲ Tribhuwan Pandey,‡,▲ Damien Voiry,§ Jin Liu,∥ Samuel T. Moran,† Ankit Sharma,† Cheng Tan,¶ Chang-Hsiao Chen,§ Lain-Jong Li,‖ Manish Chhowalla,§ Jung-Fu Lin,‖⊥ Abhishek K. Singh,*‡ and Deji Akinwande*†

†Department of Electrical and Computer Engineering, The University of Texas at Austin, Austin, Texas 78712, United States.
‡Materials Research Center, Indian Institute of Science, Bangalore 560-012, India
§Department of Materials Science and Engineering, Rutgers University, Piscataway Township, New Jersey 08854, United States
¶Institute of Atomic and Molecular Sciences, No. 1, Roosevelt Rd., Sec. 4, Taipei 10617, Taiwan
‖Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201900, China
○Physical Science and Engineering Division, King Abdullah University of Science & Technology (KAUST), Thuwal 23955, Saudi Arabia

ABSTRACT: Controlling the band gap by tuning the lattice structure through pressure engineering is a relatively new route for tailoring the optoelectronic properties of two-dimensional (2D) materials. Here, we investigate the electronic structure and lattice vibrational dynamics of the distorted monolayer 1T-MoS2 (1T′) and the monolayer 2H-MoS2 via a diamond anvil cell (DAC) and density functional theory (DFT) calculations. The direct optical band gap of the monolayer 2H-MoS2 increases by 11.7% from 1.85 to 2.08 eV, which is the highest reported for a 2D transition metal dichalcogenide (TMD) material. DFT calculations reveal a subsequent decrease in the band gap with eventual metallization of the monolayer 2H-MoS2, an overall complex structure−property relation due to the rich band structure of MoS2. Remarkably, the metastable 1T′-MoS2 metallic state remains invariant with pressure, with the J2, A1g, and E2g modes becoming dominant at high pressures. This substantial reversible tunability of the electronic and vibrational properties of the MoS2 family can be extended to other 2D TMDs. These results present an important advance toward controlling the band structure and optoelectronic properties of monolayer MoS2 via pressure, which has vital implications for enhanced device applications.

KEYWORDS: 2D Materials, MoS2, Transition Metal Dichalcogenide, Strain, Hydrostatic Pressure, Diamond Anvil Cell, Pressure Engineering, Photoluminescence

Among the great variety of exfoliable materials, transition metal dichalcogenides (TMD) have demonstrated promising optoelectronic properties. Interestingly, these properties can be largely tuned by varying the thickness,1 by modifying the crystal structure,2 or by applying strain on the TMDs.3 Pressure engineering of the two-dimensional (2D) layered crystals is still a relatively new field with many possible routes for further investigations and optimization to fully realize their potential in materials engineering.4–8 Being able to reversibly tune the band gap and structure of 2D materials by inducing pressure allows for exploring changes in photonic,9 mechanical,10 and electronic11 properties at different hydrostatic pressures. The

Received: September 22, 2014
Revised: November 10, 2014
The effects of hydrostatic pressure on 2D materials are important to understand, particularly for applications such as flexible electronics.5 The transition metal dichalcogenide family, which consists of 2D layered compounds, exhibits a laminar structure similar to that of graphene and has been investigated for several optoelectronic1,12−14 and flexible5,15 electronics. One representative TMD that has gained significant interest is molybdenum disulfide (MoS2), which is composed of a single layer of Mo atoms covalently bonded between two laminar sheets of S atoms. The natural bulk 2H-MoS2 is a semiconductor that has an indirect band gap of 1.3 eV, whereas its monolayer form has a direct band gap of 1.85 eV due to the lack of interlayer interactions in thinner layers.1 Furthermore, depending on the arrangements of sulfur atoms in the lattice, Mo can be coordinated either by six sulfur atoms in an octahedral (1T), a distorted 1T (1T′), or a trigonal prismatic (2H) polytype13 (Figure 1a). This different coordinated structure also changes the electronic structure of the material. The 1T′-MoS2 is metallic, whereas the 2H-MoS2 is semiconducting.

The two main Raman modes in the monolayer 2H-MoS2 are the A1g and the E2g mode. The out-of-plane A1g mode occurs due to opposing vibrations of the two S atoms with respect to the Mo atom. The E2g mode is associated with the in-plane vibration of the Mo and S atoms, in opposite directions from one another. For the 1T′-MoS2, the J1 mode involves two different types of vibrations: one at 152.68 cm−1, which is an out-of-plane motion of each stripe of the Mo atoms inside the zigzag chain, and the other mode at 157.64 cm−1, which is an in-plane shearing vibration of one stripe of atoms with respect to the other atom in the chain. Both of these modes appear as a single peak at room temperature. The J2 peaks at ~226 cm−1 from the motion of two zigzag chains relative to each other, whereas the mode 330.29 cm−1, named J3, tends to break each zigzag chain in two stripes with a slight out-of-plane component (Figure 1b). Due to the atomic arrangements of the 1T′-MoS2 and 2H-MoS2 phases, these Raman modes with various magnitudes of activities can be used to decipher the lattice dynamics of the monolayer polytypes (Figure 1c).

It has been found experimentally that these two phases can transition to one another via interlayer atomic plane gliding, which displaces one of the S planes and changes its electronic state.2,13,16 Another way to controllably alter the electronic properties is to mechanically distort the lattice structure by applying uniaxial, biaxial, or hydrostatic strain.17−19 The majority of research in this field pertains to theoretical calculations on how the distortion of the 2H and 1T′-MoS2 lattice can lead to changes in their photonic and electronic properties.5

Figure 1. Structural and vibrational properties of monolayer MoS2 polytypes. (a) Schematic atomic arrangements of the monolayer MoS2 showing the a (in-plane direction) and the cross section c (out-of-plane) view of the monolayer 1T-MoS2, 1T′-MoS2, and 2H-MoS2. (b) Raman active modes of the MoS2 family. For the 1T′-MoS2, the J1 mode is composed of two Raman active modes that are close to one another and appear as one peak at room temperature. (c) Raman active modes for the restacked monolayer 1T′-MoS2 and monolayer and bulk 2H-MoS2. The J1, J2, and J3 modes are only prominent in the 1T′-MoS2 phase.
Experimentally, it has been a challenge to exert hydrostatic pressure homogeneously across a 2D sample, and only a nominal compressive strain of 0.2% or a uniaxial strain of 10% can be exerted with elaborate setups. In the present study, we have investigated the MoS$_2$ family ($1T'$-MoS$_2$ and both monolayer and bulk 2H-MoS$_2$) under extreme hydrostatic pressures up to 30 GPa. A diamond anvil cell (DAC) with a soft neon pressure medium was used to apply a hydrostatic pressure uniformly across the sample. The DAC experiments allow fundamental studies of the effects of high strain levels on the properties of materials, MoS$_2$ in this case. This sort of study is important for probing the intrinsic response of the strain-property relations in a controlled environment. The insights provided by this study can guide practical realization of strained MoS$_2$ devices. The DAC methodology also permits us to investigate the modulation of the band gap, the shift from a direct to an indirect band gap, and the altered phononic properties of both the monolayer 2H-MoS$_2$ and 1T'-MoS$_2$ under applied hydrostatic pressures. These results show that for the monolayer 2H-MoS$_2$ polytype a $\sim$12% increase in band gap is observed. Although a higher pressure is not experimentally achievable for the time being, a metallization at 68 GPa is predicted by theoretical calculations. The semiconductor to metal transition occurs at a much higher pressure than that in the bulk counterpart which metalizes at $\sim$19 GPa. For the 1T'-MoS$_2$ polytype, the out-of-plane vibrations are hindered by the hydrostatic pressure, allowing only the $J_2$, $A_{1g}$ and $E_{2g}$ vibrational modes to become dominant at pressures past 27 GPa. Our combined experimental and theoretical results allow for a coherent understanding of the vibrational, optical, and electronic properties of TMD materials as a function of the number of layers and layer geometry under hydrostatic pressure.

Raman spectroscopy, being fast and nondestructive, is a powerful diagnostic tool to investigate the vibrational and physical properties of MoS$_2$. Raman spectroscopy has been used to study 2H-MoS$_2$ to determine the number of layers, to determine the effect of pressure on the 2H-MoS$_2$ lattice, and to determine the level of doping and defects. To understand the electronic and mechanical stability of the MoS$_2$ polytypes, we have studied the monolayer and bulk 2H-MoS$_2$ as well as restacked monolayer 1T'-MoS$_2$ under hydrostatic pressure.

The lattice vibrations detected by Raman spectroscopy can reveal key changes occurring to the lattice at high pressures. In particular, hydrostatic pressure can induce a blue shift (phonon hardening) in MoS$_2$. For the 2H-MoS$_2$ monolayer polytype, the intensity of in-plane Raman mode ($E_{2g}$) starts to diminish at pressures above 16 GPa (Figure 2a). The intensity ratio of $A_{1g}/E_{2g}$ also increases with pressure (Supporting Information Figure S1a) above 16 GPa. The diminishing intensity of the $E_{2g}$ mode is attributed to the dominance of normal compressive strain on the monolayer 2H-MoS$_2$ under large hydrostatic pressures, which hinders the in-plane $E_{2g}$ movement, whereas...
the A_{1g} out-of-plane vibrational mode is still prominent at pressures up to 30 GPa.

Although the rate of increase is higher for A_{1g} mode (Supporting Information Figure S1b), the E_{2g} mode also increases linearly. This distinct rate of increase can be explained by analyzing the type of vibrations involved in A_{1g} and E_{2g} modes. The A_{1g} modes originate from transverse vibrations of the S−S atom; however, the E_{2g} mode emerges from longitudinal vibrations of Mo and S atoms in opposite directions. The change in Mo−S bond length (in-plane movement of atoms) plays a significant role in determining the behavior of the E_{2g} mode. As the hydrostatic pressure increases, the out-of-plane (A_{1g}) compression becomes more favorable than the in-plane (E_{2g}) compression, indicating that at higher pressures, the transverse moment of the S−S atom is faster than the in-plane movement of the Mo−S atom (Supporting Information Figure S2a). This results in a higher rate of increase of A_{1g} mode with increasing pressure in comparison to E_{2g} mode.

Although several studies have been done on the synthesis and characterization of the distorted octahedral 1T′-MoS_{2} polytype, the lattice vibrations at extreme hydrostatic pressure conditions have not yet been studied. Previous theoretical studies have shown the breaking of lattice symmetry in 1T′-MoS_{2} when tensile and compressive strain are applied. The 1T′-MoS_{2} phase shows three Raman active modes that are not present in the trigonal prismatic 2H-MoS_{2} polytype. These three extra modes are the J_{1}, J_{2}, and J_{3}, which show up at 150 cm⁻¹, 225 cm⁻¹, and 325 cm⁻¹, respectively, at ambient pressure. As the hydrostatic pressure increases, J_{3} becomes indistinguishable from the E_{2g} mode at ∼10 GPa, whereas J_{1} and J_{2} are still prominent at higher pressures. The broadening of the J_{3} mode with pressure further supports the merging phenomenon of the J_{3} and E_{2g} modes (Supporting Information Figure S3). In order to confirm this phonon merging, theoretical calculations have been carried out to investigate the effect of pressure on the vibrational properties of the monolayer 1T′-MoS_{2}. The calculated phonon dispersion curves (Supporting Information Figure S4) at ambient pressure are consistent with the previously reported results and were used to identify all the Raman active modes. The theoretically derived pressure-dependent Raman frequencies show good qualitative agreement with experimental observation. The Raman intensity increases for the J_{1}, A_{1g}, and E_{2g} modes and shows the merging of the J_{3} and E_{2g} modes (Supporting Information Figure S5). The J_{1} Raman mode also diminishes at

Figure 3. Pressure modulated photoluminescent properties of monolayer 2H-MoS_{2}. (a) Representative PL spectra as a function of pressure. An increase in the band gap with increasing pressure and then the diminishing of the PL signals at ∼16 GPa indicates a direct-to-indirect band gap shift. (b) Derived band gap at high pressures. Extracted from the Lorentzian fit to the PL peaks, the band gap is shown to increase as a function of pressure. Red solid line: a polynomial fit to the experimental data described by \( E_g = 1.88 + 0.03P - 8.5 \times 10^{-4}P^2 \) where \( E_g \) is optical band gap and \( P \) is pressure. Inset: The theoretical prediction of the direct-to indirect band gap transition. (c) Band gap diagrams at M, K, Λ, and Γ point at two representative pressures of 0 and 22.3 GPa depicting the direct to indirect transition. Here, D and I indicate the direct and indirect band gaps, respectively. The observed direct and indirect band gap values are also presented for clarity. At 0 GPa, the E−k diagram indicates a direct-band gap between the CBM and the VBM, whereas at 22.3 GPa, band gap shift form direct (from in between K−K’ points) to indirect in between K−Λ points at 22.6 GPa that agrees with the experimental observations. At around 67.9 GPa the valence band maxima (VBM) and the conduction band minima (CBM) cross the Fermi level, leading to a semiconductor-to-metal transition.

dx.doi.org/10.1021/nl5036397 | Nano Lett. XXXX, XXX, XXX–XXX
pressures above 22 GPa, leaving just the $J_2$, the $A_{1g}$ and the $E_{2g}$ Raman modes dominant at pressures past 27 GPa (Figure 2b). To investigate the $E_{2g}$ and $J_3$ merging in further detail, theoretical calculations were performed to find the dependence on pressure compared to the other modes (Figure 2c). As the hydrostatic pressure increases, the out-of-plane compression becomes more favorable (0.08 Å/GPa) than the in-plane compression (0.03 Å/GPa), suggesting that at higher pressures the out-of-plane moment of the S=S atom is faster than the Mo=S movement leading to a smaller rate of increase of the $E_{2g}$ mode (1.3 cm$^{-1}$/GPa) compared to the $A_{1g}$ mode (2.5 cm$^{-1}$/GPa) (Figure 2d). The pressure-dependent rate of increase for the $J_1$ and $J_2$ Raman mode is 0.9 cm$^{-1}$/GPa, whereas the $J_3$ mode increases at 3.90 cm$^{-1}$/GPa. For the 2H-MoS$_2$ polytype, the pressure dependence on the Raman modes of the monolayer 2H-MoS$_2$, 1T’-MoS$_2$ and the bulk 2H-MoS$_2$ show that the $A_{1g}$ and $E_{2g}$ modes for both the monolayer 2H-MoS$_2$ and 1T’-MoS$_2$ polytypes are similar (Supporting Information Figure S6). For the 2H-MoS$_2$ monolayer, the shift in Raman peak position increases linearly with applied pressure. The Raman shift with pressure for the $A_{1g}$ mode is 2.6 cm$^{-1}$/GPa, whereas the $E_{2g}$ mode increases at a rate of 1.7 cm$^{-1}$/GPa (Supporting Information Figure S1b). The distance between $A_{1g}$ and $E_{2g}$ Raman modes increases at a rate of 1.2 cm$^{-1}$/GPa (Supporting Information Figure S1c). The $A_{1g}$ shift for monolayer MoS$_2$ with pressure, in comparison with other 2D materials such as MoSe$_2$, MoTe$_2$, and ReS$_2$, is higher, signifying that the monolayer MoS$_2$ has a strong dependence on pressure.

The deviation from the bulk MoS$_2$ is mainly attributed to the interlayer interactions along the out-of-plane axis, which is absent in the monolayer. Unlike the bulk 2H-MoS$_2$, no intermediate phase region between the semiconducting and metallic region is observed, indicating that the monolayer MoS$_2$ does not undergo metallization or a structural transition at pressures up to 30 GPa. Theoretically, we predict the metallization of 2H-MoS$_2$ to be at ~68 GPa.

Due to the inherent direct band gap (1.85 eV) of the monolayer 2H-MoS$_2$, the photonic and electronic band structure can be probed by photoluminescence (PL) spectroscopy. This strong PL emission is only observed in the monolayer 2H-MoS$_2$ and is attributed to the slow electronic relaxation that is unique to its electronic structure. The PL signal for the bilayer and trilayer are much weaker. Our PL spectral measurements on the monolayer 2H-MoS$_2$ show that the electronic band structure can be significantly modulated by hydrostatic pressure (Figure 3a) at a rate of 30 meV/GPa below 5 GPa. At higher pressures, the direct band gap gradually increases to 2.08 eV at ~12 GPa, showing a significant 11.7% change in band gap (Figure 3b), while increasing the PL full width half-maximum (fwhm) (Supporting Information Figure S1d). Although this increase in the direct band gap is reversible (Supporting Information Figure S7), the rate of increase can be altered depending on the pressure medium. This can significantly modify the photonic and electronic characteristics of 2D materials under high pressure. Because we have used an inert, soft Ne pressure medium in our experiments, our results therefore represent more intrinsic features of the system without dopant effects. The polynomial increase in the band energy is in agreement with theoretical DFT calculations, which show an increase in the direct band gap at the K–K’ point. The theoretical band gap is underestimated due to the presence of artificial self-interaction and the absence of the derivative discontinuity in the exchange-correlation potential with the PBE/GGA methods. The initial trend in band gap as supported by the PL experiments (Figure 3b) shows an increase at the K–K’ point. The in situ fwhm map of PL Spectra (Supporting Information Figure S8) increases from 24.7 nm at 0.6 GPa to 58.7 nm at 12.5 GPa and diminishes to the background noise level at pressures over 16 GPa at room temperature. This increase in the fwhm implies a crossover point to the direct-to-indirect band gap at the K–K’ point at approximately 16 GPa. This direct to indirect band gap shift was further confirmed by DFT calculations. The ambient theoretical band gap initially lies in-between K–K’ point until a pressure of 22.3 GPa is reached. At 22.3 GPa, a direct-to-indirect transition indicates that the conduction band minima (CBM) and the valence band maxima (VBM) are no longer at the K–K’ interband (Figure 3c), but rather shift to the K–Λ point. Theoretical calculations reveal that the band gap of 2H-MoS$_2$ monolayer first increases until a pressure of ~22 GPa is reached. Beyond this pressure, the band gap gradually
decreases, eventually leading to the metallization of monolayer 2H-MoS₂ at around 68 GPa.

To understand the mechanism for this band gap change and the semiconductor to metal (S–M) transition under hydrostatic pressure, we analyze the contribution from different molecular orbitals by performing angular momentum projected density of states (LDOS) calculations. At lower pressures, both valence (VB) and conduction bands (CB) are mainly composed of Mo\(_{d_{x^2-y^2}}\), \(d_{z^2}\), and \(p_{xy}\) orbitals (Figure 3c).

With increasing pressure, these orbitals move away from the Fermi level, resulting in an increase in band gap up to 22.3 GPa pressure. At higher pressure, the out-of-plane compression becomes more dominant (Supporting Information Figure S2b), which makes the Mo \(d_{z^2}\), \(d_{xy}\), and \(p_z\) orbitals interact strongly with S \(p_x\) and \(p_y\) orbitals. This strong intralayer hybridization between the orbitals mentioned above leads to a decrease in band gap after ~22 GPa pressure and finally closing of the band gap at higher pressure (68 GPa). For the monolayer 2H-MoS₂, in-plane intralayer interactions play a dominant role in the metallization at 67.9 GPa.

It was found in our previous study of the bulk MoS₂ that interlayer interactions play a critical role in the metallization.\(^{17}\) It is therefore expected that as the number of layers increases, the critical pressure or critical volume strain (Supporting Information Figure S10) at which the metallization occurs decreases (Figure 4a). The metallization of the bilayer, trilayer, and bulk 1T′-MoS₂ (Figure 4a and b) under high pressure can be understood by the interaction of electron-donating sulfur atoms between the van der Waals gaps.\(^{17,21}\) The transition pressure for MoS₂ therefore decreases as the number of layers increases. As experimentally observed, the monolayer 1T′-MoS₂ shows metallic behavior (Supporting Information Figure S7), unlike the 2H-MoS₂ polytype which is semiconducting in nature. For the 2H-MoS₂, the valence and conduction bands are mainly composed of the \(d\) orbitals of Mo and \(p\) orbitals of S atoms (Supporting Information Figure S11a). Upon application of hydrostatic pressure the extent of hybridization between Mo \(d\) orbitals (mainly \(d_{x^2}\), \(d_{xy}\), and \(d_{z^2}\)) and S \(p\) orbitals increases, thus increasing the overlap between conduction and valence bands resulting in an enhanced metallization (Supporting Information Figure S11b).

We have measured an 11.7% in the direct band gap of the 2H-MoS₂ from 1.85 eV at ambient pressure to 2.08 eV at 16 GPa before the PL signal diminished and could no longer be resolved at higher pressures and room temperature. For comparison, a 3.3% difference in direct band gap was found by S.P. Lau et al.,\(^{13}\) a 3.0% difference by G. A. Steele et al.,\(^{36}\) and a 5.4% difference by Dou et al.\(^{9}\) for the monolayer 2H-MoS₂. To further understand the electronic and phononic properties, DFT calculations were conducted to show that a critical pressure of 67.9 GPa is required to metallize the monolayer 2H-MoS₂. The 1T′-MoS₂ behaves as a metal at ambient pressure and exhibits three more Raman active modes (\(J_1\), \(J_2\), and \(J_3\)) in comparison to the 2H-MoS₂, which exhibits only the \(A_{1g}\) and \(E_{2g}\) modes. At pressures above 10 and 27 GPa, we have observed the diminishing of the out-of-plane \(J_1\) and \(J_3\) Raman modes, respectively, due to higher susceptibility to hydrostatic pressure along the out-of-plane axis. At 10 GPa, the \(J_1\) mode starts to merge with the \(E_{2g}\) mode. The suppression of the \(J_1\) mode at ~27 GPa is attributed to the large hydrostatic pressure on the lattice implying that the effect of pressure is more pronounced for this mode and is more sensitive to pressure. Because this process is reversible for both the 2H-MoS₂ and the 1T′-MoS₂, the distortion of the lattice is predicted to be a transitory structural modification. The total energy calculation also reveals that monolayer MoS₂ is the most stable phase under the applied pressure range (Supporting Information Figure S12), and confirms that there is no phase transformation between 2H and 1T′ phase within the studied range of pressure.

Strain engineering of 2D layered materials is a relatively new field with possible routes for further investigations to fully realize their potential in customizing material behavior. Here, the interplay of the structural and optoelectronic properties is successfully described for the MoS₂ family. The monolayer 2H-MoS₂ differs from its bulk counterpart because the bandgap increases by ~12% with applied hydrostatic pressure due to the absence of interlayer interactions. For the intrinsically metallic 1T′-MoS₂, interlayer structural distortion is prevalent resulting in phonon merging of two Raman active modes (\(J_1\) and \(E_{2g}\)) at high pressures. The large reversible bandgap modulation of semiconducting MoS₂ is attractive for highly tunable optoelectronics, nanoelectronics, and flexible electronics and can enable new opportunities based on the dynamic strong electron–phonon coupling.

**Experimental Methods. Sample Preparation.** The 2H-MoS₂ monolayer was synthesized based on our previous work.\(^{37}\) In brief, 300 nm SiO₂ substrates were placed in the center of a tubular furnace. Precursors of 0.3 g MoO₃ (Sigma-Aldrich, 99.5%) in Al₂O₃ crucible was placed 12 cm away from the furnace. Because this process is reversible for both the 2H- and bulk 1T′-MoS₂, interlayer structural distortion is prevalent resulting in phonon merging of two Raman active modes (\(J_1\) and \(E_{2g}\)) at high pressures. The large reversible bandgap modulation of semiconducting MoS₂ is attractive for highly tunable optoelectronics, nanoelectronics, and flexible electronics and can enable new opportunities based on the dynamic strong electron–phonon coupling.

**Characterization.** For the Raman spectroscopic studies on the 2H and 1T′ polytypes, a green 532 nm Coherent Verdi V2 laser was used at the Mineral Physics Laboratory of the University of Texas at Austin. The scattered light was dispersed by a 1800 grooves/mm grating and collected by an EMCCD (Andor Technology) resulting in a spectral resolution of approximately 1 cm⁻¹. To avoid potential overheating or oxidizing of the samples, the highest laser power level used was 20 mW with a focused laser beam size of 10 μm. Ruby fluorescence spectra were also collected using the same system for pressure calibrations.\(^{58}\) (Supporting Information Figure S8).

For the photoluminescence (PL) and Raman in situ mapping studies on the 2H-MoS₂ a grating of 900 grooves/mm was used. A long working-distance (LD EC) objective, Epiphan-NeoFluar (20×/0.22 DIC M27), was used. The Witec Alpha 300 micro-Raman confocal microscope with a 488 nm laser was used for the in situ PL and Raman mapping studies. To better understand the band gap energy of the system, a Lorentzian
Theoretical Calculations. Modeling of Hydrostatic Pressure on Monolayer MoS$_2$. The hydrostatic pressure on the monolayer was modeled by calculating the ease of compression along the $x$, $y$, and $z$ direction. First, we checked the individual energy costs for in-plane ($x$, $y$) and out of plane compression ($z$). Based on the energy cost calculation we calculated the compression along all directions for hydrostatic pressure modeling (Supporting Information Figure S2a and S2b). A similar procedure was followed for 1T‘- MoS$_2$ monolayer.

For 2L, 3L, and bulk MoS$_2$, first we approximate the in-plane (change in $a$, $b$) and out-of-plane (change in slab thickness $c$) compression by performing total energy calculation. First, we apply a uniform strain in all directions calculate the energy cost. By comparing the energy cost for biaxial and normal compressive strain, we extract the atomic displacement. Due to presence of weak van der Waals (vdW) interaction in between the layers the slab thickness decreases more rapidly in comparison to in plane lattice parameter $a$ and $b$ as shown in Supporting Information Figure S13 (a) for 2L MoS$_2$.

In order to correlate the theoretical finding with experiments, it is important to estimate applied hydrostatic pressure. The applied pressure was calculated from the energy cost per unit volume as per the following equation for 1L, 2L, 3L, and bulk MoS$_2$

$$P = \frac{E - E_0}{V - V_0}$$

where, $E$ ($E_0$) and $V$ ($V_0$) are the energy and volume for the unstrained (strained) systems. The volume of a hexagonal lattice can be defined as $V = a^2 c \sin (60)$ where $a$ is the in-plane lattice parameter and $c$ is thickness of slab. The thickness of various structures is defined as shown in Supporting Information Figure S13. As shown in our previous work, the theoretical calculated pressure agrees well with the experimental pressure for bulk MoS$_2$.

First-Principles Theoretical Calculations. Theoretical calculations were performed using first-principle ab initio density functional theory (DFT) using Vienna Ab Initio Simulation Package (VASP). All-electron projector augmented wave potentials and the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) were used to account for the electronic exchange and correlation. The structure of the 1T‘- MoS$_2$ monolayer is generated by following the approach of Calandra. All the structures were relaxed in the $x$-$y$ plane while constraining the $z$ coordinates by employing a conjugate gradient scheme until the forces on every atom were minimized to be less than 0.005 eV/Å. A well-converged Monkhorst-Pack $k$ point set of $15 \times 15 \times 1$ was used for this procedure. The phonon dispersion of monolayer MoS$_2$ was calculated using density functional perturbation theory (DFPT) as implemented in VASP. An additional tool, Phonopy, supports the VASP interface, was used for extracting the phonon frequencies. The force constants were calculated with a supercell of $2 \times 2 \times 1$ and the $k$ point set of $13 \times 13 \times 1$. In order to obtain accurate phonon frequencies, a high energy cutoff of 600 eV and strict energy convergence criterion of $10^{-11}$ eV were used.

References


Pressure-Dependent Optical and Vibrational Properties of Monolayer Molybdenum Disulfide

Avinash P. Nayak\textsuperscript{1}, Tribhuwan Pandey\textsuperscript{2*}, Damien Voiry\textsuperscript{3}, Jin Liu\textsuperscript{4}, Samuel T. Moran\textsuperscript{1}, Ankit Sharma\textsuperscript{1}, Cheng Tan\textsuperscript{1}, Chang-Hsiao Chen\textsuperscript{6}, Lain-Jong Li\textsuperscript{7}, Manish Chhowalla\textsuperscript{3}, Jung-Fu Lin\textsuperscript{4,5}, Abhishek K. Singh\textsuperscript{2*}, Deji Akinwande\textsuperscript{1*}

SUPPLEMENTARY INFORMATION
Figure S1. Vibrational and Optical Properties of Bulk and Monolayer 2H-MoS$_2$ at High Pressures. (a) Intensity ratio of the A$_{1g}$ and E$_{2g}$ peaks. The E$_{2g}$ mode is observed to diminish in comparison to the A$_{1g}$. The insets show the relative intensities of the E$_{2g}$ and A$_{1g}$ peaks at selected pressures. (b) Pressure dependence of the Raman frequencies of the A$_{1g}$ and the E$_{2g}$ modes as a function of pressure. The behavior of these vibrational Raman modes in monolayer 2H-MoS$_2$ at high pressures (blue circles) deviates significantly from that of the bulk counterpart (red circles) due to the absence of interlayer interactions. Inset: representative vibrations involved in A$_{1g}$ and E$_{2g}$ modes. The A$_{1g}$ modes originate from transverse vibrations of S-S atom, however the E$_{2g}$ mode emerges from longitudinal vibrations of Mo and S atoms in opposite directions. (c) Raman frequency separation between the A$_{1g}$ and E$_{2g}$ peak as a function of pressure for monolayer and bulk 2H-MoS$_2$. Inset: representative Raman spectra highlighting the separation at 0 GPa and 30.8 GPa. The in-plane A$_{1g}$ mode becomes more dominant in intensity than the E$_{2g}$ past ~16 GPa for the monolayer 2H-MoS$_2$. (d) PL FWHM with pressure up to 16 GPa. The black lines serves as visual guidelines.
**Figure S2. Modeling of hydrostatic pressure on monolayer MoS$_2$.** (a) Compression of atoms plotted with respect to energy required to compress the in-plane ($x$, $y$) and out of plane ($z$) bonds. (b) Compression of atoms is plotted with respect to pressure. Till 20 GPa pressure there is equal compression in all the three direction. After 18 GPa. Compression along the $z$ direction becomes more favorable. Inset: Schematic representing the compression of atoms in the in-plane direction (upper inset) and out-of-plane directions.

![Figure S2](image)

---

**Figure S3. Raman Spectroscopic Results of Restacked 1T'-MoS$_2$ and monolayer 2H-MoS$_2$ at High Pressures.** (a) FWHM of $J_1$, $J_2$ and $J_3$ Raman modes. The $J_3$ mode tends to saturate at 10 GPa while $J_2$ and $J_3$ increase in FWHM. (b) The FWHM of the $E_{2g}$ and $A_{1g}$ increases with pressure. (c) The FWHM of the $E_{2g}$ and $A_{1g}$ Raman modes for 2H-MoS$_2$. The FWHM is notably smaller for the 2H-MoS$_2$ monolayer than the 1T'-MoS$_2$ since the $J_3$ mode merges with the $E_{2g}$ mode.

![Figure S3](image)
Figure S4. Phonon Dispersions for Monolayer 1T'-MoS$_2$ at Representative Pressures. The Raman active modes for 1T'-MoS$_2$ are highlighted with different colors for clarity at (a) 0 GPa and (b) 23 GPa. The Raman active $A_{1g}$, $E_{2g}$, $J_1$, $J_2$ and $J_3$ modes are identified from the dispersion curves at the $\Gamma$ point. As can be seen in case of 1T'-MoS$_2$ three new modes $J_1$, $J_2$ and $J_3$ appear, whereas the frequency of the $E_{2g}$ mode decreases significantly compared to bulk MoS$_2$. The $J_3$ mode merges with the $E_{2g}$ mode at ~10 GPa.
Figure S5. Raman Intensity Map of 1T'-MoS$_2$. The pressure dependent Raman shows the shift and broadening of the 1T'-MoS$_2$ Raman active modes. The dominant Raman active modes at high pressure are J$_2$, E$_{2g}$, and A$_{1g}$. 
Figure S6. Raman Shift with Pressure. The pressure dependence of the Raman modes for the monolayer 2H and 1T'-MoS$_2$ polytypes compared to the bulk 2H-MoS$_2$ analog in their semiconducting (SC) and metallic (M) regime.
Figure S7. Reversible Pressure Effects on Monolayer MoS$_2$. (a) PL from monolayer MoS$_2$ before and after hydrostatic pressure of 30 GPa is applied across the monolayer 2H-MoS$_2$. (b) The PL for the 1T$'$-MoS$_2$ and 2H-MoS$_2$ at 0 GPa. The 1T$'$-MoS$_2$ does not show PL behavior. (c) Upon decompression, the Raman active A$_{1g}$ and E$_{2g}$ modes compare well with the Raman spectra with increasing pressure, suggesting that the pressure effects are reversible. (d) Pristine and relaxed 1T$'$-MoS$_2$ show the J$_1$, J$_2$, and J$_3$ active modes, indicating that the pressure effects are reversible.
Figure S8. FWHM of the PL Spectra from Monolayer MoS$_2$. (a) The FWHM map showing an increase with hydrostatic pressure at (a) 0.6 GPa (b) 12.5 GPa and (c) 21.3 GPa the diminishing of the PL peak that suggest the PL at high pressures is unresolvable past 16 GPa at room temperature. The black dots represent where the peaks are diminished into the background noise.
Figure S9. Fluorescence Spectra Shift in Ruby. The $R_2$ and $R_1$ ruby luminescence peaks are used to measure the pressure shift. The evolution of the PL spectra from ruby is used as a calibrant to measure the pressure experienced by the sample.
Figure S10. Relation between Volume Strain and Pressure for 2H-MoS$_2$ Family. 2L, 3L and Bulk follow the same trend and the data can be fitted to a third order polynomial as $P = -0.36 + 59.81\varepsilon + 137.96\varepsilon^2 + 325.93\varepsilon^3$. However 1L depicts a completely different behavior, the polynomial fit of 1L data can be given as $P = 0.39 + 101.24\varepsilon - 220.72\varepsilon^2 + 446.7\varepsilon^3$. These different behaviors arise due to absence of interlayer interaction for monolayer MoS$_2$. Inset: 2L, 3L and bulk have almost same dependence between volume strain and pressure.
Figure S11. Band Structure and Density of States for the 1T’-MoS$_2$ Monolayer. (a) At 0 GPa pressure and (b) 30 GPa. The monolayer 1T’-MoS$_2$ is metallic and becomes more metallic under hydrostatic pressure. Upon application of hydrostatic pressure the hybridization between Mo $d$-orbitals (mainly $d_{z^2}$, $d_{xy}$ and $d_{x^2-y^2}$) and S $p$-orbitals increases, there is an increase in the overlap between conduction and valence bands, increasing the extent of metallization.
Figure S12. Stability of Different MoS$_2$ Monolayer Polytypes with Respect to the 2H-MoS$_2$ Monolayer as a Function of Volume Strain. Monolayer 2H-MoS$_2$ (i.e. 1H-MoS$_2$) is the most stable phase at ambient conditions and remains energetically favorable even under high strains. The absence of cross over between the various energy plots indicates the absence of phase transformation between 2H and monolayer 1T'-MoS$_2$ which is in agreement with our Raman spectra.

Figure S13. Compression of the in-plane and out-of-plane axis. (a) Variation in slab thickness ($c_{2L}$) and in-plane lattice parameter $a$ under hydrostatic pressure. Illustration of slab thickness for (b) bulk and (c) 1L, 2L, and 3L MoS$_2$. 