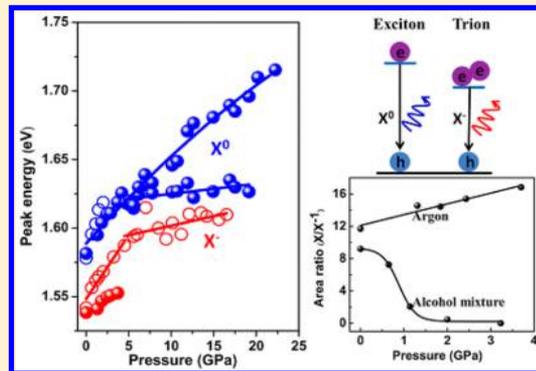


Pressure-Dependent Light Emission of Charged and Neutral Excitons in Monolayer MoSe₂Xinpeng Fu,[†] Fangfei Li,^{*,†,‡} Jung-Fu Lin,[‡] Yuanbo Gong,[†] Xiaoli Huang,[†] Yanping Huang,[†] Bo Han,[†] Qiang Zhou,^{*,†} and Tian Cui^{†,‡}[†]State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China[‡]Department of Geological Sciences, The University of Texas at Austin, Austin, Texas 78712, United States

Supporting Information

ABSTRACT: Tailoring the excitonic properties in two-dimensional monolayer transition metal dichalcogenides (TMDs) through strain engineering is an effective means to explore their potential applications in optoelectronics and nanoelectronics. Here we report pressure-tuned photon emission of trions and excitons in monolayer MoSe₂ via a diamond anvil cell (DAC) through photoluminescence measurements and theoretical calculations. Under quasi-hydrostatic compressive strain, our results show neutral (X⁰) and charged (X⁻) exciton emission of monolayer MoSe₂ can be effectively tuned by alcohol mixture vs inert argon pressure transmitting media (PTM). During this process, X⁻ emission undergoes a continuous blue shift until reaching saturation, while X⁰ emission turns up splitting. The pressure-dependent charging effect observed in alcohol mixture PTM results in the increase of the X⁻ exciton component and facilitates the pressure-tuned emission of X⁻ excitons. This substantial tunability of X⁻ and X⁰ excitons in MoSe₂ can be extended to other 2D TMDs, which holds potential for developing strained and optical sensing devices.



Atomically thin transition metal dichalcogenides (TMDs) 2H-MX₂ (M = Mo, W, and etc.; X = S, Se, and Te) have attracted widespread attention owing to their unusual optical and electronic properties.^{1–6} The fundamental optical excitation of semiconductors is an exciton (X⁰) associated with the Coulomb-bound excited electron and hole. Trions can be formed by extra capture of one electron or hole when the Coulomb interaction is strong enough. The latter term divides into two states: two electrons and one hole correspond to a negatively charged trion (X⁻), and one electron and two holes correspond to a positively charged trion (X⁺). Binding energies of excitons and trions in 2D TMDs are as high as a few hundred meV, which is an order of magnitude larger than conventional semiconductor quantum wells. This property originates from the large carrier effective masses, strong quantum confinement, and reduced dielectric screening due to the monolayer thickness.^{7–10} Strong Coulomb interactions make these quasiparticles stable at room temperature and relevant for optoelectronic devices.^{11–15} As a consequence, monolayer TMDs have potential applications in controllable 2D electronic systems. Recently, increasing attention is being paid to their excitonic physics including interexcitonic scattering,¹⁶ exciton-carrier broadening,^{17,18} biexciton formation,¹⁹ as well as exciton valley relaxation dynamics.²⁰

MoSe₂, a member of the group-VI TMDs, is composed of a single layer of Mo atoms covalently bonded between two laminar sheets of Se atoms. Monolayer MoSe₂ has a direct band gap at the K points in the first Brillouin zone. The emission of

X⁰ and X⁻ excitons generated by the direct interband transition at room temperature has been observed in previous reports. Their well-separated excitonic features possess advantages for exploring excitonic physics. Recently, electrical control of the excitonic species among positively charged (X⁺), neutral (X⁰), and negatively charged (X⁻) excitons of monolayer MoSe₂ has been achieved using a back-gated field-effect transistor (FET) device.⁷ By setting V_g to be negative or positive, X⁰ excitons were turned into X⁺ or X⁻ excitons, respectively. On the other hand, strain engineering via application of hydrostatic pressure has been shown to be an effective means to modulate electronic band gaps and charges in monolayer MoS₂, heterostructured MoS₂, and graphene. The direct band gap increased from 1.85 to 2.08 eV when the monolayer MoS₂ was exposed over a pressure range of 0–16 GPa.²¹ p-Type doping of graphene was observed in graphene/MoS₂ heterostructures due to the charge transfer and reached a doping concentration of ~3.2 × 10¹³ cm⁻² at 30 GPa.²² These studies have demonstrated that strain engineering is an important routine to control behaviors of excitons and trions. More importantly, the strain-induced charging effect enables simultaneous tuning of the content and energy of excitons and trions in monolayer 2D TMDs, which holds potential for light-emitting device applications.^{23,24}

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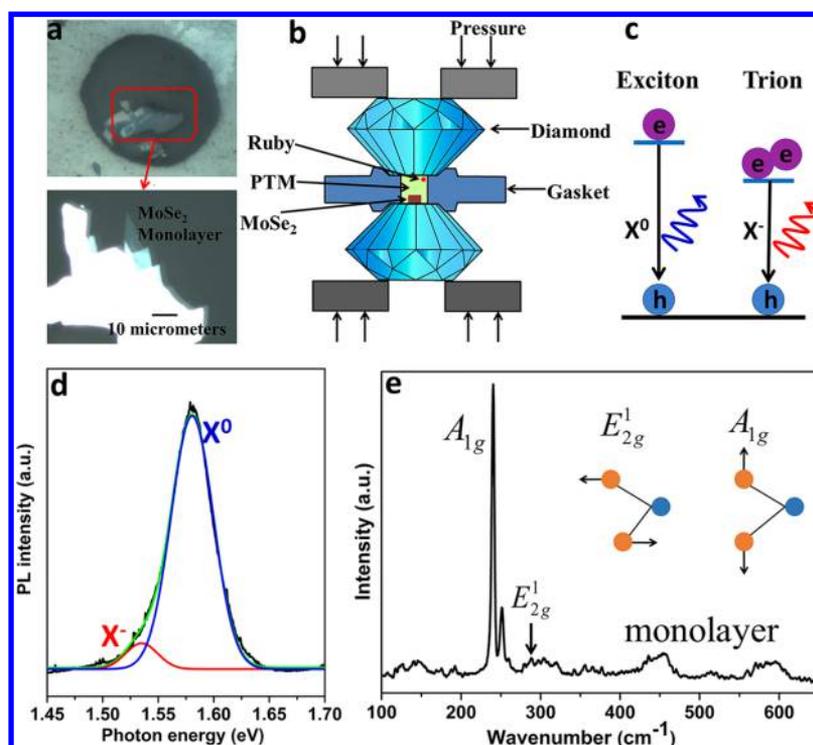


Figure 1. (a) Representative photo of the monolayer MoSe₂ placed in the sample chamber of the DAC in alcohol mixture PTM. The photo of the monolayer 2H-MoSe₂ film shown in the red box is enlarged in the image below. The sample can be easily distinguished in an optical microscope with its distinct optical contrast (lower figure). (b) Schematic diagram of the DAC for PL and Raman experiments. (c) Illustration of the transition processes for neutral (X⁰) and charged (X⁻) excitons in monolayer 2H-MoSe₂. (d) PL spectrum of monolayer 2H-MoSe₂ at ambient conditions. The neutral exciton emission (blue curve) is very dominant, while the charged exciton (red curve) is weak at ambient conditions. (e) Raman spectrum of monolayer 2H-MoSe₂ at ambient conditions. The insets show the normal vibrational modes of monolayer 2H-MoSe₂. Blue and orange circles represent Mo and Se atoms, respectively.

In this work, we report the first study on effective tuning of exciton and trion emission of the exfoliated monolayer MoSe₂ via hydrostatic pressure and charging effects using photoluminescence (PL) spectra in a diamond anvil cell (DAC) loaded with argon or alcohol mixture pressure transmitting media (PTM). We found a pressure-dependent charging effect in alcohol mixture PTM, which led to the increase of the X⁻ exciton component and facilitated the emission of X⁻ excitons being modulated continuously to high pressure. Meanwhile, the tunability of X⁰ emission at high pressure can be achieved by employing argon as PTM. At low pressure, the energies of X⁻ and X⁰ emission exhibit an approximately similar blue shift rate, and then X⁻ emission gradually reaches saturation, whereas pressure-induced splitting of X⁰ emission appears at high pressure. The obtained strain-related response of X⁰ and X⁻ exciton emission in monolayer MoSe₂ in a controlled environment is helpful for developing strained MoSe₂ devices. In addition, the ability of switching between these two distinctly different pressure-dependent evolutions of the PL spectrum by controlling the contents of X⁰ and X⁻ excitons is significant for optoelectronic applications.

Monolayer 2H-MoSe₂ film was prepared by mechanically exfoliating a MoSe₂ single crystal (2D Semiconductor Supplies, USA) using GEL film (Gel-Pak).^{25,26} The monolayer MoSe₂ was transferred onto a diamond anvil surface, which also served as the substrate in the sample chamber. Regions of monolayer MoSe₂ were identified by their optical contrasts with the background using an optical microscope. Further confirmation was followed by employing PL measurements (Figure 1d) and Raman spectra measurements (Figure 1e). The DAC device

provides hydrostatic pressure, and its schematic diagram is shown in Figure 1b. The top-view microscope image of the pressure chamber is exhibited in Figures 1a and S1. Two different types of PTMs, argon and alcohol mixture, were used in this work. The optical response of monolayer MoSe₂ is dominated by excitonic transitions. As illustrated in Figure 1c, the emission of X⁰ and X⁻ excitons originates from the transition of Coulomb-bound electron–hole and 2electron–hole quasiparticles in the band gap, respectively, and the emission of X⁻ excitons red shifts from the X⁰ excitons.

Figure 1d shows the typical PL spectrum of a monolayer MoSe₂ at ambient conditions, which has been well fitted using two Gaussian functions. The two fitted peaks, a small one located at the lower energy side and a main broad peak located at the higher energy side, are assigned to negatively charged exciton X⁻ (at 1.54 eV) and neutral exciton X⁰ (at 1.58 eV) emission, respectively, which is in agreement with previous reports.^{7,27–30} The existence of X⁻ emission suggests an unintentional doping effect related to the structural defects.^{31–33}

The Raman spectrum of bulk 2H-MoSe₂ is shown in Figure S2, and the vibrational normal modes are illustrated in the inset. Four normal vibrational modes were studied in bulk 2H-MoSe₂, including B_{2g}¹ at 351.03 cm⁻¹, E_{1g} at 169.77 cm⁻¹, E_{2g}¹ at 284.5 cm⁻¹, and A_{1g} at 242.02 cm⁻¹. The E_{1g}, E_{2g}¹, and A_{1g} modes originate from the in-plane vibration of Se–Se atoms, in-plane vibration of Mo–Se atoms, and out-of-plane vibrations of Se–Se atoms in opposite directions, respectively. The B_{2g}¹ mode is expected to be present in multilayer MoSe₂ because it arises from out-of-plane (breathing) vibration and has been used as

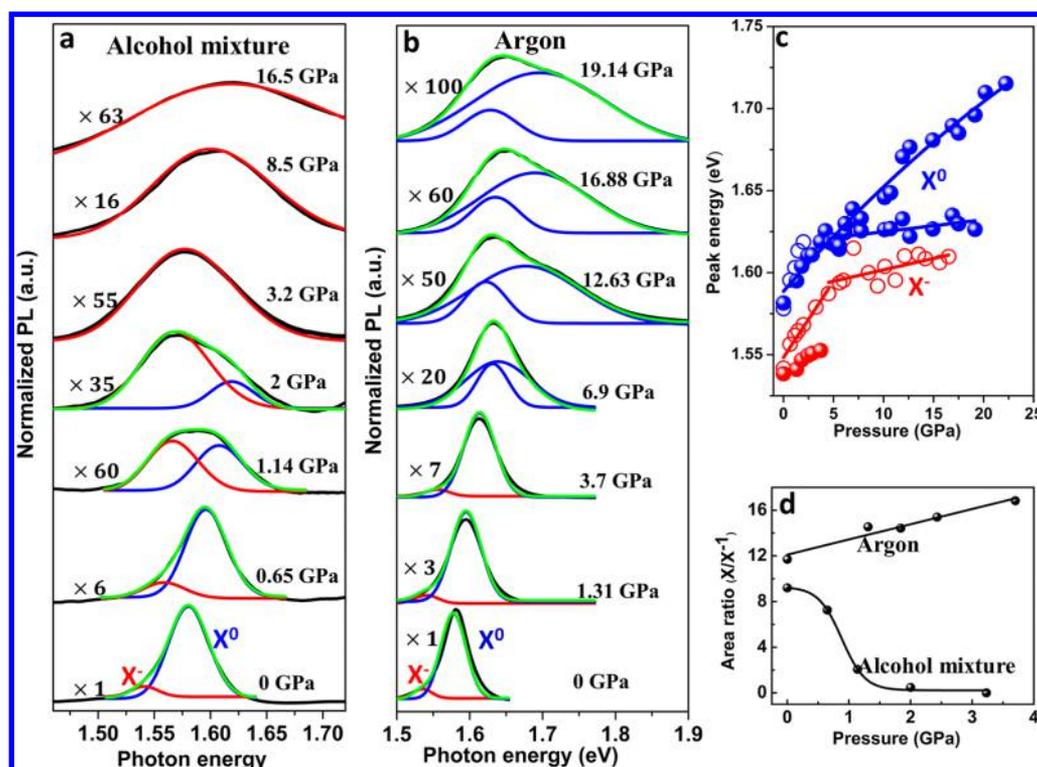


Figure 2. (a) PL spectra of monolayer 2H-MoSe₂ immersed in alcohol mixture PTM at high pressure. (b) PL spectra of monolayer 2H-MoSe₂ in argon PTM at high pressure. The spectra are normalized to show characteristic features at high pressure. Panels (a) and (b) show experimental spectra (black lines) with spectral fits to X⁰ exciton emission (blue lines), X⁻ emission (red line), and overall fitted spectra (green lines). (c) Peak energy evolution of PL peaks fitting as a function of pressure in two PTM. Solid circles represent X⁻ (red ●) and X⁰ (blue ●) excitons in argon PTM, and hollow circles represent X⁻ (red ○) and X⁰ (blue ○) excitons in alcohol mixture PTM. (d) Pressure-dependent area ratio of exciton/trion emission (X⁰/X⁻) versus pressure.

an important criterion in distinguishing the monolayer from multilayers. In our monolayer MoSe₂, intense A_{1g} peaks are observed, and the B_{2g}¹ mode is not observed as expected (Figure 1e). When the bulk was thinned to a monolayer, a 1.8 cm⁻¹ red shift of the A_{1g} mode and a 3.83 cm⁻¹ blue shift of the E_{2g}¹ mode were observed because of the competition between surface effects and thickness effects,³⁴ which are consistent with the previous results.^{27,35,36}

After confirming that the prepared sample was indeed monolayer 2H-MoSe₂, the pressure-dependent PL measurement was conducted using alcohol mixture PTM, and the normalized PL spectra of monolayer MoSe₂ are presented in Figure 2a. The scaling factors for the normalization are listed on the left side of the corresponding curves, and a larger factor corresponds to a smaller PL intensity. The raw data in Figure 3a were fitted with a multi-Gaussian function, and individual component X⁰ and X⁻ emission is displayed in blue curves and red curves for pressures of 0 GPa and above. As the pressure increases, both X⁻ and X⁰ peaks exhibit blue shifts, but the relative intensity evolutions give an obvious contrary transition. The integrated intensity of the X⁻ peak tended to increase with pressure, while that of the X⁰ peak showed the opposite trends. When the pressure was increased to 3.2 GPa, the neutral exciton X⁰ peak disappeared, leaving the X⁻ peak to become the main emission. Then, with further compression, the X⁻ emission vanished above 16.5 GPa. The unusual behaviors of PL have never been observed in any previous study of pressure-tuning monolayer TMDs and present a pressure-enhanced charging effect in monolayer MoSe₂, which facilitates the high-pressure modulation of X⁻ excitons. We suppose that the

charging effect in monolayer MoSe₂ is closely related with the alcohol mixture PTM.

To rationalize the charging effect and investigate the high-pressure tuning behaviors of X⁰ in PL spectra, we utilized inert argon as PTM to eliminate the interference from PTM itself and obtain intrinsic features of the system. As shown in Figure 2b, the X⁻ and X⁰ peak evolutions under pressure exhibit obviously different behaviors in the two PTM experiments. Enhancement of X⁻ emission is never observed in argon. Instead, it diminishes gradually with pressure, which indicates that the pressure-dependent charging effect was interdicted when PTM was replaced by argon. Therefore, emission of X⁰ excitons at high pressure has been effectively tuned using argon PTM. Interestingly, a new splitting of neutral exciton X⁰ emission appears above 3.7 GPa.

The PL intensity exhibits an oscillating trend as pressure increases in the alcohol mixture experiment, whereas there are monotonous decreases in the argon experiment (Figure 2a,b). In alcohol mixture PTM, the inhibitory effect of pressure on the exciton emission and the pressure-dependent charging effect together contribute to the oscillating intensity of X⁻ peaks, represented as the oscillation of PL intensities. However, because of blocking of the charging effect in liquid argon PTM, the intensity of exciton emission is dominated by the inhibitory effect of pressure, displaying a monotone decrease with increasing pressure. In addition, the width of peaks is observed to broaden with increasing pressure, which may be partly ascribed to the inhomogeneity of pressure arising from solidification of the pressure medium.

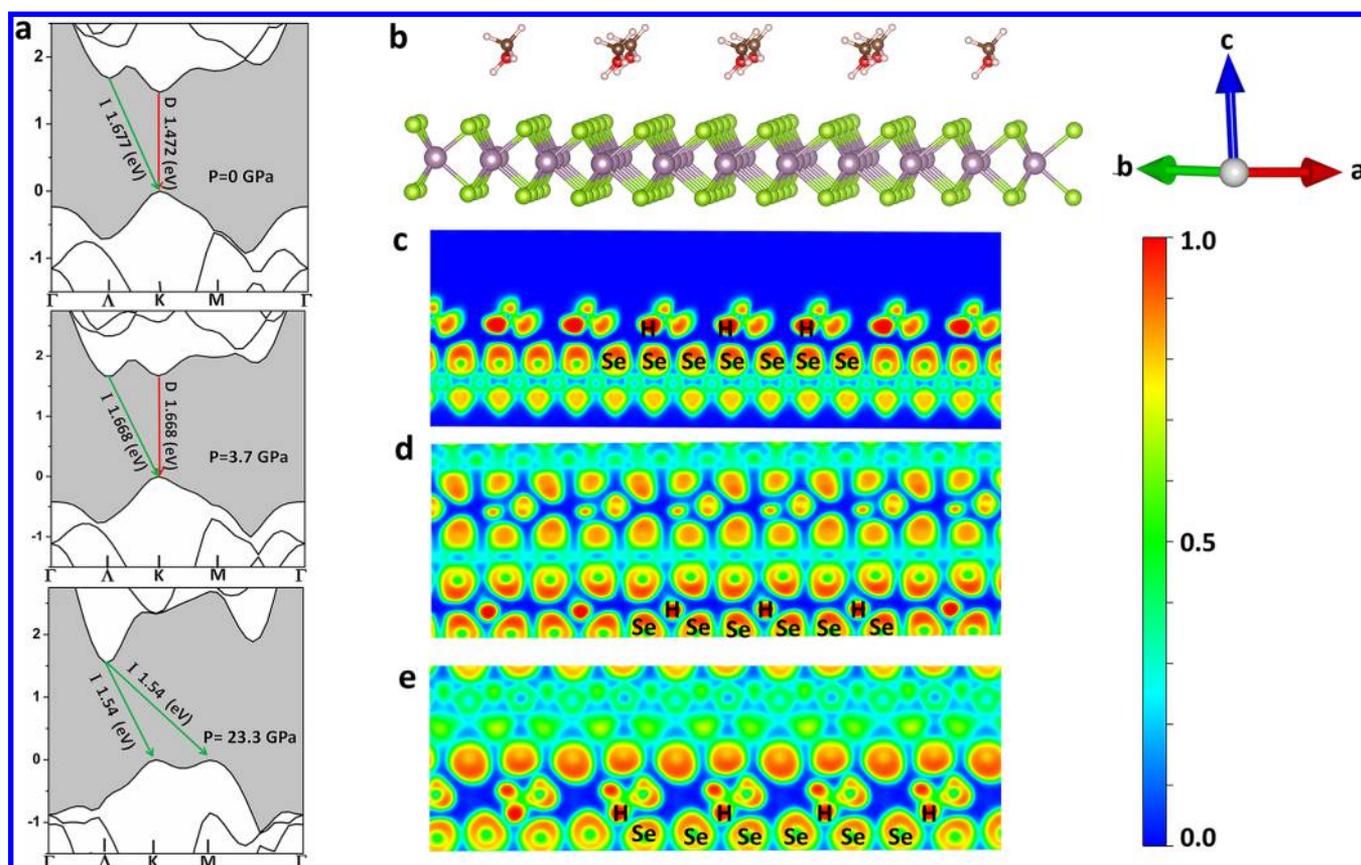


Figure 3. (a) Band structures of monolayer MoSe₂ at three representative pressures of 0, 3.7, and 23 GPa, depicting K–K direct interband transitions, conduction band K– Λ crossover, and valence band K–M crossover, respectively. Here, D indicates the direct band gaps and I indicates indirect band gaps. The values of D and I are also shown in the figure. (b) Calculated methanol molecule adsorption on monolayer MoSe₂ at 0 GPa. (c–e) ELF of the calculated structure at 0, 30, and 50 GPa.

Two opposite evolutions of area ratio of the exciton/trion (X^0/X^-) versus pressure in both PTMs are shown in Figure 2d. The area ratio of X^0/X^- declined quickly and finally disappeared with increasing pressure in the alcohol mixture PTM, while the trend of the area ratio in argon PTM was upward. These results reveal that the occurrence of the charging effect is closely related to the alcohol mixture PTM. We propose that the charging effect is derived from the interaction between H atoms of alcohol mixture PTM and Se atoms of monolayer MoSe₂ at high pressure, and the related DFT calculations are described in the following.

The energy evolutions of X^- and X^0 exciton emission as a function of pressure in two PTMs are illustrated in Figure 2c. In the alcohol mixture PTM experiment, the neutral exciton X^0 emission disappeared at 3.2 GPa, and a turning point in pressure evolution of negatively charged exciton X^- emission can be observed. The sectionalized linear equation, $E_g = 1.548 + 0.009P$ ($P < 3.7$ GPa) and $E_g = 1.588 + 0.001P$ ($P \geq 3.7$ GPa), fits the experimental data well. On the other hand, in argon PTM, it gives three main PL peaks, as shown by solid circles. The X^- emission (blue solid circle) diminishes and disappears after 3.7 GPa, while the X^0 emission presents a continuous blue shift with pressure up to 23.3 GPa, which is diametrically opposed to that in alcohol mixture PTM. A second-order polynomial fit $E_g = 1.589 + 0.007P - 5.867 \times 10^{-5}P^2$ can be applied to describe the pressure dependence of the main peak. After 3.7 GPa, a new split peak appears at the lower energy side and gives a pressure evolution expressed by

linearly fitting $E_g = 1.618 + 7.365 \times 10^{-4}P$. Notably, the novel emerged PL emission in argon PTM and the X^- emission in alcohol mixture PTM ($P \geq 3.7$ GPa) give a similar pressure trend but with an energy discrepancy of about 30 meV. It is worth mentioning that the monolayer MoSe₂ in either alcohol mixture PTM or argon PTM displays discontinuous changes at 3.7 GPa, which indicates that it is a key point in the process of the hydrostatic pressure-modulated electronic band structure.

First-principles DFT calculations were employed to calculate the band structure of monolayer MoSe₂ with CASTAP code for a better understanding of the energy evolutions of X^- and X^0 emission during compression,³⁷ and the obtained results are shown in Figure 3a. At 0 GPa, the direct band gap of 1.472 eV initially lies in K–K points. Both X^0 and X^- excitons exit in K–K points, and their energy tuned by pressurization presents a trend of increase. When the pressure reaches up to 3.7 GPa, a conduction band K– Λ crossover behavior is observed, and the direct band gap of K–K points coincides with the indirect band gap of Λ –K points of 1.668 eV. The pressure value of conduction band K– Λ crossover obtained from theoretical calculation matches well with the experimental key point of 3.7 GPa. Upon further increasing the pressure, the conduction band minimum at the Λ point continues dropping and becomes much lower than that of the K point, and the monolayer MoSe₂ then transforms into an indirect band gap semiconductor (Figure S3). During this process, X^0 emission is divided into indirect Λ –K and direct K–K interband transitions, and the energy of X^0 existing in these two parts

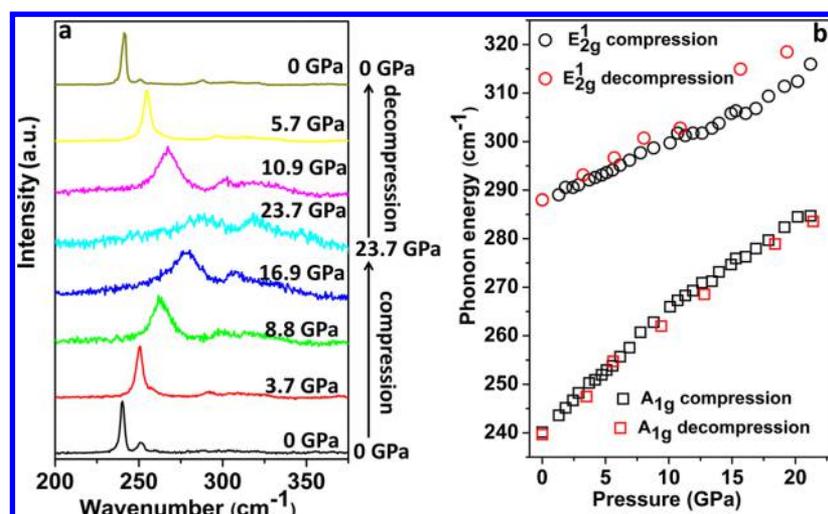


Figure 4. (a) Raman spectra of monolayer MoSe₂ in argon PTM during a pressure cycle. (b) Pressure dependence of Raman frequencies for A_{1g} and E_{2g}¹ modes during compression and decompression in argon PTMs.

tends to increase and remain nearly unchanged, respectively, with the pressure modulation. In the case of X⁻ emission, it only lies in the indirect Λ -K interband transition, and the corresponding energy shows a similar evolving model with that of X⁰ located at the Λ -K interband transition. These calculated results are in good agreement with experimental phenomenon of X⁰ emission splitting and X⁻ exciton energy reaching saturation. Up to 23.3 GPa, the indirect band gaps of Λ -K points and Λ -M points match the value of 1.54 eV. The pressure-induced valence band K-M crossover turns up, and indirect interband transition shifts from Λ -K to Λ -M points afterward (Figure 3a).

Now, the evolutions of X⁻ and X⁰ emission are clear by combining the experimental and calculated results. Pressure-induced conduction band K- Λ crossing occurred at 3.7 GPa, which is related to its direct band gap to indirect band gap transition. For monolayer MoSe₂ in argon PTM, the novel emerging PL emission on the left side of the original main peak is attributed to the Λ -K interband transitions after the conduction band K- Λ crossover at 3.7 GPa, and the original main X⁰ emission peak existing in the whole pressure ranges comes from K-K transitions. The fitted polynomial to the original main X⁰ emission matches well with the K-K interband transitions of theoretical calculations, even though it turns from a direct band gap (before 3.7 GPa) to an indirect band gap transition due to the existence of conduction band K- Λ crossover.

For monolayer MoSe₂ in alcohol mixture PTM, when conduction band K- Λ crossover occurs, the blue shift of negatively charged exciton X⁻ emission slows down obviously above 3.7 GPa, implying that the X⁻ emission transitions occur in K-K points at low pressure but occur in Λ -K points at high pressure. This behavior matches with a previous report on monolayer WSe₂ that X⁻ emission transitions occur only in Λ -K points not in K-K points after conduction band K- Λ crossover because the ionized electrons populate the conduction band minimum to form X⁻ emission.³⁸ Besides, as we mentioned before, there is about a 30 meV energy discrepancy between the novel emerged PL emission in argon PTM and the X⁻ emission in alcohol mixture PTM ($P \geq 3.7$ GPa), but they possess a similar pressure trend. This is because they both come from the indirect transitions in Λ -K points

after 3.7 GPa, and the 30 meV energy discrepancy is known as the trion dissociation energy. It should be noted that the conduction band K- Λ crossover phenomenon in monolayer MoSe₂ occurs at a smaller pressure (3.7 GPa) than that of MoS₂ (22.3 GPa),²¹ indicating that the X⁰ and X⁻ exciton emission of MoSe₂ is easily tuned to undergo the transformation from direct to indirect band gap transition compared with monolayer MoS₂. This might partly be ascribed to the fact that the separation of the energy difference between the conduction band minimum at K and Λ points is smaller, that is, 0.04 eV for monolayer MoSe₂ in comparison with 0.2 eV for monolayer MoS₂. Because the PL spectra of the monolayer 2H-MoS₂ diminish to the background noise level at pressures over 16 GPa at room temperature, the behaviors of excitons after conduction band K- Λ crossover in monolayer MoS₂ were not observed. For monolayer MoSe₂, the behaviors of X⁰ and X⁻ excitons lying in indirect Λ -K interband transition were successfully observed and investigated in this work, and Figure 2c is plotted to schematically illustrate their energy variations with pressure.

The content of X⁻ excitons can be tuned by pressure-dependent charging effects in the surroundings of the alcohol mixture, in which the electron charge was injected into alcohol-immersed MoSe₂ to form X⁻ excitons by interaction between H atoms of PTM and Se atoms of monolayer MoSe₂ at high pressure. This mechanism of charging effects is verified by DFT calculations performed with the VASP code.³⁹ As shown in Figure 3b, we place methanol molecules on the surface of monolayer MoSe₂ and relax the atomic structure until stable configurations are found. We calculated the electron localization function (ELF) for this atomic structure. Then, the structure was regarded as the crystal structure of a bulk material to obtain a uniform pressure from all directions. The electron with an ELF value close to 0.5 is regarded as a free electron. As shown in Figure 3c, at 0 GPa, the free electrons of H atoms in methanol molecules and Se atoms are isolated. When a pressure of 30 GPa was applied to the atomic structure from all directions, a union of free electrons derived from H and Se atoms was formed (Figure 3d). Further increasing the pressure to 50 GPa, the union of the free electrons was further strengthened due to the pressurizing-induced declination of interaction distance (Figure 3e). Despite the fact that the

theoretical model could not exactly simulate the complex system of the alcohol mixture-immersed sample, it still convincingly reveals the mechanism of the charging effect and the enhanced trend during compression observed in the experiment. When the PTM was replaced by argon, the pressure-dependent charging effect was interdicted because inert properties blocked the interaction between the sample and PTM. The calculated simulation of the pressure-induced charging effect provides an excellent strategy for achieving controllable modulation of excitons and trions in 2D TMDs at extreme environments.

Another important property of monolayer MoSe₂ is the behavior of lattice vibrations under high pressure. We also investigate the Raman spectra of monolayer MoSe₂ at high pressures employing alcohol mixture and argon as PTM. Figure 4a displays a series of Raman spectra with different pressure coefficients obtained in argon PTM, in which Raman peaks exhibits a blue shift with the pressure increasing up to 23.7 GPa. Figure 4b reveals that the pressure-induced evolutions of A_{1g} and E_{2g}¹ modes are reversible, and the resulting blue shifts from 0 to 23.7 GPa are 44.6 and 28 cm⁻¹, respectively. Altering PTM with the alcohol mixture, the obtained Raman spectra did not present any observable disparity (Figure S4), which suggests that a change of PTM has a slight influence on the pressure-dependent lattice vibrations. Therefore, we conclude that the Raman mode shift based on the diamond substrate exhibits uniform change, offering a continuous excitonic tuning process upon pressurizing for the following PL measurement. In addition, a control experiment was performed by altering diamond with a Si/SiO₂ substrate, and the results are exhibited in Figure S5. The occurrence of a nonuniform Raman mode shift and softening phenomenon observed from the SiO₂/Si substrate-based experiment was supposed to be related to unit cell reduction and phase transition of the Si/SiO₂ substrate at high pressure. This nonuniform change in the volume largely limits the energy tunability of excitons and trions for potential optoelectronic applications. Therefore, we are convinced that diamond is the appropriate choice of window material for high-pressure experiments due to its outstanding resistance to pressure. In addition, using diamond as the substrate is of benefit to the optical measurements in the transmission mode and largely improves the pressure that samples could achieve, which may significantly advance the study on pressure-induced semiconducting to metallic transition in few-layered TMDs.

In conclusion, we investigated the tuning process of X⁰ and X⁻ exciton emission by hydrostatic pressure and charging effects through PL spectra. Samples were transferred into a DAC and immersed in two kinds of PTM including a standard mixture of (4:1) methanol/ethanol and argon. Using diamond as the substrate, monolayer MoSe₂ shows different evolutions of pressure-dependent PL spectra in two PTMs. The content of charged exciton X⁻ emission increases dramatically in the alcohol mixture PTM-based experiment during compression. When the pressure goes up to the key point of 3.7 GPa, only indirect Λ -K transition-related X⁻ emission is observed in the alcohol mixture experiment. In contrast, in the argon experiment, the content of charged exciton X⁻ emission decreases and the X⁰ emission corresponding to direct K-K transition and indirect Λ -K transition is observed at 3.7 GPa and above. Moreover, theoretical calculation, consistent with the experimental results, helps us to analyze the behaviors of the exciton in PL spectra during recompression. The result of DFT calculations with VASP code reveals that the pressure-

dependent charging effect observed in the alcohol mixture PTM experiment is induced by the interaction between H atoms of PTMs and Se atoms at high pressure.

EXPERIMENTAL METHODS

Sample Preparation and Characterizations. Monolayer 2H-MoSe₂ film was obtained from a MoSe₂ single crystal (2D Semiconductor Supplies, USA) by mechanical exfoliation technology on GEL film (Gel-Pak).^{25,26} Afterward, the monolayer MoSe₂ was transferred onto a diamond anvil surface serving as the substrate in the sample chamber. A symmetric DAC with a pair of 300 μ m culet anvils was used for the high-pressure experiments. A T301 stainless steel gasket with an initial thickness of 250 μ m was preindented to 50 μ m thick and was subsequently drilled in the center to form a hole 120 μ m in diameter. The pressure of the sample chamber in DAC was measured by collecting ruby fluorescence spectra from ruby spheres loaded in the chamber.⁴⁰ The PTM, either a standard mixture of (4:1) methanol/ethanol or argon, was also loaded in the sample chamber to provide a hydrostatic pressure condition for the samples.

Raman, PL spectroscopy, and optical contrast were used to determine the layers of MoSe₂. Raman and PL measurements were conducted using a micro-Raman spectrometer (Horiba-JY T64000) equipped with a solid-state green laser ($\lambda = 532$ nm) in a backscattering configuration. The signals were dispersed by an 1800 g mm⁻¹ (Raman) and a 600 g mm⁻¹ (PL) grating and collected via a 50 \times objective lens under atmospheric conditions and high pressures, respectively. Considering the probable damage from heating or oxidizing under exposure, the estimated laser power at the surface of the sample was set to be less than 0.5 mW.

Theoretical Calculations. The first-principles calculations based on DFT were performed to provide insight into the energy band of monolayer MoSe₂ at high pressure. Perdew-Burke-Ernzerh (PBE) of generalized gradient approximation (GGA) functional with the exchange-correlation functional and norm-conserving was used as the type of pseudopotential during the whole computational procedure. Calculation of the energy band was performed with a plane-wave cutoff energy of 800 eV and a K-point set of 18 \times 18 \times 1. A 20 \AA vacuum spacing was set as the interatomic spacing to avoid artificial couplings between adjacent atomic layers. The self-consistent field (SCF) was managed to be less than 5 \times 10⁻⁷ eV/atom to ensure the accuracy of calculated results. The band structure of monolayer MoSe₂ can be calculated via the modulated lattice parameter *a* at selected pressures obtained by applying the procedure of geometry optimization. All of the calculations were performed in the CASTEP code.

The stable structure of methanol molecule adsorption on monolayer MoSe₂ was obtained using DFT within the PBE of parametrization of the GGA, as implemented in the Vienna ab initio simulation package VASP code. A 20 \AA vacuum spacing was set as the interatomic spacing to acquire the stable structure at 0 GPa. Then, the structure was regarded as the crystal structure of a bulk material to obtain the uniform pressure from all directions. A plane-wave cutoff energy of 900 eV was sufficient for the initial search over structures. The ELF calculations were introduced to analyze the behaviors of free electrons existing in H and Se atoms. A well-converged Monkhorst-Pack k point set of 5 \times 5 \times 1 was used for this procedure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01374.

Photo of the monolayer MoSe₂ on a diamond substrate in liquid argon PTM; Raman spectrum of bulk 2H-MoSe₂ at ambient conditions; band structures of monolayer MoSe₂ at representative pressures; comparison of Raman in two PTMs; comparison of Raman on diamond and SiO₂/Si substrates (PDF)

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Notes

The authors declare no competing financial interest.

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