Coupling-Assisted Renormalization of Excitons and Vibrations in Compressed MoSe$_2$–WSe$_2$ Heterostructure

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Supporting Information

ABSTRACT: Vertical heterostructures (HSs) constructed with two-dimensional (2D) materials is expected to generate fascinating properties due to interlayer coupling between neighboring layers. However, interlayer coupling can be easily obscured by cross-contamination during transfer processes, rendering their experimental demonstration challenging. Here, we explore the coupling-assisted renormalization of excitons and vibrations in a mechanically fabricated MoSe$_2$–WSe$_2$ HS through high-pressure photoluminescence, Raman spectra, and density functional theory calculations. Accompanied by the interlayer coupling enhancement, the excitonic and vibrational renormalizations involving dimensionality and composition variations were achieved. A cycle of 2D–3D–2D excitonic evolution was disclosed and pressure-induced emergence of $X^-$ exciton of MoSe$_2$ in HS was found reflecting the band structure transition in the MoSe$_2$–WSe$_2$ HS. The Raman spectra reveals that the coupled A$_2^+$ vibrations of WSe$_2$ and MoSe$_2$ in HS got coherent upon pressure modulation. This coupling-assisted renormalization in MoSe$_2$–WSe$_2$ HS can be extended to other 2D layered HSs, which indicates the possibility to design a flexible HS with controlled excitonic and vibrational system for light-emitting diodes, excitonic, and photovoltaic devices.

INTRODUCTION

Transition metal dichalcogenides (TMDs) 2H-MX$_2$ (M = Mo, W, etc., X = S, Se, and Te) have received considerable interests in recent years due to their excellent optical and electronic properties. In natural bulk 2H-MX$_2$, many alternating sandwiched X–M–X layers are loosely coupled to each other by van der Waals (vdW) forces. Due to the effect of the interlayer coupling, optical properties of TMDs can be tuned largely by varying the atomic thickness. A strong photoluminescence (PL) can be obtained by thinning down bulks to monolayers due to the consequent indirect to direct band gap transition process in TMDs, which gives rise to many potential applications in optoelectronics. Because the large binding energy exists in these two-dimensional (2D) semiconductors, exciton dominates the optical response, exhibiting strong light–matter interactions that are electrically and strain tuned. The discovery of excitonic valley physics and pseudospin physics in 2H-TMDs expands device concepts nonexistent in other material systems.

Interestingly, utilizing van der Waals interlayer coupling offers the possibility to form vertical TMDs heterostructures (HSs) by stacking different TMD monolayers together. One highly coveted is that of differing monolayer MoSe$_2$ and WSe$_2$ with type II band alignment. The MoSe$_2$ and WSe$_2$ share the approximately same crystalline structure; however, their physical properties such as spin–orbit coupling strength, band gap, and exciton resonance vary significantly. Particularly, their distinct well-separated excitonic features are available to explore excitonic physics and functionalities of vertically stacked monolayer TMDs HSs. The energy band structure of MoSe$_2$–WSe$_2$ HS is renormalized by the interlayer coupling effect, which can lead to a crossover from a 2D excitonic system in the monolayer to a three-dimensional (3D) excitonic system in the HSs. The 3D excitonic system possesses concomitant 2D excitonic physics and functionalities of vertically stacked monolayer and 3D interlayer exciton that is bound hole and electron localized in individual monolayers. Controlling of the interlayer coupling signifies the ability of effectively modulating the quantity, energy, and even dimensionality of the exciton in HSs; it is significant to give insight into the low-dimensional physics, and discover new phenomena with rich functionalities and novel physical effects.

In addition to the excitonic explorations on HS, seeking electronic band structure renormalization, the vibrational explorations are necessary to demonstrate their lattice structure renormalization, elaborating on the structural stability, and...
dimensional crossover. As is reported, the $B_{2g}^{1}$ mode that arises from out-of-plane (breathing) vibration has been observed in few-layer TMDs. The $B_{2g}^{1}$ mode involves interlayer interaction from restoring force existed in several component layers, and can be regarded as an important criterion for distinguishing monolayer from multilayers. The way of stacking in HS causes its symmetry to change to the one similar to homostructural stacking. Indeed, exploring the existence of such vibrational modes and their dependence on the interlayer coupling intensity in an atomic clean HS is attractive and concerned for probing dimensionality effects of 2D materials. As we know, an effective way for tuning the interlayer coupling intensity is to alter the interlayer distance of HS by applying uniaxial, biaxial, or hydrostatic strain. In particular, hydrostatic pressure applied on in-plane and out-of-plane generates diverse compressive strains, it is conducive to revealing unique physical phenomena and realizing an optimized potential of vertically stacked monolayer TMDs HSs in extremes.

In this work, we investigated the coupling-assisted renormalized excitonic and vibrational evolutions in compressed MoSe$_2$–WSe$_2$ HS using a diamond anvil cell (DAC) in conjunction with theoretical calculations. Through vacuum annealing process and application of hydrostatic pressure, interlayer coupling was enhanced across the van der Waals gap between neighboring layers, the excitonic system and vibrational motions were renormalized with variations in dimensionality and compositions. The pressure-induced evolutions of interlayer and intralayer excitons energies and Raman vibrational frequencies obtained here hold the potential for developing optoelectronic devices such as p–n junctions and flexible excitonic circuits.

### RESULTS AND DISCUSSION

Monolayer 1H-MoSe$_2$ and WSe$_2$ films were prepared by mechanical exfoliation of bulk crystals (2D Semiconductor supplies) using a Gel Film (Gel-Pak). Through the optical contrast, Raman spectroscopy, and PL spectroscopy-based appraisal (Figure 1), the monolayer MoSe$_2$ and WSe$_2$ processing strong excitonic effect were confirmed, the $X^0$ and $X^-$ emissions are located at about 1.58 and 1.54 eV for monolayer MoSe$_2$, and about 1.66 and 1.64 eV for monolayer WSe$_2$ at room condition, which are consistent with previous reports (Figure 1d). The fact that monolayer WSe$_2$ owns 5 times higher PL yield than the monolayer MoSe$_2$ indicates a stronger nonradiative recombination in the MoSe$_2$. The flake with a high-quality WSe$_2$ monolayer region was selectively transferred onto the MoSe$_2$ monolayer to form a MoSe$_2$–WSe$_2$ HS sample (Figure 1a), followed by mild vacuum annealing (<0.133 Pa, 120 °C, 6 h) to remove redundant interspace (see Experimental Methods and Figure S1). First principles
calculation shows that MoSe$_2$−WSe$_2$ HS has a type II band alignment, where the highest valence band and the lowest conduction band lie in WSe$_2$ and MoSe$_2$ layers, respectively. The type II band alignment induces the photoexcited electrons and holes relaxing to the conduction band edge of MoSe$_2$ and the valence band edge of WSe$_2$, respectively (Figure 1b). The interlayer exciton is derived from the Coulombic attraction between electrons in the MoSe$_2$ and holes in the WSe$_2$, which is similar to spatially indirect excitons in coupled quantum wells (Figure 1c).

Before vacuum annealing, the as-transferred HS gives two PL peaks located at $\sim$1.66 and 1.58 eV, consistent with the $X^0$ exciton emissions of the individual monolayer MoSe$_2$ and WSe$_2$, respectively. It is in a state of "spotty-coupled", namely an unintentional redundant interspace trapped between the monolayers. This indicates a spatially inhomogeneous HS composed of strongly and weakly coupled regions. Through vacuum annealing, it effectively decreases the redundant interspace trapped between the monolayers, and converts the luminescence spectrum of the HS’s from spotty-coupled profile to a new profile assisted with charge transfer and band renormalization, as shown in Figure 1d. The converted state gets a strong electronic coupling in major regions to become a true heterobilayer with the band structure transformation. Employing a multiple-peak fitting to analyze the measured PL spectra, the overall phenomena were summarized as follows:

1. The PL intensity of WSe$_2$ in the annealed HS is 10 times lower than that of individual WSe$_2$. This pronounced PL...
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The high-pressure experiments are presented in Experimental Methods and Figure S2 in the Supporting Information). The raw data in the panel are fitted with multi-Gaussian functions. The red and blue curves represent individual components $X_0$ exciton emissions of MoSe$_2$ and WSe$_2$ in HS, and the green curves represent an overall fitted spectra. As indicated by blue dashed lines in Figure 2a, the $X_0$ emission of WSe$_2$ first exhibits a blue-shift as the pressure increases and then exhibits a linear red-shift above 2.43 GPa. However, the $X_0$ emission of MoSe$_2$ only shows a nearly linear blue-shift from 0 to 2.43 GPa (red dashed lines). The integrated relative intensity of the $X_0$ peak of MoSe$_2$ decreases gradually with pressure and almost disappeared up to 2.43 GPa. Interestingly, a new emission peak fitted by the orange curve appears at this pressure point, and it is located at the lower-energy side than the $X_0$ emission of individual MoSe$_2$ and WSe$_2$. On the other hand, the interlayer exciton emission (3D exciton) continues to weaken under pressure and vanishes above 2.43 GPa. Inset in Figure 2a shows the images of the 3D exciton emissions at 10 times magnification with pressures ranging from 0 to 2.43 GPa. As guided by black dashed line, the evolution of 3D interlayer exciton emission also experiences a transformation from linear blue-shifts to red-shifts with the increasing pressure. The whole PL of MoSe$_2$—WSe$_2$ HS also attenuates and finally diminishes to the background noise level upon continuous pressurizing (Figure S4). The widths of the excitons peaks are observed to broaden with increasing pressure, which may be partly ascribed to the inhomogeneity of pressure arising from the solidification of the pressure medium.

Before analyzing the behaviors of 2D and 3D excitons in HS, we clarify the high-pressure behaviors of excitons in separate monolayer WSe$_2$ and MoSe$_2$. As shown in Figure 2ef, the emissions of both $X_0$ and $X'$ components in the monolayer WSe$_2$ exhibit a linear blue-shift before 2.43 GPa and turn to red-shift at pressure of 2.43 GPa and above. The energy evolution of $X_0$ versus pressure can be expressed by $E_{\text{g}[X_0(WSe_2)\text{mono}]} = 1.656 + 0.009P$ ($P < 2.43$ GPa) and $E_{\text{g}[X'(WSe_2)\text{mono}]} = 1.687 - 0.001P$ ($P \geq 2.43$ GPa), where $E_g$ represents the exciton energy and $P$ represents the pressure, respectively. Likewise, the energy evolution of $X'$ emission is expressed as $E_{\text{g}[X'(WSe_2)\text{mono}]} = 1.642 + 0.008P$ ($P < 2.43$ GPa) and $E_{\text{g}[X'(WSe_2)\text{mono}]} = 1.667 - 0.003P$ ($P \geq 2.43$ GPa). The turning point at 2.43 GPa reflects a pressure-induced conduction band $K$—$\Lambda$ crossing of monolayer WSe$_2$, i.e., the $X_0$ and $X'$ excitons lie in direct $K$—$K$ interband transition below 2.43 GPa, and then switch to indirect $K$—$\Lambda$ interband transition above 2.43 GPa, which has been convinced by both experiments and theoretical simulations.19,40 For monolayer MoSe$_2$, pressure-induced conduction band $K$—$\Lambda$ crossover leading to its direct band gap to indirect band gap transition occurs at 3.7 GPa.40 Its $X_0$ emissions show a blue-shift with pressure and a novel $X'$ split peak emerges above 3.7 GPa, as shown in Figure 2c,d. These two energy evolutions can be expressed by $E_{\text{g}[X_0(MoSe_2)\text{mono}]} = 1.589 + 0.007P - 5.867 \times 10^{-3}P^2$ and $E_{\text{g}[X'(MoSe_2)\text{mono}]} = 1.618 + 7.365 \times 10^{-3}P$, respectively. The energy evolution of $X_0$ emission is described as $E_{\text{g}[X_0(MoSe_2)\text{mono}]} = 1.538 + 0.005P$. The original $X_0$ emission exists in the whole pressure ranges and the $X'$ emission is ascribed to $K$—$K$ transitions, whereas the novel $X'$ split emission is derived from the $K$—$\Lambda$ interband transition.

Now, we turn back to the evolutions of the 3D interlayer and 2D intralayer excitons in MoSe$_2$—WSe$_2$ HS under compression.
According to Figure 2b, the X° emission of WSe₂ in HS exhibits a sectionalized linear shift versus pressure with the equation

\[ E_g[X°(WSe₂)HS] = 1.581 + 0.015P \quad (P < 2.43 \text{ GPa}) \]

and

\[ E_g[X°(WSe₂)HS] = 1.686 - 0.003P \quad (P \geq 2.43 \text{ GPa}) \]

This equation confirms an almost same pressure assignment of state with that of the monolayer WSe₂, indicating that the vDW force in HS has a faint influence on the 2D exciton in the contributing WSe₂ layer. For the X° emission of MoSe₂ in HS, the energy shows a blue-shift expressed by

\[ E_g[X°(MoSe₂)HS] = 1.529 + 0.015P \quad (P \leq 2.43 \text{ GPa}) \]

and

\[ E_g[X°(MoSe₂)HS] = 1.418 - 0.005P \quad (P > 2.43 \text{ GPa}) \]

due to trion dissociation energy. Notably, a new emission peak appeared above 2.43 GPa, which is assigned to the X0 emission under compression suggested a dimensional transformation from 3D to 2D excitonic system. Besides, the asymmetric character of the X+ exciton emission in HS is due to trion dissociation energy. Thus, the enhanced interlayer coupling in hydrostatic pressure conditions opens a door for trion dissociation energy. Thus, the enhanced interlayer relaxation is enhanced and causes a charging effect leading to the emergence of X° emissions. A second-order polynomial fit of

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interlayer exciton evolution. The turning points for $X_0^*$ exciton emissions of WSe$_2$ and MoSe$_2$ in the HS here appear a bit earlier compared with the experimental observations, this discrepancy is due to the fact that the experimentally fabricated HS may process a low-symmetry stacking configuration and a mismatched atomic alignment, whereas the AB stacking order used in the simulation has a perfect symmetry, which may not match with the experimental case. However, it reveals the intrinsic mechanism of controllable modulation of excitons and trions, which is helpful for developing flexible excitonic devices and provides a promising platform for exploring new excitonic phenomena.

Apart from the electronic structure transitions of HS under pressure, its lattice structural variation can be judged by high-pressure Raman spectra. As shown in Figure 4, there are two obvious Raman peaks for annealed HS located at 352.8 and 308.8 cm$^{-1}$. A comparison of the Bernal-stacked bilayer MoSe$_2$ and WSe$_2$ samples (Figure 4c–f) showed that they are close to the $B_{2g}^1$ modes of the bilayer MoSe$_2$ and WSe$_2$ emerging at $\sim 353.3$ and 309 cm$^{-1}$. The $B_{2g}^1$ mode is regarded as a characteristic feature to distinguish monolayer from other few layers because its equivalent mode in monolayers MoSe$_2$ and WSe$_2$ are Raman inactive and denoted as the $A_{2g}^\prime$ mode. On these basis, the 352.8 and 308.8 cm$^{-1}$ vibrations in HS were assigned to the $A_{2g}^\prime$ modes of MoSe$_2$ and WSe$_2$ in the vdW HS.

Figure 4. Raman spectra (a) and schematics (b) for $A_{2g}^\prime$ modes in MoSe$_2$–WSe$_2$ heterobilayer; (c) and (d) for $B_{2g}^1$ mode in Bernal-stacked bilayer MoSe$_2$; (e) and (f) for $B_{2g}^1$ mode in Bernal-stacked bilayer WSe$_2$. (g) Raman spectra of $A_{2g}^\prime$ vibrational modes of MoSe$_2$ and WSe$_2$ in HS versus pressure. The dashed lines are guides to the eye. (h) Pressure dependence of Raman frequencies for $A_{2g}^\prime$ modes during compression, color-coded by blue ($A_{2g}^\prime$ mode of WSe$_2$ in the HS) and red ($A_{2g}^\prime$ mode of MoSe$_2$ in the HS).

Figure 5. (a) Raman spectra of MoSe$_2$–WSe$_2$ HS versus pressure. The dashed lines are guides to the eye. (b) Raman frequencies of the $E_1'$ and $A_1'$ vibration modes at a series of pressures, color-coded by blue (WSe$_2$ in the HS), red (MoSe$_2$ in the HS), and black (both in the monolayers).
and these $A_2^\prime$ modes of the annealed HS are activated by a finite restoring force existing between the two-component layers. Thus, from the renormalized vibrational spectra, we believe the spotty-coupled HS turns into a true 3D heterobilayer system in annealed HS.

As pressure can effectively reduce the interlayer distance and strengthen the interlayer coupling and restoring force, the $A_2^\prime$ modes give a blue-shift during compression, accompanied by peak broadening. The shifting corresponding to the MoSe$_2$ and WSe$_2$ in HS are 1.86 and 1.64 cm$^{-1}$ respectively, and results in 42.7 cm$^{-1}$ shifts from 0 to 26.82 GPa for MoSe$_2$ and 17.8 cm$^{-1}$ shifts from 0 to 9.47 GPa for WSe$_2$. Therefore, the $A_2^\prime$ modes of MoSe$_2$ and WSe$_2$ in HS observed in our research can be used as a sensitive probe to investigate the interlayer interactions existing in van der Waals materials.

For other normal vibrations, namely the out-of-plane $A_1^\prime$ and in-plane $E'$ vibrational modes of HS, a blue-shift is observed upon compression. For single-monolayer WSe$_2$, the pressurization can stiffen its Raman response and causes $A_1^\prime$ and $E'$ vibrations to go apart; obviously, finally the $A_1^\prime$ mode vibrational frequency is about 10 cm$^{-1}$ higher than the $E'$ mode frequency at 15 GPa. For monolayer MoSe$_2$ on the other hand, its $A_1^\prime$ mode vibrational frequency is about 30 cm$^{-1}$ lower than that of the $E'$ mode vibrational frequency at 15 GPa. Moreover, though the $A_1^\prime$ mode of MoSe$_2$ vibration is slower than that of WSe$_2$ at ambient pressure, a higher pressure coefficient of MoSe$_2$ makes these two $A_2^\prime$ modes cross together up to 15 GPa. For annealed HS, it is noticed that the stiffer $A_1^\prime$ mode of WSe$_2$ [$A_1^\prime$(WSe$_2$)$_{HS}$] is shifted up and the softer $A_1^\prime$ mode of MoSe$_2$ [$A_1^\prime$(MoSe$_2$)$_{HS}$] is pushed down, which shows quite different pressure-evolved paths compared with individual monolayers. However, the $E'$ modes of annealed HS are almost the same with those of the individual monolayers, exhibiting a linear pressure dependence. All of the vibrational modes can be easily distinguished from each other (Figure S5), and the details on identification and peak fitting of these Raman peaks are provided in Figure S6.

In the absence of external pressure, the $A_1^\prime$ modes of the two layers in HS vibrate separately and are same with that of monolayer MoSe$_2$ and WSe$_2$, though the two layers have coupled together after annealing. However, the annealing-induced coupling is weak to an extent. The interlayer coupling is strengthened when an external pressure is introduced. Then, the $A_1^\prime$ vibrations of the two layers in HS will switch to two coherent vibration modes where the Se atoms in both WSe$_2$ and MoSe$_2$ layers move in concert, with one vibrating in phase and the other vibrating $180^\circ$ out of phase (shown Figure S8). The stiffened $A_1^\prime$(WSe$_2$)$_{HS}$ mode compared to that of individual WSe$_2$ monolayer $A_1^\prime$(WSe$_2$)$_{monolayer}$ originates from the Se atoms vibrating along the opposite direction in the coherent in-phase modes, whereas the softened $A_1^\prime$(MoSe$_2$)$_{HS}$ mode comes from the Se vibrations in consistent direction in the coherent out-of-phase modes.

As the pressure increases, the distance reduces further between the two layers and interlayer coupling is enhanced. The renormalization of these two coherent $A_1^\prime$ HS vibrational modes becomes prominent. On the contrary, the in-plane $E'$ modes of the two layers are not coupled with each other even at high pressures, indicating that the intraplane W–Se or Mo–Se covalent bonds are less influenced. These results prove that the three-dimensional vibrational $A_2^\prime$ modes in HS, as well as the degree of $A_2^\prime$ mode stiffening or softening offer a possible way to evaluate the interlayer coupling interactions in the HS’s system.

In conclusion, we fabricated a MoSe$_2$–WSe$_2$ HS through mechanical exfoliation and vacuum annealing treatment, and high-pressure PL and Raman spectra of the annealed HS were measured in diamond anvil cell. The interlayer coupling was enforced externally with vacuum annealing, leading to a crossover in the electronic structure and lattice vibration from a spotty-coupled status to a true coupled heterobilayer status. The 3D interlayer exciton is observed in the PL spectrum, and coupled $A_2^\prime$ vibrations of WSe$_2$ and MoSe$_2$ are detected in Raman spectrum. Hydrostatic pressure enforced the interlayer coupling further; evidently, a pressure-induced K–A crossing process was found and the 3D interlayer exciton experienced a turn from blue-shift to red-shift upon compression and finally diminished to the background noise at about 2.43 GPa, only leaving 2D intralayer excitons of WSe$_2$ and MoSe$_2$. This coupling-assisted renormalization of electronic system disclosed a cycle of 2D–3D–2D excitonic evolution. The pressure-induced lattice vibrational renormalization represents as linear stiffness of $A_2^\prime$ mode of WSe$_2$ and MoSe$_2$ in HS, and coherency of out-of-plane $A_1^\prime$ vibrations of WSe$_2$ and MoSe$_2$ in HS. As the pressure can decrease the interlayer distance more effectively than thermal treatment, the interlayer coupling effect is modulated to a great extent. It provides an excellent strategy for exploring the coupling-assisted renormalization of excitonic and vibrational system in TMD van der Waals HS. Overall, our work offers the fundamental understanding of coupling-assisted renormalization and gives a convenient way to probe the interlayer coupling intensity, which provides access to design future optoelectronic devices performance.

**EXPERIMENTAL METHODS**

**Sample Preparation and Characterizations.** MoSe$_2$ and WSe$_2$ flakes first were mechanically exfoliated from the bulk crystals onto clear and flexible poly(dimethylsiloxane) (Ge Film) substrates using adhesive tapes to achieve the monolayer samples. Optical contrasts through an optical microscope, photoluminescence (PL), and Raman measurements (Figure 1d,e) indicated the good quality of exfoliated monolayer crystals. Afterward, a monolayer MoSe$_2$ was transferred onto a diamond anvil surface in the sample chamber via a micromanipulator. Then, a WSe$_2$ monolayer flake was precisely transferred onto the MoSe$_2$ flake (Figure S1). The heterostructure flake is finally thermally annealed at 120 °C for 6 h under a vacuum environment below a base pressure of about 0.133 Pa.

A series of high-pressure experiments were performed using a symmetric diamond anvil cells (DAC) with a pair of 300 μm culet anvils. A T301 stainless steel gasket was preindented to reduce its thickness from 250 to 50 μm and subsequently drilled in the center to form a hole of 160 μm diameter. Measurement of the pressure of the sample chamber in DAC was achieved by collecting ruby fluorescence spectra from ruby spheres loaded in the chamber. Inert argon as pressure transmission medium (PTM) was compressively loaded in the sample chamber to offer a continuous hydrostatic pressure applied on the samples.

Raman and PL measurements were carried out using a micro-Raman spectrometer (Horiba-HR-Evolution) equipped with a solid-state green laser ($\lambda = 532$ nm) in a back-scattering configuration. The PL signal was dispersed by a 600 g mm$^{-1}$ grating and the Raman signal was dispersed by an 1800 g mm$^{-1}$ grating. The laser power applied on the surface of the sample

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was set to be no more than 0.5 mW to avoid the probable damage from heating or oxidizing under exposure. The Gaussian spot diameter used in the fluorescence measurement system is about 1 μm.

**Theoretical Calculations.** The calculations of the energy band of MoSe₂−WSe₂ heterostructure (HS) at different pressures are performed using the QUANTUM ESPRESSO code, within the density functional theory (DFT). Perdew−Burke−Ernzerhof of generalized gradient approximation functional with the exchange−correlation functional was used as the type of pseudopotential during the whole computational procedure. The AB stacking order is adopted for our model systems. The norm-conserving ultrasoft with energy (charge density) cutoff up to 60 Ry (600 Ry) is employed in this work. The first Brillouin zone is sampled with a 20 × 20 × 1 Monkhorst−Pack grid. The vacuum region thickness is greater than 25 Å. The structures are relaxed when the forces exerted on the atoms are less than 1 × 10⁻² eV Å⁻¹. To obtain a good accuracy of calculated results, the self-consistent field was set to be < 1 × 10⁻⁵ eV Å⁻¹. The hydrostatic pressure applied on HS was modeled by calculating the ease of compression along the x-, y-, and z-direction. The force constants were calculated with a unit cell. Despite the fact that the unit cell could not exactly simulate the large supercell of the periodic structure in an experimentally fabricated HS and the AB stacking order used in the simulation has a perfect symmetry that may not match with the experimental case, the calculation still convincingly reveals the intrinsic mechanism of controllable modulation of energy band observed in the experiment.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b01453.

Schematic of the MoSe₂−WSe₂ heterobilayers preparation on a diamond substrate; schematic diagram of the DAC; PL intensity of HS and monolayers; band structures of HS at different pressures; Lorentzian fittings for normalized Raman spectra of HS at different pressures; selected experimental Raman spectra of monolayer WSe₂ and MoSe₂ at different pressures; the schematics of the coherent in-phase and out-of-phase modes (PDF)

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**Notes**

The authors declare no competing financial interest.

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