1. Introduction

Molybdenum disulfide (MoS₂) is the most commonly studied two-dimensional (2D) transition metal dichalcogenide (TMD). Monolayer MoS₂ exhibits a S–Mo–S trigonal prismatic (1H) structure with a lack of inversion symmetry (figure 1). The non-centrosymmetric crystalline structure, combined with 2D quantum confinement and strong spin–orbit coupling, produce many remarkable properties in monolayer MoS₂, including the direct band gap [1, 2], spin-valley coupling [3], optical harmonic generation [4, 5], magnetoelectricity [6], and piezoelectricity [7]. Beyond monolayer, MoS₂ commonly exhibits the hexagonal 2H stacking order, in which the adjacent layers are rotated by 180° and stack directly upon one another (figure 1). For even numbers of layers, 2H MoS₂ restores the inversion symmetry and hence loses many interesting valleytronic, piezoelectric and nonlinear optical properties [4, 5, 7–9]. This greatly limits the applications of MoS₂. Fortunately, MoS₂ hosts another stable polytype with the rhombohedral 3R stacking order, in which the adjacent layers displace slightly without any rotation [10, 11] (figure 1). This distinct polytype can break the inversion symmetry, and hence retain excellent valleytronic, piezoelectric and nonlinear optical properties, for all layer numbers [10–14]. In addition, 3R MoS₂ shows superior catalytic properties to 2H MoS₂ [15] and can possibly host distinctive excitonic states [16]. These recent developments have stimulated much scientific interest in 3R MoS₂.

Although 3R MoS₂ atomic crystals exhibit attractive properties, there is a lack of efficient and reliable methods to characterize their layer number and stacking order. Conventional methods such as transmission electron microscopy, x-ray diffraction, and scanning probe measurements cannot determine both the layer...
number and stacking order accurately for multi-layer crystals; they are also difficult to apply to microscale samples. In this respect, Raman spectroscopy of interlayer phonons can provide rapid and nondestructive identification of the layer number and stacking sequence. 2D materials generally exhibit two types of interlayer phonon modes, namely the shear (S) and breathing (B) modes, which arise from interlayer vibrations with tangential and vertical layer displacement, respectively. As they are generated entirely by interlayer coupling, the interlayer phonons are highly sensitive to the layer thickness \[17\], stacking order \[18\], and surface environment \[19\]. Therefore, ultralow-frequency Raman spectroscopy of interlayer phonons has been widely applied to characterize the interlayer coupling and stacking structure in many 2D materials, including graphene \[17–26\], TMDs \[27–61\], boron nitride \[62, 63\], and black phosphorene \[64–68\]. Researchers have just recently studied the interlayer Raman modes in 3R TMD atomic crystals \[56–61\]; however, the results are ambiguous because they used either natural crystals or samples grown by chemical vapor deposition (CVD), both of which contain random mixture of different stacking sequences. To this point, a comprehensive investigation of interlayer phonons in pure 3R MoS\(_2\) atomic crystals is still lacking.

Here, we report a comparative Raman study of interlayer phonon modes in pure 3R and 2H MoS\(_2\) atomic crystals with thickness from 2 to 13 layers. We observe up to four breathing branches and three shear branches in the low-frequency Raman spectra. The interlayer shear modes exhibit distinct layer-number dependence and branch dependence between the 3R and 2H polytypes. While 2H MoS\(_2\) exhibits the strongest Raman signal in the highest-frequency shear branch, 3R MoS\(_2\) exhibits the strongest Raman response in the lowest-frequency shear branch. Such opposite Raman behavior reflects the different crystal structure in the 3R and 2H phases. On the other hand, the breathing modes exhibit similar layer-number and branch dependence for both polytypes, but the 2H breathing modes are consistently higher in frequency (\(~3\ \text{cm}^{-1}\)) than the 3R breathing modes. This result indicates a small but detectable difference in the interlayer coupling strength between the 3R and 2H stacking order. We can explain all major observations by a combined analysis of the linear chain model, group theory, effective bond polarizability model and first-principles calculations.

### 2. Experimental methods

We fabricated 2H and 3R MoS\(_2\) samples with layer number \(N = 1\) to 13 (labeled as 1L–13L) by mechanical exfoliation of bulk crystals onto Si/SiO\(_2\) substrates. We used natural 2H MoS\(_2\) crystals from HQ Graphene Inc, and grew 3R MoS\(_2\) single crystals by the chemical vapor transport (CVT) method \[11\]. In the synthesis of 3R MoS\(_2\) crystals, we used MoCl\(_3\) as the transport agent. The stoichiometric amount of Mo:S:MoCl\(_3\) is 9:20:1 and the total mass is 450 mg. They were sealed in an evacuated 20 cm-long quartz tube under vacuum of \(10^{-6}\) Torr. The tube was placed in a three-zone furnace. The reaction zone was pretreated at 850 °C for 30 h with the grown zone at 900 °C. The reaction zone was then programmed at a higher temperature 1060 °C with the growth zone at a lower temperature 920 °C for six...
days to provide a temperature gradient for the crystal growth. Finally, the furnace was naturally cooled down to room temperature and the 3R MoS$_2$ single crystals were collected in the growth zone. Our crystals show uniform 3R stacking order with almost no mixture of other phases. Such high-quality 3R MoS$_2$ crystals enable us to exfoliate atomically thin layers with pure 3R stacking order.

We measure the Raman spectra of MoS$_2$ samples using a commercial Horiba LabRam HR Raman microscope in the back-scattering geometry at room temperature. The excitation light source is a 532 nm continuous laser. The incident laser power on the samples was below 1 mW, with a spot diameter of $\sim 1 \text{ \mu m}$. We measure both unpolarized and polarized Raman spectra. In the former case, we collect Raman signals of all polarizations. In the latter case, we excite the samples with either horizontally (H) or vertically (V) polarized laser and collect the Raman signals at only the vertical (V) polarization. Correspondingly, we obtain the parallel-polarized (VV) and cross-polarized (HV) Raman spectra. The shear modes in MoS$_2$, being doubly-degenerate, have 2D group representations with finite diagonal and off-diagonal elements in their Raman tensors; they are therefore observed in both the VV and HV geometries. But the breathing modes, being non-degenerate, have 1D group representations with only diagonal elements in the Raman tensors; they only appear in the VV geometry.

3. Experimental results

We first present the unpolarized Raman spectra of 3R and 2H MoS$_2$ bilayers, the simplest pair to compare the two polytypes (figures 2(a) and (c)). Both polytypes exhibit a shear mode and a breathing mode, but their spectra show two different features. First, while the frequencies of their shear modes are nearly the same ($22 \text{ cm}^{-1}$), the 3R breathing mode ($37 \text{ cm}^{-1}$) is lower in frequency than the 2H breathing mode ($40 \text{ cm}^{-1}$). This implies that the 3R layers are less strongly bound than the 2H layers. Second, the intensity ratio between the breathing and shear modes is much higher in 3R MoS$_2$ than in 2H MoS$_2$. The breathing-mode peak intensity is $\sim 70\%$ ($\sim 25\%$) of the shear-mode intensity for the 3R (2H) MoS$_2$ bilayers.

We have calculated the unpolarized Raman spectra of the shear and breathing modes for both 3R and 2H MoS$_2$ bilayers by density functional theory (DFT) (figures 2(b) and (d); see supplementary material (stacks.iop.org/TDM/6/025022/mmedia)). Our calculations reproduce the two spectral features discussed above. First, the separation between the shear and breathing modes is $3 \text{ cm}^{-1}$ smaller in 3R MoS$_2$ than in 2H MoS$_2$; in our simulated spectra. This result matches the observed $3 \text{ cm}^{-1}$ red shift of the 3R breathing mode relative to the 2H breathing mode. Second, the intensity ratio between the calculated breathing and shear modes agrees well with the experimental ratio.
Our experiment and calculation therefore consistently show that 3R and 2H MoS₂ have noticeable difference in the interlayer coupling strength and Raman response. We can use the above two major spectral features to distinguish the two types of MoS₂ bilayers.

Thicker MoS₂ samples display more interlayer Raman modes. Figure 3 displays the logarithmic parallel-polarized (VV) and cross-polarized (HV) Raman spectra for both 3R and 2H MoS₂ with layer numbers \( N = 1–13 \). We have subtracted the broad Raman background to display the weak interlayer modes (see supplementary material for details). We observe up to three branches of shear modes and four branches of breathing modes in thick MoS₂ samples. The 3R and 2H breathing modes have similar thickness dependence. For both polytypes, the strongest breathing Raman peak redshifts as the layer number increases (blue squares in figures 3(a) and (c)). In contrast, the 3R and 2H shear modes show strikingly different spectra as the layer thickness increases. Figures 3(b) and (d) display the shear-mode spectra in the HV geometry, in which all breathing modes are suppressed. For the 2H polytype, the shear Raman peaks blueshift as the layer number increases. But for the 3R polytype, the shear Raman peaks redshift as the layer number increases. Therefore, the 2H and 3R shear Raman modes evolve oppositely with the layer number.

4. Theoretical discussion and analysis

4.1. Linear chain model

We can describe the frequencies of the breathing (shear) modes by a simple linear chain model in which adjacent layers are coupled harmonically with the same force constant [17]. An \( N \)-layer system hosts \( N − 1 \) breathing modes and \( N − 1 \) doubly-degenerate shear modes. Their mode frequencies are:

\[
\omega_{j,b}^{(j)} = \omega_b \cos \left( \frac{j\pi}{2N} \right)
\]

\[
\omega_{j,s}^{(j)} = \omega_s \cos \left( \frac{j\pi}{2N} \right)
\]

Here \( j = 1, 2, \ldots, N − 1 \) is the branch index, counting from the highest-frequency to the lowest-frequency branch; \( \omega_b \) (\( \omega_s \)) is the frequency of the highest breathing (shear) branch in the bulk limit. These two bulk frequencies are the only fitting parameters in the linear chain model.

Figure 4 compares the observed breathing and shear mode frequencies (symbols) with the prediction...
of the linear chain model (lines). The observed breathing modes in 3R and 2H MoS₂ can be fit well with a bulk breathing-mode frequency of $\omega_B = 53.85 \text{ cm}^{-1}$ and $57.40 \text{ cm}^{-1}$, respectively. The strongest breathing Raman mode corresponds to the lowest breathing branch ($j = N - 1$), and other weaker breathing Raman modes correspond to higher branches with $j = N - 3, N - 5, N - 7 \ldots$ (solid blue lines in figure 4). Other breathing branches with $j = N - 2, N - 4, N - 6 \ldots$ are Raman inactive (dashed blue lines in figure 4).

For the shear modes, the observed Raman frequencies in 3R and 2H MoS₂ can be fit well with a bulk frequency $\omega_S = 31.85 \text{ cm}^{-1}$ and $32.85 \text{ cm}^{-1}$, respectively. Both values match closely the measured shear frequency (32.9 cm$^{-1}$) of bulk 2H MoS₂ (the top spectrum in figures 3(c) and (d)). The linear chain model shows that the observed shear modes in 2H MoS₂ correspond to low-frequency shear branches with $j = 1, 3, 5$ (red open dots and solid lines in figure 4). The branches with $j = 2, 4, 6 \ldots$ are Raman inactive (red dashed lines). In contrast, the observed shear modes in 3R MoS₂ correspond to low-frequency shear branches with $j = N - 1, N - 3, N - 5$ (red solid dots). The branches with $j = N - 2, N - 4, N - 6 \ldots$ are Raman inactive (red dashed lines). The observed 2H and 3R shear modes therefore cover the high and low shear branches, respectively. For MoS₂ with odd layer numbers, the observable 2H and 3R shear modes complement each other. By combining the 2H and 3R data, we can reveal all the shear branches ($j = 1$ to $N - 1$) in MoS₂ with odd layer numbers $N = 3, 5, 7$.

4.2. Interlayer force constants and elastic moduli

Our measured interlayer mode frequencies allow us to calculate the interlayer force constants and elastic moduli of 3R and 2H MoS₂ (table 1). The interlayer force constant ($K$) is related to the bulk interlayer vibration frequency ($\omega$) as $K = (\omega \pi c)^2 \mu$, where $c$ is the speed of light and $\mu = 3.068 \times 10^{-6} \text{ kg m}^{-2}$ is the mass per unit area of MoS₂ monolayer [17, 31]. By using the extracted 3R and 2H bulk shear mode frequencies, we obtain the interlayer shear force constants: $K_x = 2.76 \times 10^{19} \text{ Nm}^{-3}$ for 3R MoS₂ and $K_x = 2.94 \times 10^{19} \text{ Nm}^{-3}$ for 2H MoS₂. The elastic modulus ($C$) is related to the force constant as $C = KT$, where $t$ is the interlayer separation. 2H and 3R MoS₂ have slightly different interlayer distance: 5.

![Figure 4](image_url)

Figure 4. Frequencies of the observed shear modes (S; red) and breathing modes (B; blue) in figure 3 as a function of MoS₂ layer number. The solid (open) symbols are experimental data for 3R (2H) MoS₂. The blue (red) lines are the predicted frequencies of the breathing (shear) modes by the linear chain model, as described in the text. The solid (dashed) lines denote the Raman active (inactive) branches. The 2H breathing modes are consistently higher in frequency than the 3R breathing modes, whereas the shear modes have almost the same frequencies for both polytypes.

| Table 1. Elastic parameters of 2H and 3R MoS₂ calculated from the interlayer phonon frequencies. |
|---|---|---|
| Elastic parameters | 3R MoS₂ | 2H MoS₂ |
| Shear properties | $\omega_S (\text{cm}^{-1})$ | 31.85 | 32.85 |
| | $K_x (10^{19} \text{ Nm}^{-3})$ | 2.76 | 2.94 |
| | $C_{44} (\text{GPa})$ | 16.90 | 18.08 |
| Compressive properties | $\omega_B (\text{cm}^{-1})$ | 53.85 | 57.40 |
| | $K_z (10^{19} \text{ Nm}^{-3})$ | 7.89 | 8.98 |
| | $C_{33} (\text{GPa})$ | 48.32 | 55.19 |

---
t = 6.148 Å for 2H MoS₂ and t = 6.123 Å for 3R MoS₂. Correspondingly, we obtain the shear modulus \( C_{44} = K_{st} = 16.90 \text{ GPa} \) (18.08 GPa) for 3R (2H) MoS₂ and the compressive modulus \( C_{33} = K_{zt} = 48.32 \text{ GPa} \) (55.19 GPa) for 3R (2H) MoS₂ (table 1). Our 2H results agree with prior works [30, 31]. Notably, the 2H compressive modulus is 14% higher than the 3R modulus; this ratio matches roughly the prediction of recent first-principles calculations [69].

4.3. Group-theory analysis

After calculating the elastic parameters, we examine the Raman properties of interlayer phonons. The interlayer phonon modes in 2H MoS₂ have been well studied in the literature [28, 31, 70, 71]. Their Raman activity behavior can be understood from their point group symmetry. 2H MoS₂ with even (odd) layer numbers have the \( D_{3d} \) (\( D_{3h} \)) point group. From the representations of the shear (breathing) modes, we can easily deduce that they are Raman active in every other branch, counting from the highest (lowest) branch, while being Raman inactive in other branches (see the supplementary material for a summary of group-theory analysis for 2H MoS₂). However, the point-group analysis is not applicable in the 3R structure, which has lower symmetry than the 2H structure. 3R MoS₂ has the \( C_{3v} \) point group for all the layer numbers, with no inversion nor mirror symmetry. All breathing modes have the \( A_{1} \) representation and all shear modes have the \( E \) representation. They are all Raman active in the group-theory analysis. Therefore, a simple point-group symmetry analysis cannot explain the observed alternating appearance of the interlayer branches in the 3R Raman spectra.

Figure 5. (a) Layer displacement of the two shear modes in 3R and 2H MoS₂ trilayers. By comparing the atomic configuration at opposite normal displacements (\( Q > 0 \) and \( Q < 0 \)) near the equilibrium position (\( Q = 0 \)), we can deduce whether the differential polarizability (\( \partial \alpha / \partial Q \)) (hence, the Raman tensor) is zero or finite. (b) and (c) The experimental and simulated cross-polarized Raman shear modes for trilayer 2H and 3R MoS₂. In the simulation, the shear-mode frequency is predicted by the linear chain model (highlighted by the yellow bars) and the relative mode intensity is determined by the bond polarizability model. The high and low shear modes appear exclusively in the 2H and 3R trilayer, respectively.
4.4. Qualitative description of Raman activity

To reveal the underlying physics of interlayer Raman modes in the 3R structure, we directly examine the influence of stacking order on the Raman tensor of the phonon modes. For a vibration mode $k$, its Raman intensity ($I_k$) is proportional to [72, 73]:

$$I_k \propto \left( n_k + 1 \right) \frac{\omega_k}{\omega_k} \left| \vec{e}_i \cdot \vec{R}_k \cdot \vec{e}_s \right|^2. \quad (3)$$

Here $\omega_k$ is the phonon frequency; $n_k$ is the phonon occupation according to the Bose–Einstein distribution; $\vec{e}_i$ and $\vec{e}_s$ are the polarization unit vectors of the incident and scattered light, respectively; $\vec{R}_k$ is the Raman tensor. In a classical picture, $\vec{R}_k$ can be expressed as:

$$\vec{R}_k = \frac{\partial \vec{\alpha}}{\partial Q_k} \Delta Q_k. \quad (4)$$

Here $\vec{\alpha}$ is the polarizability tensor; $Q_k$ is the normal coordinate of the vibration normal mode; $\partial \vec{\alpha}/\partial Q_k$ is the derivative of the polarizability tensor at the equilibrium lattice position ($Q_k = 0$).

To determine the Raman activity of a phonon mode, we can directly examine the atomic configuration during the vibration. As an illustration, figure 5(a) shows the interlayer atomic configurations of the two shear modes $S_{13}^3$ and $S_{23}^3$ in 3L MoS$_2$ at positive ($Q > 0$) and negative ($Q < 0$) normal displacement. The 3R and 2H structures have distinct atomic configurations during the vibration. For the 3R $S_{13}^3$ mode, the interlayer atomic configurations are the same for $Q > 0$ and $Q < 0$. The differential polarizability $\partial \vec{\alpha}/\partial Q$ is thus zero; this mode is Raman inactive. But the $S_{23}^3$ mode in the 2H structure has distinct atomic configurations for $Q > 0$ and $Q < 0$. This mode thus has non-zero $\partial \vec{\alpha}/\partial Q$ and is Raman active. In contrast, the lower $S_{13}^2$ mode has opposite stacking dependence. The 3R $S_{13}^2$ mode exhibits different interlayer atomic configurations for $Q > 0$ and $Q < 0$, leading to finite $\partial \vec{\alpha}/\partial Q$ and Raman response. However, the 2H $S_{13}^2$ mode has the same atomic configurations for $Q > 0$ and $Q < 0$, leading to zero $\partial \vec{\alpha}/\partial Q$ and no Raman response. This simple analysis illustrates why the high and low shear branches appear exclusively in the Raman spectra from 3L MoS$_2$ of 2H and 3R phases, respectively (figure 5(b)). The above pictorial analysis can be applied to explain the Raman activity of shear and breathing modes in 2H and 3R structures with any number of layers (e.g. see the analysis of 5L MoS$_2$ in the Supplementary Material). Similar stacking-dependent shear modes are also observed in few-layer graphene with ABA and ABC stacking order [18, 26].

4.5. Quantitative bond polarizability model

Our qualitative analysis above can be quantified in an effective bond polarizability model [72, 73], which predicts the relative Raman intensity of different shear modes. This model considers the distortion of interlayer bonds by the interlayer vibration. The Raman tensor $\vec{R}$ is the sum of contributions from each interlayer bond. The diagonal element $R_{xx}$ is responsible for parallel-polarized Raman response; the off-diagonal element $R_{xy}$ is responsible for cross-polarized Raman response. For a shear mode $k$ with $x$-direction layer displacement in an $N$-layer structure, the tensor element $R_{\mu\nu}$ ($\mu, \nu = x, y, z$) may be expressed as:

![Figure 6. Schematic representation of interlayer bonds for (a) 3R and (b) 2H MoS$_2$. The interlayer bonds have the same lateral orientation for 3R stacking, but alternate lateral orientation for 2H stacking, resulting in their distinct shear-mode Raman response. The blue/red dashed lines highlight the interactions between adjacent layers.](image-url)
Here \( l \) denotes the layer index; \( x_l \) is the lateral displacement of layer \( l \) from the equilibrium position; \( \alpha_l \) is the \( \mu \nu \)-element of the polarizability tensor of the interlayer bond between layers \( l \) and \( l+1 \). \( \alpha'_l = \frac{\partial \alpha_l}{\partial x_l} \) is the derivative of \( \alpha_l \) with respect to \( x_l \).

For a shear mode \( S_j \) with branch index \( j \) in an \( N \)-layer structure, the displacement of layer \( l \) is:

\[
x_l \propto \cos \left( \frac{(N-j)(2l-1)}{2N} \pi \right).
\]

(6)

The 3R and 2H structure have the same layer displacement pattern in vibration, but different configurations of interlayer bonds. In 3R MoS\(_2\), all the layers have the same orientation and identical interlayer bonds, and hence the same \( \alpha'_l \) (figure 6(a)). We may thus remove the \( l \) index and name it as \( \alpha'_R \). By equation (5), the 3R Raman tensor element is:

\[
R_{\mu\nu}(k) = \sum_{l=1}^{N-1} \alpha'_R (x_l - x_{l+1}). \tag{5}
\]

It depends only on the displacement of the top and bottom layers.

In contrast, the adjacent layers in 2H MoS\(_2\) have opposite orientation. The interlayer bonds thus exhibit alternate lateral orientation for successive layer pairs, leading to opposite signs of \( \alpha'_l \) (figure 6(b)). By setting \( \alpha'_{l=1} = \alpha'_H \), the other \( \alpha'_l \) would be \((-1)^{l+1} \alpha'_H \). By equation (5), the 2H Raman tensor element is:

\[
R_{\mu\nu}(k) = \sum_{l=1}^{N-1} (-1)^{l+1} \alpha'_H (x_l - x_{l+1}) \nonumber \\
= \alpha'_H [(x_1 - x_2) + (x_2 - x_3) + \ldots + (x_{N-1} - x_N)]. \tag{7}
\]

(8)

We can combine equation (3), (6)–(8) to obtain the Raman intensity. After some algebraic derivation (see supplementary material), the Raman intensities of the 3R and 2H shear modes \( S_j \) show the following analytic forms:

\[
R_{\mu\nu}(k) = \sum_{l=1}^{N-1} \alpha'_R (x_l - x_{l+1}) \nonumber \\
= \alpha'_R [(x_1 - x_2) + (x_2 - x_3) + \ldots + (x_{N-1} - x_N)]. \tag{5}
\]

(7)

It depends only on the displacement of the top and bottom layers.
In equation (9), the factor \(1 - (-1)^{N-j}\) is zero when \(N - j\) is an even number; the 3R shear mode is non-zero only when the branch index \(j = N - 1, N - 3, N - 5, \ldots\). In equation (10), the factor \(1 - (-1)^j\) is zero when \(j\) is an even number; the 2H shear mode is non-zero only when \(j = 1, 3, 5, \ldots\). Such stacking-dependent Raman activity exactly matches our experimental results (figures 3 and 4).

In addition to accounting for the Raman activity, the above analytical theory enables us to quantitatively simulate the Raman spectra of shear modes for each layer number and stacking order. In the simulation, we use the linear chain model (equations (1) and (2)) to determine the mode frequencies and the bond polarizability model (equations (9) and (10)) to determine the Raman intensity ratio of different branches. The calculation gives the same results for parallel and cross polarizations. For comparison with experiment, we plot the theoretical Raman modes as Gaussian functions with the same width as the experimental peaks. Figures 5 and 7 compare our simulations with experiment for 3L, 5L and 9L MoS\(_2\), which exhibit one, two and three shear modes, respectively, for both the 3R and 2H phases in our observed Raman spectra. Our calculated spectra show reasonably accurate intensity ratio between different shear branches (see supplementary material for simulations for other layer numbers).

Our model can be readily extended to explain the breathing modes by redefining \(\alpha_l' = \partial \alpha_l / \partial z_l\), where \(z_l\) is the vertical displacement of layer \(l\). In this case, \(\alpha_l'\) does not depend on the lateral orientation of the interlayer bonds, so \(\alpha_l'\) is the same for all layer indices \(l\) in either stacking order. As a result, for both 2H and 3R breathing modes, their Raman tensor and intensity follow the same forms as those of 3R shear modes in equations (7) and (9). For instance, figure 8 displays our calculated breathing-mode Raman spectrum for 10L MoS\(_2\) (the same for 2H and 3R phases), in comparison with the measured parallel-polarized (VV) spectrum of 10L 3R MoS\(_2\). Our calculation quantitatively reproduces the experimental spectrum, which exhibits four breathing modes \((B_{10}^9, B_{10}^7, B_{10}^5, B_{10}^3)\) from low to high frequency and strong to weak intensity.

5. Conclusion

We have carried out a comprehensive experimental and theoretical investigation of the interlayer Raman modes in 3R and 2H MoS\(_2\) atomic layers. The 3R and 2H polytypes exhibit similar breathing-mode spectra but distinct shear-mode spectra. Prior research has measured the interlayer Raman modes in various 2D materials with different stacking order, such as few-layer graphene with ABA and ABC stacking order [18, 26, 74], TMDs with 2H structure [27–31], TiSe\(_2\) with 3R stacking order [51], etc. Nonetheless, due to the difficulties in sample preparation and Raman experiment, no prior work could systematically
measure both the shear and breathing modes in the same material at two distinct stacking orders and all layer numbers. Our comparative analysis of 3R and 2H MoS$_2$ of layer number $N = 1–13$ thus represents a key Raman study to address the role of stacking order and layer number in 2D materials. In addition, our results serve to facilitate the research of 3R TMD materials, whose general lack of inversion symmetry may enable many novel valleytronic, piezoelectric, and nonlinear optical applications.

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Competing interests

The authors declare no competing interests.

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