Interlayer Breathing and Shear Modes in Few-Trilayer MoS₂ and WSe₂

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Supporting Information

ABSTRACT: Two-dimensional (2D) layered transition metal dichalcogenides (TMDs) have recently attracted tremendous interest as potential valleytronic and nanoelectronic materials, in addition to being well-known as excellent lubricants in the bulk. The interlayer van der Waals (vdW) coupling and low-frequency phonon modes and how they evolve with the number of layers are important for both the mechanical and the electrical properties of 2D TMDs. Here we uncover the ultralow frequency interlayer breathing and shear modes in few-layer MoS₂ and WSe₂, prototypical layered TMDs, using both Raman spectroscopy and first principles calculations. Remarkably, the frequencies of these modes can be perfectly described using a simple linear chain model with only nearest-neighbor interactions. We show that the derived in-plane (shear) and out-of-plane (breathing) force constants from experiment remain the same from two-layer 2D crystals to the bulk materials, suggesting that the nanoscale interlayer frictional characteristics of these excellent lubricants should be independent of the number of layers.

KEYWORDS: Transition metal dichalcogenides, shear modes, breathing modes, Raman spectroscopy, first principle calculations, linear chain model

Bulk transition metal dichalcogenides (TMDs) represent a family of about 40 layered compounds, with wide-ranging electronic properties and excellent mechanical properties as lubricants due to their weak interlayer interactions.¹ Few-layer 2D TMD crystals, motivated by the experimental isolation² and recent scaled-up synthesis,³–⁵ have been shown to have unique electronic and optical properties. For instance, the bandgap of 2D MoS₂ crystals exhibits an indirect-to-direct transition from a few-layer to monolayer sample,⁶ while monolayer MoS₂ and several related TMDs have been proposed as possible valleytronics materials⁷–¹¹ and were demonstrated as field-effect transistors.¹²,¹³ Recent calculations predict that the carrier mobility in a MoS₂ monolayer is limited by optical phonon scattering due to deformation potential and Fröhlich interactions.¹⁴ Similarly, we expect low-frequency interlayer phonons to especially affect the low bias electron transport behavior via electron–phonon coupling interactions. The possible application of 2D TMDs as components in nanoscale electromechanical systems implies that a systematic understanding of their mechanical properties is required. Recently, frictional characteristics of 2D TMDs, as measured using atomic force microscopy (AFM), were found to be highly dependent on the number of layers.¹⁵ However, the AFM measured friction between the tip and the entire 2D crystal, involving a negligible interlayer sliding.¹⁵ The interlayer interactions are dominated by weak van der Waals interactions that are inherently nonlocal. It is thus an open and important question to understand how the interlayer interactions evolve from 3D bulk to 2D TMDs, thus elucidating the interlayer sliding contributions in friction. Therefore, probing low frequency interlayer phonon modes and interlayer force
constants in 2D TMD crystals and their evolution as a function of the number of layers have become increasingly important.

Raman spectroscopy has been very successful in studying phonons and their couplings to electrons in 2D crystals like graphene in the few-layer regime. The probing of the interlayer phonons through Raman spectroscopy is challenging, since these phonon modes are usually of very low frequencies (several to tens of wavenumbers) and are difficult to distinguish from the Rayleigh background scattering. The low-frequency characteristic of the interlayer phonon modes results from the weak interlayer vdW restoring force. By using a triple-grating micro Raman spectrometer and effective filters (see Methods), we can detect frequencies as low as ~5 cm⁻¹, providing a unique capability of probing low energy phonon modes. In this work, we uncover, using a combination of Raman spectroscopy and first principles calculations, the existence of two shear modes and two breathing modes in the ultralow frequency (~55 cm⁻¹) region for few-layer MoS₂ and WSe₂. Similar interlayer shear modes have been identified by Raman spectra in a series of bulk layered materials such as graphite, h-BN, NbSe₂, GaSe, MoS₂, and WSe₂ and recently in both few-layer graphene and MoS₂ crystals. The “organ pipe” or “breathing” modes as reported here cannot be optically probed in bulk layered materials because of their optical inactivity, but they might become IR or Raman active as theoretically predicted by Michel and Verberck in multilayer graphene and BN.

Although a few experimental works on few-layer graphene have reported the overtones of the interlayer breathing modes (ZO, ZA) and other high-frequency phonon modes (LO, oTO) through combination mode Raman scattering, so far, the interlayer breathing modes have not yet been directly probed by any optical techniques in the low-frequency region. Here, we find that the frequencies of the experimentally observed shear modes in few-layer MoS₂ and WSe₂ redshift as the number of layers decreases, while the observed breathing modes evolve with an opposite trend. These frequencies can be perfectly described using a simple linear chain model with only nearest-neighbor interactions, with each constituent of the chain representing one layer. Using this model, we can extract both the in-plane (shear) and out-of-plane (breathing) force constants from experiment. Remarkably, these force constants remain the same from two-layer 2D crystals to the bulk materials, suggesting that the nanoscale interlayer frictional characteristics of these excellent lubricants should be independent of the number of layers.

Layered TMDS, that is, MX₂ (M = transition metal, X = S, Se, Te), are composed of hexagonal close-packed atomic layers. Each layer, henceforth referred to as “trilayer (TL),” consists of three atomic layers, covalently bonded to one another, and the adjacent TLs are coupled via weak vdW interactions. The MX₂ compounds investigated here are of the most common 2H type (atomic layers arranged in /AbA BaB/ stacking, as shown in Figure 2a), which belongs to the non-symmorphic space group D₆h (P63/mmc). The primitive unit cell consists of two TLs (six atoms), resulting in 18 Brillouin zone center (Γ) phonons. The irreducible representations of the phonon modes are shown as F₁b = A₁ + 2A₂ + B₁ + 2B₂ + E₁ + 2E₂ + E₃ + 2E₄, among which 2E₂, E₁, and A₁ are Raman active modes. The 2-fold degenerate E symmetry modes represent in-plane (shear) vibrations, while the A modes vibrate in the out-of-plane (breathing) direction along the z-axis. In the few-TL samples prepared by mechanical exfoliation, we believe the /AbA BaB/stacking order is maintained. The symmetry along

- the z-axis is reduced in few-TL crystals due to the lack of translation in its direction, and therefore the symmetry operations are reduced from 24 in the bulk to 12 in even- and odd-TLs each, with symmetry groups different from that for the bulk 2H materials (D₆h). The symmetry operations in few-TLs are demonstrated in Figure 1, using 1TL and 2TL as examples for odd- and even-TLs, respectively. The 12 symmetry operations in odd-TLs are: E (identity symmetry), 2C₃ (the axis of the clockwise and anticlockwise rotations is denoted as the black line. The horizontal (σ₃) and vertical (σᵥ) reflection operations are shown as the gray and yellow planes, respectively, or “breathing” modes as reported here cannot be optically probed in bulk layered materials because of their optical inactivity, but they might become IR or Raman active as theoretically predicted by Michel and Verberck in multilayer graphene and BN. Although a few experimental works on few-layer graphene have reported the overtones of the interlayer breathing modes (ZO, ZA) and other high-frequency phonon modes (LO, oTO) through combination mode Raman scattering, so far, the interlayer breathing modes have not yet been directly probed by any optical techniques in the low-frequency region. Here, we find that the frequencies of the experimentally observed shear modes in few-layer MoS₂ and WSe₂ redshift as the number of layers decreases, while the observed breathing modes evolve with an opposite trend. These frequencies can be perfectly described using a simple linear chain model with only nearest-neighbor interactions, with each constituent of the chain representing one layer. Using this model, we can extract both the in-plane (shear) and out-of-plane (breathing) force constants from experiment. Remarkably, these force constants remain the same from two-layer 2D crystals to the bulk materials, suggesting that the nanoscale interlayer frictional characteristics of these excellent lubricants should be independent of the number of layers.

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through Raman spectroscopy depends on the symmetry selection rules as well as the scattering geometry. The Raman scattering intensity is proportional to \(|t_0|^2 \bar{R} \cdot e_1|^2\), where \(e_1\) is the polarization vector of the incident light and \(e_0\) is that of the scattered light. \(\bar{R}\) is the Raman tensor. A given phonon mode can be observed by Raman scattering spectroscopy only when \(|t_0|^2 \bar{R} \cdot e_1|^2\) has a nonzero value. Raman tensors of the Raman-active interlayer vibrational modes can be predicted by group theory analysis as follows:

\[
A_1' = \begin{pmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & b
\end{pmatrix}
\]

\[
E_1 = \begin{pmatrix}
c & 0 & 0 \\
0 & -c & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

\[
E_2 = \begin{pmatrix}
c & d & 0 \\
0 & -c & 0 \\
0 & 0 & d
\end{pmatrix}
\]

for MoS\(_2\)/WSe\(_2\) crystals with an odd number of TLs, and

\[
A_{1g} = \begin{pmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & b
\end{pmatrix}
\]

\[
E_{g} = \begin{pmatrix}
c & d & 0 \\
0 & -c & 0 \\
0 & 0 & c
\end{pmatrix}
\]

for even TLs.

The experimental geometrical scatters of our Raman measurements can be represented by the Porto notations \(\bar{e}(xx)z\) and \(\bar{e}(xy)z\), which correspond to parallel and perpendicular polarization configurations, respectively, in our back-scattering geometry. Considering the Raman tensors of all of the Raman active modes, the polarization dependence of the modes can be predicted, as summarized in Table 1: the interlayer breathing modes \(A_1'\) and \(A_{1g}\) can only be observed under the \(\bar{e}(xx)z\) polarization configuration; the interlayer shear modes \(E_1\) and \(E_{g}\) can be observed under both \(\bar{e}(xx)z\) and \(\bar{e}(xy)z\) polarization configurations; while the other interlayer shear mode \(E_2\) cannot be observed under either configuration.

Few-TL MoS\(_2\) and WSe\(_2\) crystals are prepared by mechanical exfoliation\(^2\) with the thickness determined by optical contrast and AFM measurements (see Figure 2b and Supporting Information, Figure S-1). Figure 2c (left) shows typical anti-Stokes and Stokes Raman spectra of 1TL, 2TL, 4TL, and bulk MoS\(_2\) in the low frequency region (\(-55\) to \(55\) cm\(^{-1}\)) taken with the \(\bar{e}(xx)z\) polarization configuration. The spectra for the high frequency \(E_{2g}\) and \(A_{1g}\) modes (Figure 2c, right) exhibit a blueshift and redshift, respectively, from bulk to 1TL (in which these two modes actually have \(E_1\) and \(A_1'\) vibrational symmetries, respectively), in agreement with a previous report.\(^29\) The Raman-active bulk mode \(E_{2g}\) (labeled as S1) corresponds to an interlayer shear mode where the adjacent TLs are vibrating out-of-phase by 180°. The S1 peak evolves to lower frequencies from bulk (\(-32\) cm\(^{-1}\)) to 2TL (\(-22\) cm\(^{-1}\)). Density functional theory (DFT) calculations indicate that the S1 peak corresponds in the NTL system to the highest frequency shear mode. We also observe a broader peak in 2TL and 4TL (labeled as B1), which can be assigned to the lowest frequency interlayer out-of-plane breathing mode by DFT. This assignment is consistent with the disappearance of B1 in the \(\bar{e}(xy)z\) perpendicular polarization configuration (Figure 2d), in accordance with the Raman selection rule, where the Raman scattering intensity of a phonon mode is strictly determined by its Raman tensor and the polarization configuration of the experimental setup. Group theory predicts that, under the \(\bar{e}(xy)z\) configuration, the Raman scattering intensity is zero for all of the breathing modes and nonzero for some shear modes; while under the \(\bar{e}(xx)z\) configuration, both breathing and shear modes could have nonzero Raman scattering intensities. Consequently, the out-of-plane \(A_{1g}\) mode disappears in the
Figure 2. Raman spectra of few-trilayer and bulk MoS2 and WSe2. (a) Crystal structure of 2H-MoS2/WSe2. The primitive unit cell runs over two trilayers (TLs). (b) Optical images of 1 – 4TL MoS2 on 90 nm SiO2/Si substrates. The scale bar is 5 μm. (c–d) Stokes and anti-Stokes Raman spectra of 1TL, 2TL, 4TL, and bulk MoS2 taken under the (c) \( \overline{z(x)z} \) polarized backscattering configuration and (d) \( \overline{z(x)y}z \) polarization configuration. (e–f) Stokes and anti-Stokes Raman spectra of 1TL, 2TL, 4TL, and bulk WSe2 under (e) \( \overline{z(xx)z} \) configuration and (f) \( \overline{z(xy)y} \) configuration. For increased clarity, all of the spectra in the low-frequency region are normalized by the intensity of the S1 peak, and the spectra in the high frequency region are normalized by the intensity of the E2g peak. The experimental scattering geometries of our Raman measurements are represented by the Porto notations28 \( \overline{z(xx)z} \) and \( \overline{z(xy)y} \), where \( \overline{z} \) and \( z \) indicate wave vectors of the incident laser beam and the collected scattered light, respectively. The two alphabets in parentheses represent the polarizations of incident and scattered light, respectively: We note that the high frequency spectra will be discussed in further detail in future manuscripts.

\( \overline{z(xy)z} \) configuration, while the in-plane \( E_{2g} \) and \( \overline{E_{2g}} \) shear modes remain because of their nonzero off-diagonal matrix elements in the Raman tensors.30 It is important to note that both the B1 and S1 peaks are absent for samples with 1TL, which further confirms them as interlayer vibrational modes. Figure 1e, f shows similar Raman spectra for WSe2, with all the Raman peaks red-shifted with respect to those of MoS2, consistent with the larger mass per unit area in WSe2. Moreover, we observed another weak peak, labeled B2, around 35 cm\(^{-1}\) in 4TL WSe2 under the \( \overline{z(xx)z} \) configuration. For increased clarity, all of the spectra in the low-frequency region are normalized by the intensity of the S1 peak, and the spectra in the high frequency region are normalized by the intensity of the E2g peak. The experimental scattering geometries of our Raman measurements are represented by the Porto notations28 \( \overline{z(xx)z} \) and \( \overline{z(xy)y} \), where \( \overline{z} \) and \( z \) indicate wave vectors of the incident laser beam and the collected scattered light, respectively. The two alphabets in parentheses represent the polarizations of incident and scattered light, respectively: We note that the high frequency spectra will be discussed in further detail in future manuscripts.

We next conduct a systematic thickness-dependent Raman study on both materials. For the MoS2 sample, as the thickness decreases from bulk to 2TL, the S1 peak redshifts from \( \sim 32 \) cm\(^{-1}\) to \( \sim 22 \) cm\(^{-1}\), as guided by the red dashed line (Figure 3a, b). In contrast, the second strongest peak B1 blueshifts from \( 9TL \left( \sim 10 \right. \) cm\(^{-1}\)) to 2TL (\( \sim 40 \) cm\(^{-1}\)) and crosses the S1 peak at 3TL. The high frequency modes \( E_{2g} \) and \( A_{1g} \) are also dispensed as a function of TL scaling, with a blueshift of \( \sim 3 \) cm\(^{-1}\) and a redshift of \( \sim 3.5 \) cm\(^{-1}\), respectively, from bulk to 1TL samples. The frequency dispersions of \( E_{2g} \) and \( A_{1g} \) have been proposed to determine the thickness of few-TL MoS2\(_{2}\), which, however, are much less sensitive than using the S1 and B1 frequencies. The B1 peak is not observed in 10TL and above, because of an inadequate signal-to-noise ratio. Two weak peaks, labeled S2 and B2, can also be identified for samples with a thickness larger than 3 TLs, showing similar trends versus thickness with S1 and B1 (shown clearly in the Supporting Information, Figure S-4, spectra before normalization). In WSe2, we observe the same Raman-active modes with similar trends of evolution versus thickness (Figure 3c, d). The pronounced difference is that the B2 peak is much stronger in WSe2 (Figure 3e). In both materials, the B1 and S2 modes are strongly suppressed in the \( \overline{z(xy)z} \) configuration, in agreement with Raman selection rules for breathing modes, as discussed above.

The Raman spectra of these layered systems are computed from density functional perturbation theory as implemented in the Quantum-Espresso,3 within the local density approximation (LDA). Highly accurate convergence thresholds are required (see Methods and Supporting Information). Our calculations indicate, as expected, that all low frequency modes (\( < 55 \) cm\(^{-1}\)) correspond to interlayer vibrations in which each TL moves as a single unit. Furthermore, the low-frequency phonon modes are essentially the same in both MoS2 and WSe2 except that the frequencies are lower for WSe2. Figure 4a shows the two interlayer modes in the bulk material, that is, the Raman active shear mode \( E_{2g}^{2} \) and the optically inactive breathing mode \( B_{2g}^{2} \). For the NTL systems, we obtain N–1 2-fold degenerate interlayer shear modes and N–1 interlayer breathing modes, as expected. We find that the observed S1 and S2 modes are interlayer shear modes with the highest and third highest frequencies for each NTL system, while the B1 and B2 modes are interlayer breathing modes with the lowest and third lowest frequencies. This explains why S1 and B1 are observed in NTLs with \( N \geq 2 \), while S2 and B2 are only observed for \( N \geq 4 \). We note that the breathing modes with the second lowest frequencies are missing because they are Raman-inactive, belonging to the symmetry groups \( A''_{2} \) for odd \( N \) and \( A_{2g} \) for even \( N \) (see Table 1). Shear modes with the second highest frequencies belong to the symmetry groups \( E''_{g} \) for odd \( N \) and \( E_{g} \) for even \( N \) and, thus, cannot be observed in our Raman measurements (see Table 1). Our DFT calculations further predict that there are, in fact, other shear and breathing modes (Figure S6–S7 in the Supporting Information) that have the correct symmetry for observation; however, the calculated
nonresonant Raman intensities, obtained within the Placzek approximation,\textsuperscript{31,32} are essentially zero, consistent with the experimental findings. In all cases, the computed LDA frequency behavior matches very well with the experiment (Figure 5a, b), with discrepancies of ∼4, ∼1.5, and ∼2 cm\(^{-1}\) for the S1, B1, and B2 modes, respectively, for MoS\(_2\) and even better agreement for WSe\(_2\). Since LDA does not treat vdW interactions, we also compute the phonon frequencies using the vdW-DF functional,\textsuperscript{33,34} with Cooper’s exchange interaction term.\textsuperscript{35} Interestingly, we find that, although LDA underestimates the interlayer distance in comparison with the vdW-DF functional, the vdW-DF calculation overestimates the phonon frequencies compared with experiment (see Supporting Information, Table S-2 and Figure S-8). Similar good agreement with experiment was obtained for LDA calculations on the shear mode in multilayer graphene, suggesting that, although vdW-DF gives a more accurate description of the forces, LDA better describes the derivative of the forces with respect to displacements.

In Figure 4b, we schematically display the normal vibrational displacements of the S1 and B1 modes in the NTL crystals (2 ≤ N ≤ 9). In the S1 mode, adjacent TLs are distinctly out-of-phase, while in the B1 mode, the TLs can be divided into two groups, with TLs in each group being approximately in-phase with one another. This picture is consistent with the fact that S1 is the highest frequency shear mode while B1 is the lowest frequency breathing mode, because the frequency of an interlayer phonon mode is larger if the adjacent TLs have more out-of-phase displacement. Furthermore, in the case of S1, a larger N implies more out-of-phase displacement between adjacent layers, leading to higher frequencies. In the case of B1, a larger N implies a greater proportion of approximately in-phase displacement, leading to lower frequencies. Similar arguments can be made for S2 and B2 (Figure 4c). Comparing the S1 mode with the bulk \(E_{2g}^2\) mode, it is clear that the S1 mode evolves to the Raman-active \(E_{2g}^2\) mode in the bulk, although the vibration amplitudes of the surface layers are slightly smaller than for layers in the middle of the few-layer materials. The reason for this difference is that the TLs at the surface have only one nearest neighbor TL, in contrast to TLs in the bulk that have two nearest neighbor layers. The excellent agreement between calculated and measured frequencies suggest that the TLs are weakly coupled to the silicon substrate, which is consistent with measurements obtained for suspended samples (see section V in Supporting Information) and a recent report on frictional properties.\textsuperscript{15}

To quantify the aforementioned arguments, we consider a simple linear chain model (Figure 5c) for the interlayer modes, with each TL moving as one unit. The model further assumes that only interactions between the nearest-neighbor layers are
important, and the substrate effects are neglected. The force constant $K$ is the out-of-plane constant per unit area, $K_z$, for the breathing modes, and the in-plane (shear) force constant per unit area, $K_x$, for the shear modes. A similar model has previously been used to explain the observed breathing mode in epitaxial thin films and shear modes in multilayer graphene.

Solving this model, we obtain the eigenmodes

$$u_j' \propto \cos \left( \frac{(\alpha - 1)(2j - 1)\pi}{2N} \right)$$

and the corresponding phonon frequencies (in cm$^{-1}$)

$$\omega_{j\mu} = \sqrt{\frac{K}{2\mu c^2}} \left(1 - \cos \left( \frac{(\alpha - 1)\pi}{N} \right) \right)$$

where $j$ denotes the layer number and $\alpha = 1, 2, ..., N$. The $\alpha = 1$ mode corresponds to the acoustic mode and $\alpha = 2, ..., N$ correspond to the breathing modes ($K = K_z$) or shear modes ($K = K_x$), $\mu$ is the mass per unit area of the TMDs, and $c$ is the speed of light in cm/s. The eigenvector $u$ is in the $z$ direction for the breathing mode and the $x$ direction for the shear mode. The aforementioned expressions fit both the measured and computed frequencies perfectly (Figure 5a, b; $\alpha = N, N-2, 2, 4$ for $S1, S2, B1$, and $B2$, respectively), and the resulting force constants are shown in Table 2. $K_z$ values derived from fits to experimental data are almost the same in both materials ($8.6 \times 10^{19}$ N m$^{-3}$), while the in-plane (shear) force constant $K_x$ in WSe$_2$ is 13% larger than in MoS$_2$ ($3.1 \times 10^{19}$ N m$^{-3}$ versus $2.7 \times 10^{19}$ N m$^{-3}$); both are about 3 times smaller than $K_z$ and much larger than that reported in few-layer graphene ($1.28 \times 10^{19}$ N m$^{-3}$). We can also derive the corresponding elastic constants, $C_{33}$ and $C_{44}$, $C_{33} = K_z \nu$ and $C_{44} = K_x / \nu^2$, $\nu$ being the equilibrium distance between the center of each TL. This gives experimental values of $C_{33} = 2.0$ GPa and $C_{44} = 16.4$ GPa for MoS$_2$, and $C_{33} = 2.1$ GPa and $C_{44} = 18.6$ GPa for WSe$_2$.

We note that the good fits imply not only that interlayer interactions are dominated by interactions between nearest-neighbor layers, but also that the force constants $K_x$ and $K_z$ do

Figure 4. Vibrational normal modes of the interlayer shear and breathing modes in MoS$_2$/WSe$_2$. (a) The vibrational normal modes of the interlayer shear ($E_{2g}^2$) and breathing modes ($B_{2g}^2$) in bulk 2H-MoS$_2$/WSe$_2$. The shear mode is Raman-active, and the breathing mode is optically inactive. (b) Vibrational normal modes of the highest frequency shear mode $S1$ (top) and the lowest frequency breathing mode $B1$ (bottom) from 2TL to 9TL. (c) Vibrational normal modes of the minor shear mode $S2$ (top) and the minor breathing mode $B2$ (bottom) from 4TL to 9TL. The arrows indicate the direction of motion of the whole TL, and the length of the arrows represents the magnitude. The denoted frequencies are results of the first principles calculations for both MoS$_2$ (in purple) and WSe$_2$ (in black).
Here, we show that these important recent report, AFM measurements15 indicated that friction principles calculation results (open squares) match very well. The discrepancies for the S1, B1, and B2 modes in MoS2 are around 4 cm−1, 1.5 cm−1, and 2 cm−1, respectively. All of the fitting results in a and b are shown as the red solid lines for experimental data and black solid lines for DFT results. The equations for the fits are based on the linear chain model as described in the text.

Remarkably, we note that in the limit, as TL number increases, the measured (right column) for the bulk material.

not change significantly as N is increased from 2 to 9 in NTLs; this is consistent with fits obtained for all computed interlayer mode frequencies with the different N (see Supporting Information, Figures S-9 and S-10), using a single K parameter. Remarkably, we note that in the limit, as N → ∞, the linear chain model with the above Kc values predicts S1 (E1) frequencies in very good agreement with the actual calculated/measured E1 frequencies (Table 2), indicating that Kc is essentially unchanged from 2TLs to the bulk material. In a recent report, AFM measurements15 indicated that friction increased monotonically with decreasing number of layers in MoS2, and this was attributed to increased elastic compliance of thinner films. We note that our results are not contradictory to, and in fact complement, these findings. As discussed by the authors,15 there was relatively little interlayer sliding in the AFM measurements (indeed, the displacement in both in-plane and out-of-plane directions would be negligible under a ~10 nN lateral frictional force or normal load assuming the typical AFM tip radius of 5 nm, using the force constants we extracted). Therefore the frictional characteristics probed by the AFM experiments correspond to the limit where tip-layer interactions are much weaker than interlayer interactions. However, the well-known lubricating properties of layered TMDs are in fact related to the weak interlayer interactions, and here, we show that these important interlayer interactions are essentially unchanged from 2 TLs to the bulk.

Table 2. Force Constants Per Unit Area Derived from Fits to the Linear Chain Model and the Corresponding Predicted S1 Frequencies in the Bulk

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<thead>
<tr>
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<th>DFT (LDA)</th>
<th>experiment</th>
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<tr>
<td>MoS2</td>
<td>Kx (10^15 N m^-1)</td>
<td>9.26</td>
</tr>
<tr>
<td></td>
<td>Ky (10^15 N m^-1)</td>
<td>3.51</td>
</tr>
<tr>
<td></td>
<td>bulk S1 frequency (cm^-1)</td>
<td>36.1° (35.7)</td>
</tr>
<tr>
<td>WSe2</td>
<td>Kx (10^15 N m^-1)</td>
<td>8.38</td>
</tr>
<tr>
<td></td>
<td>Ky (10^15 N m^-1)</td>
<td>3.41</td>
</tr>
<tr>
<td></td>
<td>bulk S1 frequency (cm^-1)</td>
<td>24.8° (24.6)</td>
</tr>
</tbody>
</table>

“Values predicted by the linear chain model. The values in parentheses are explicitly calculated by DFT (left column) or experimentally measured (right column) for the bulk material.

In conclusion, we have uncovered the Raman signature of both interlayer shear and breathing modes in 2H-MoS2/WSe2 few-TL crystals. Two breathing modes are reported for the first time, where their appearance critically depends on the polarization used in the Raman experiment. Such organ pipe breathing modes are expected to exist in many other 2D crystals. The shear and breathing modes provide effective probes of the interlayer interactions that have important implications for both mechanical and electrical properties.

Methods. Sample Preparation. Single- and few-TL MoS2 and WSe2 films were isolated from bulk crystals by Scotch tape-based mechanical exfoliation2 and were then deposited onto freshly cleaned Si substrates with a 90 nm thick SiO2. The layer numbers can be determined by optical contrast and thickness measurements using atomic force microscopy (Dimension 3100 with a Nanoscope IIIa controller, Veeco, CA, USA) operated in a tapping mode under ambient conditions. More details regarding sample preparation and characterization can be found in the Supporting Information.

Raman Spectroscopy. Raman scattering spectroscopy measurements were carried out at room temperature using a micro-Raman spectrometer (Horiba-JY T64000) equipped with a liquid nitrogen cooled charge-coupled device. The measurements were conducted in a backscattering configuration excited with a solid state green laser (λ = 532 nm). We used a reflecting Bragg grating (OptiCrate) followed by another ruled reflecting grating to filter the laser side bands, and as such we can achieve ~5 cm−1 limit of detection using most solid state or gas laser lines. We find our signal-to-noise ratio is adequate which rules out the necessity of using a single monochromator configuration with three notch filters as recently reported.23 The backscattered signal was collected through a 100x objective and dispersed by a 1800 g/mm grating under a triple subtractive mode with a spectra resolution of 1 cm−1. The laser power at the sample surface was less than 1.5 mW for MoS2 and 0.3 mW for WSe2. Control measurements were conducted using very low excitation power levels of 0.03 mW for both materials. No detectable difference of the peak position and full width half-maximum (fwhm) intensity was observed between Raman spectra using high and low excitation power.
levels. Thus, the laser heating effect can be excluded in our measurements.

**Calculation Details.** First-principles calculations of vibrational Raman spectra are performed within density-functional theory (DFT) as implemented in the plane-wave pseudopotential code QUANTUM-ESPRESSO. The local density approximation (LDA) to the exchange-correlation functional is employed in the norm-conserving (NC) pseudopotential throughout the calculation. For the purpose of comparison, the LDA calculations with projector-augmented wave (PAW) potentials for the electron-ion interaction are performed to test the pseudopotential methods. To get converged results, plane-wave kinetic energy cutoffs of 65 and 550 Ry are used for the wave functions and charge density, respectively. The slabs are separated by 16 Å of vacuum to prevent interactions between slabs (this value has been tested for convergence of phonon frequencies). A Monkhorst-Pack k-point mesh of 17 × 17 × 5 and 17 × 17 × 1 is used to sample the Brillouin Zones for the bulk and thin films systems, respectively. In the self-consistent calculation, the convergence threshold for energy is set to 10⁻¹⁹ eV. All of the atomic coordinates and lattice constants are optimized with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm. During the structure optimization, the symmetry of D_{3h} (P6_3/mmc) is imposed on the bulk, while the symmetry of D_{3d} (P6m2) and D_{3d} (P3m1) is imposed on the odd number TLs and even number TLs, respectively. The structures are considered as relaxed when the maximum component of the Hellmann–Feynman force acting on each ion is less than 0.003 eV/Å.

With the optimized structures and self-consistent wave functions, the phonon spectra and Raman intensities are calculated within density-functional perturbation theory (DFPT) as introduced by Lazzeri and Mauri. For the DFPT self-consistent iteration, we used a mixing factor of 0.2 and a high convergence threshold of 10⁻¹⁴ which results from the long-range dipole–dipole interactions associated with long wavelength longitudinal phonons, are included in the calculation with the momentum vector q approaching zero from the x direction in the dynamical matrix. We find that the LO-TO splitting does not affect the frequencies of the low frequency Raman modes reported here.

**ASSOCIATED CONTENT**

* Supporting Information
  Sample preparation and characterization; vibrational normal modes of 1TL, 2TL, and bulk MoS₂/WSe₂; Lorentzian lineshape analysis; demonstration of breathing mode B₂ and shear mode S₂ in few-TL MoS₂; substrate effect; first-principles calculated phonon modes; linear chain model. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**
Y.Z. and X.L. contributed to this work equally. Y.Z., J.Z. and Q.X. conceived the idea. H.L., J.W., and H.Z. prepared the samples and conducted thickness measurements. Y.Z., J.Z., and Q.X. performed the Raman scattering experiments. X.L., C.K.G., and S.Y.Q. performed the first principles calculations and explained the measured and computed frequencies using the linear chain model. P.T.A. and M.S.D. conducted group theory analysis. All authors analyzed data and cowrote the manuscript.

**Notes**

The authors declare no competing financial interest.

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