Raman spectroscopy of shear and layer breathing modes in multilayer MoS$_2$

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We study by Raman scattering the shear and layer breathing modes in multilayer MoS$_2$. These are identified by polarization measurements and symmetry analysis. Their positions change significantly with the number of layers, with different scaling for odd and even layers. A chain model can explain the results, with general applicability to any layered material, allowing a reliable diagnostic of their thickness.

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I. INTRODUCTION

The fast progress of graphene research, fueled by the unique properties of this two-dimensional (2d) material, paved the way to experiments on other 2d crystals.$^{1-3}$ There are several layered materials (LMs), studied in the bulk,$^4$ retaining their stability down to a single monolayer, and whose properties are complementary to those of graphene. Transition metal oxides$^5$ and metal dichalcogenides have a layered structure.$^1$ Atoms within each layer are held together by covalent bonds, while van der Waals interactions keep the layers together.$^4$ LMs include a large number of systems with interesting properties.$^1$ For example, NiTe$_2$ and VS$_2$ are semimetals;$^3$ WS$_2$,$^6$ WS$_2$,$^7$ MoS$_2$,$^8$ MoSe$_2$,$^9$ MoTe$_2$,$^{10}$ TaSe$_2$,$^{11}$ RhTe$_2$ and PdTe$_2$ are semiconductors;$^4$ h-BN, and HfS$_2$ are insulators; NbS$_2$, NbSe$_2$,$^{12}$ NbTe$_2$, and TaSe$_2$ are superconductors;$^3$ Bi$_2$Se$_3$ and Bi$_2$Te$_3$ show thermoelectric properties$^4$ and may be topological insulators.$^{12}$ Similar to graphite and graphene, the LM properties are a function of the number of layers ($N$). The combinations of such 2d crystals in 3d stacks could offer huge opportunities in designing the functionalities of such heterostructures.$^1$ One could combine conductive, insulating, superconducting and magnetic 2d materials in one stack with atomic precision, fine tuning the performance of the resulting material,$^1$ the functionality being embedded in the design of such heterostructures.$^1$

Amongst these LMs, MoS$_2$ is a subject of intense research because of its electronic$^{13}$ and optical properties,$^14$ such as strong photoluminescence (PL),$^{14,15}$ electroluminescence,$^{16}$ controllable valley and spin polarization,$^{17-19}$ A single layer MoS$_2$ (1L-MoS$_2$) consists of two planes of hexagonally arranged S atoms linked to a hexagonal plane of Mo atoms via covalent bonds,$^{14,20-23}$ In the bulk, individual MoS$_2$ layers are held together by weak van der Waals forces,$^{20-23}$ This property has been exploited in lubrication technology$^{24}$ and, more recently, enabled the isolation of 1L-MoS$_2$. While bulk MoS$_2$ is a semiconductor with a 1.3-eV indirect band gap,$^{26}$ 1L-MoS$_2$ has a 1.8-eV direct band gap.$^{14,15}$ The absence of interlayer coupling of electronic states at the Γ point of the Brillouin zone in 1L-MoS$_2$ results in strong absorption and PL bands at $\sim$1.8 eV (680 nm).$^{14,15}$ 1L-MoS$_2$ field effect transistors (FETs) show both unipolar$^{13}$ and ambipolar$^{28}$ transport, with high mobilities and on-off ratios.$^{29,30}$ 1L-MoS$_2$ is also a promising candidate for novel optoelectronic devices,$^{16}$ such as photodetectors$^{31-33}$ and light-emitting devices operating in the visible range.$^{16}$

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15 K; \( \sim 34 \text{ cm}^{-1} \) (C), \( \sim 56 \text{ cm}^{-1} \) (LBMs) for MoS\(_2\); \( \sim 22 \text{ cm}^{-1} \) (C) for GaS; \( \sim 56 \text{ cm}^{-1} \) (C) for GaSe. Only Refs. 51 and 52 reported some of these for non-bulk samples. In particular, Ref. 51 studied the Raman spectrum of one shear mode for 2, 3, 5, 6, and 10L-MoS\(_2\). Reference 52 observed only one set of C and LB modes for 2L-MoS\(_2\) and 9L-MoS\(_2\). Both did not consider the symmetry difference between ONL-MoS\(_2\) and ENL-MoS\(_2\), e.g., they assigned the C mode in ONL MoS\(_2\) as \( E_{2g} \), but, as we show later, this is instead \( E' \). Reference 51 suggested that the scaling rule of the C mode in multilayer graphene\(^{40} \) cannot be extended to few-layer MoS\(_2\), opposite to the results presented in Ref. 52. Reference 52 wrote that LBMs scale as \( 1/N \), as predicted by Ref. 60 with an assumption of strong coupling between layers and substrate. However, it is not clear whether such strong coupling actually exists. Furthermore, even though LBMs are optical modes, an acoustic atomic displacement for such modes was presented in Fig. 1(b) of Ref. 52, with no symmetry analysis. Therefore, all symmetries, force constants, possible role of interactions between layers and substrate, and mode scaling with \( N \) still need to be fully understood. More importantly, it would be desirable to establish a general model to describe the evolution of C and LB modes with \( N \) in any LMs, not just MoS\(_2\).

Here we report the shear and layer breathing modes for NL-MoS\(_2\) up to 19L-MoS\(_2\), and bulk MoS\(_2\). We identify several groups of modes with frequencies dependent on \( N \). ONL-MoS\(_2\) and ENL-MoS\(_2\) show different scaling with \( N \), due to different symmetry. A chain model can account for the observed trends, and can be extended to other LMs.

II. RESULTS AND DISCUSSION

NL-MoS\(_2\) samples are produced from bulk MoS\(_2\) (SPI Supplies) by mechanical exfoliation, following a similar procedure to that used for graphene samples.\(^{2,6} \) NL-MoS\(_2\) are supported on a Si wafer with 93-nm SiO\(_2\), which is used as substrate in order to make the samples optically visible. The layer thickness is determined by optical contrast\(^{62} \) and atomic force microscopy.\(^{35} \) Raman measurements are performed using a Jobin-Yvon HR800 system equipped with a liquid nitrogen cooled charge-coupled detector. The excitation wavelength is 532 nm from a diode-pumped solid-state laser. A power ~0.23 mW is used to avoid sample heating. The laser plasma lines are removed using a BraggGrate bandpass filter (OptiGrate Corp), as these would appear in the same spectral range as the modes of interest. The Rayleigh line is suppressed using four BraggGrate notch filters with an optical density 3 range as the modes of interest. The Rayleigh line is suppressed using four BraggGrate notch filters with a spectral resolution of \( \sim 0.6 \text{ cm}^{-1} \), as estimated from the full width at half maximum (FWHM) of the Rayleigh peak.

Bulk MoS\(_2\) and 2L-MoS\(_2\) belong to the space group \( P6_3/mmm \) (point group \( D_{3h} \)),\(^{63} \) with unit cell consisting of two Mo atoms in sites with point group \( D_{3h} \), and four S atoms in sites with point group \( C_{3v} \),\(^{53} \) as shown in Fig. 1(a). There are 18 normal vibration modes.\(^{53} \) The factor group of bulk and 2L-MoS\(_2\) at \( \Gamma \) is \( D_{3h} \), the same as the point group.\(^{64} \) The atoms site groups are a subgroup of the crystal factor group.\(^{64} \) The correlation\(^{53} \) of the Mo site group \( D_{3h} \), S site group \( C_{3v} \), and factor group \( D_{3h} \) allows one to derive the following irreducible representations for the 18 normal vibration modes at \( \Gamma \):\(^{53,65} \) 

\[
\Gamma = A_{1g} + 2A_{2g} + 2B_{2g} + B_{1u} + E_{1g} + 2E_{1u} + 2E_{2g} + E_{2u},
\]

while \( A_{1g} \) and \( A_{1u} \) and one of the doubly degenerate \( E_{2g} \) modes, \( E_{2g} \), as shown in Fig. 1(d) for 2L and bulk MoS\(_2\), give rise to Raman modes above 200 cm\(^{-1} \).\(^{49} \) Only \( A_{1g} \) (~408 cm\(^{-1} \) in bulk and ~405 cm\(^{-1} \) in 2L-MoS\(_2\)) and \( E_{2g} \) (~382 cm\(^{-1} \) in bulk and ~383 cm\(^{-1} \) in 2L-MoS\(_2\)) can be observed when the laser excitation is normal to the sample basal plane.\(^{49} \) The other doubly degenerate \( E_{2g} \) mode, \( E_{2g} \), and one \( B_{2g} \) mode, \( B_{2g} \), are shear and LB modes.\(^{53,54,66} \) \( E_{2g} \) corresponds to a rigid-layer displacement perpendicular to the \( c \) axis (C mode), while \( B_{2g} \) corresponds to rigid-layer displacements parallel to the \( c \) axis (LBMs), as shown in Figs. 1(b) and 1(c) for 2L-MoS\(_2\).

1L-MoS\(_2\) has \( D_{3h} \) symmetry, with three atoms per unit cell.\(^{63} \) The \( \Gamma \) phonons can be expressed by the irreducible
representation of \( D_{3d} \), \( \Gamma = 2A''_1 + A'_1 + 2E' + E'' \), where \( A''_1 \) and \( E' \) are acoustic modes, \( A'_1 \) is IR active, \( A'_1 \) and \( E'' \) are Raman active, and another \( E'' \) is both Raman and IR active. The \( E' \) and \( A'_1 \) modes, Fig. 1(d), were previously detected in the Raman spectra of 1L-MoS\(_2\) at \( \sim 384 \) and \( \sim 403 \) cm\(^{-1}\). Of course, no rigid-layer vibrations can exist in 1L-MoS\(_2\).

3L-MoS\(_2\) has the same point group \( (D_{3h}) \) as 1L-MoS\(_2\), with \( A'_1 \) and \( A''_1 \) corresponding to LBMs, and \( E' \) and \( E'' \) being C modes, Figs. 1(b) and 1(c). ENL-MoS\(_2\) belongs to point group \( D_{6h} \) (without inversion symmetry), while ONL-MoS\(_2\) corresponds to \( D_{3h} \) (without inversion symmetry). Therefore, it is convenient to denote each mode of NL-MoS\(_2\) by the corresponding irreducible representation according to the their point group, and then determine if they are Raman or IR active, or inactive. NL-MoS\(_2\) has 9\( N - 3 \) optical modes: 3\( N - 1 \) are vibrations along the \( c \) axis, and 3\( N - 1 \) are doubly degenerate in-plane vibrations. For rigid-layer vibrations, there are 3\( N - 1 \) LBMs along the \( c \) axis, and 3\( N - 1 \) doubly degenerate shear modes perpendicular to it. When \( N \) is even, there are 0 Raman active LBMs and \( \frac{N-1}{2} \) doubly degenerate Raman active shear modes. When \( N \) is odd, \( \frac{N-1}{2} \) LBMs and \( 3N - 1 \) doubly degenerate shear modes are Raman active. The interlayer distance in LMs is much larger than the in-plane bond length, e.g., in MoS\(_2\), the interlayer distance is \( \sim 6.7 \) Å, while the in-plane bond length is \( \sim 3.2 \) Å. Thus, the in-plane optical modes may not strongly depend on \( N \). However, the interlayer coupling dominates the lattice dynamics of the rigid-layer vibrations, so that LB and shear modes will be very sensitive to \( N \). For example, Fig. 2(a) shows the Raman spectra of 5, 6L, and bulk MoS\(_2\). In the high-frequency region above 200 cm\(^{-1}\), the \( E'_2 \) (\( \sim 384 \) cm\(^{-1}\)), \( A_{1g} \) (\( \sim 409 \) cm\(^{-1}\)), 2LA(M) (\( \sim 453 \) cm\(^{-1}\)), and \( A_{2u} \) (\( \sim 463 \) cm\(^{-1}\)) modes are detected both in bulk and 6L-MoS\(_2\). Although the notation in 5L-MoS\(_2\) is different from 6L and bulk MoS\(_2\) because of the different crystal symmetry, the modes \( (E', A'_1) \) are observed in 5L-MoS\(_2\). The line shape and peak positions in the high-frequency region for 5L and 6L-MoS\(_2\) are almost identical, both being similar to bulk MoS\(_2\). In the low-frequency region below 100 cm\(^{-1}\), there is only one Raman peak \( \sim 33 \) cm\(^{-1}\), i.e., \( E'_{2g} \), in bulk MoS\(_2\). However, as discussed above, there should exist six Raman active modes for 5L and three for 6L-MoS\(_2\). Of these, four and three shear modes should be doubly degenerate for 5L and 6L-MoS\(_2\), respectively. Experimentally, we observe three modes below 60 cm\(^{-1}\) in 5L and four modes in 6L-MoS\(_2\), as for Fig. 2(a).

The LB \( (A'_1) \) and C \( (E', E'') \) Raman tensors in ONL-MoS\(_2\), and C \( (E'_{2g}) \) Raman tensor in ENL-MoS\(_2\) are:

\[
A'_1 \text{(LB,ONL)} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix},
\]

\[
E' \text{(C,ONL)} = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},
\]

\[
E'' \text{(C,ONL)} = \begin{bmatrix} 0 & 0 & c \\ 0 & 0 & 0 \\ c & 0 & 0 \end{bmatrix},
\]

\[
E'_{2g} \text{(C,ENL)} = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.
\]
Raman spectra of ENL-MoS\textsubscript{2}. The spectrum of bulk MoS\textsubscript{2} is also included in (a), (b). Dashed and dotted lines in (a), (b) are guides to the eye. (c) Position of typical C and LB modes as a function of \( \sim 200 \text{ cm}^{-1} \) above 100 cm\(^{-1}\) and polarized XX. All 5L-MoS\textsubscript{2} LBMs are higher than in 6L-MoS\textsubscript{2}, while all C modes at \( \sim 32 \text{ cm}^{-1} \) for 5L, and \( \sim 23 \) and \( \sim 32 \text{ cm}^{-1} \) for 6L-MoS\textsubscript{2}. According to the symmetry analysis discussed above, we assign these to \( E' \) in 5L and \( E_{2g} \) in 6L-MoS\textsubscript{2}. Two broad peaks are observed for XX measurements at \( \sim 17 \) and 47 cm\(^{-1}\) for 5L-MoS\textsubscript{2}, which we assign to \( A'_1 \). Note that the lower \( E' \) mode of 5L-MoS\textsubscript{2} at \( \sim 19 \text{ cm}^{-1} \) cannot be fully resolved for XX measurements due to the presence of the broad \( A'_1 \) mode at \( \sim 17 \text{ cm}^{-1} \). We also detect two Raman modes at \( \sim 15 \) and 41 cm\(^{-1}\) in 6L-MoS\textsubscript{2}. These are consistent with what should be optically silent \( B_{2g} \) LBMs, as discussed later. The symmetry, polarization, and mode frequency are summarized in Table I for the C and LB modes of 5 and 6L-MoS\textsubscript{2}. Although the in-plane modes in 5 and 6L-MoS\textsubscript{2} above 200 cm\(^{-1}\) are almost identical, the C and LB mode positions below 100 cm\(^{-1}\) are different. The frequencies of all 5L-MoS\textsubscript{2} LBMs are higher than in 6L-MoS\textsubscript{2}, while all C modes are lower than in 6L-MoS\textsubscript{2}. Figures 3(a) and 3(b) show the low-frequency Raman measurements for NL-MoS\textsubscript{2}, with \( N = 1–19 \), as well as bulk MoS\textsubscript{2}. Since the point group of ONL-MoS\textsubscript{2} (D\(_{3h}\)) is different from ENL-MoS\textsubscript{2} (D\(_{6h}\)), we plot the Raman spectra of ONL-MoS\textsubscript{2} [Fig. 3(a)] and ENL-MoS\textsubscript{2} [Fig. 3(b)] in two panels. Bulk MoS\textsubscript{2} is included both in ONL-MoS\textsubscript{2} and ENL-MoS\textsubscript{2} panels because we cannot distinguish its parity in a (noninfinite) bulk sample. Of course, there are no LB or C modes in 1L-MoS\textsubscript{2}, as confirmed in Fig. 3(a). The two spikes \( \sim 4.55 \text{ cm}^{-1} \), with weaker intensity for thicker flakes, are due to Brillouin scattering of the LA mode from the Si substrate.\(^70\) This is confirmed by determining the elastic constant \( C_{11} \) from the Raman measurements \( \sim 1.65 \times 10^{11} \text{ Pa} \) is consistent with \( 1.66 \times 10^{11} \text{ Pa} \) measured by ultrasonic wave propagation.\(^71\) In 2L-MoS\textsubscript{2} two Raman peaks are observed, while two overlapping bands are seen in 3L-MoS\textsubscript{2}. More Raman peaks are observed for thicker MoS\textsubscript{2} flakes.

We classify all low-frequency Raman peaks into two categories. Those that stiffen for increasing \( N \), linked by dashed lines, and those softening with \( N \), linked by dotted lines. One C mode stiffens from \( \sim 22.6 \text{ cm}^{-1} \) in 2L to 32.5 cm\(^{-1}\) in 19L-MoS\textsubscript{2}, while one LB mode softens from \( \sim 40.1 \text{ cm}^{-1} \) in 2L to 4.7 cm\(^{-1}\) in 19L-MoS\textsubscript{2}, Fig. 3(c). The two sets of modes have different FWHM, Fig. 3(d). In 2L-MoS\textsubscript{2}, FWHM

![Raman spectra](image)

FIG. 3. (Color online) (a) Stokes and anti-Stokes Raman spectra of ONL-MoS\textsubscript{2} in the low-frequency range. (b) Stokes and anti-Stokes Raman spectra of ENL-MoS\textsubscript{2}. The spectrum of bulk MoS\textsubscript{2} is also included in (a), (b). Dashed and dotted lines in (a), (b) are guides to the eye. (c) Position of typical C and LB modes as a function of \( \sim 200 \text{ cm}^{-1} \) above 100 cm\(^{-1}\) and polarized XX. All 5L-MoS\textsubscript{2} LBMs are higher than in 6L-MoS\textsubscript{2}, while all C modes at \( \sim 32 \text{ cm}^{-1} \) for 5L, and \( \sim 23 \) and \( \sim 32 \text{ cm}^{-1} \) for 6L-MoS\textsubscript{2}. According to the symmetry analysis discussed above, we assign these to \( E' \) in 5L and \( E_{2g} \) in 6L-MoS\textsubscript{2}. Two broad peaks are observed for XX measurements at \( \sim 17 \) and 47 cm\(^{-1}\) for 5L-MoS\textsubscript{2}, which we assign to \( A'_1 \). Note that the lower \( E' \) mode of 5L-MoS\textsubscript{2} at \( \sim 19 \text{ cm}^{-1} \) cannot be fully resolved for XX measurements due to the presence of the broad \( A'_1 \) mode at \( \sim 17 \text{ cm}^{-1} \). We also detect two Raman modes at \( \sim 15 \) and 41 cm\(^{-1}\) in 6L-MoS\textsubscript{2}. These are consistent with what should be optically silent \( B_{2g} \) LBMs, as discussed later. The symmetry, polarization, and mode frequency are summarized in Table I for the C and LB modes of 5 and 6L-MoS\textsubscript{2}. Although the in-plane modes in 5 and 6L-MoS\textsubscript{2} above 200 cm\(^{-1}\) are almost identical, the C and LB mode positions below 100 cm\(^{-1}\) are different. The frequencies of all 5L-MoS\textsubscript{2} LBMs are higher than in 6L-MoS\textsubscript{2}, while all C modes are lower than in 6L-MoS\textsubscript{2}. Figures 3(a) and 3(b) show the low-frequency Raman measurements for NL-MoS\textsubscript{2}, with \( N = 1–19 \), as well as bulk MoS\textsubscript{2}. Since the point group of ONL-MoS\textsubscript{2} (D\(_{3h}\)) is different from ENL-MoS\textsubscript{2} (D\(_{6h}\)), we plot the Raman spectra of ONL-MoS\textsubscript{2} [Fig. 3(a)] and ENL-MoS\textsubscript{2} [Fig. 3(b)] in two panels. Bulk MoS\textsubscript{2} is included both in ONL-MoS\textsubscript{2} and ENL-MoS\textsubscript{2} panels because we cannot distinguish its parity in a (noninfinite) bulk sample. Of course, there are no LB or C modes in 1L-MoS\textsubscript{2}, as confirmed in Fig. 3(a). The two spikes \( \sim 4.55 \text{ cm}^{-1} \), with weaker intensity for thicker flakes, are due to Brillouin scattering of the LA mode from the Si substrate.\(^70\) This is confirmed by determining the elastic constant \( C_{11} \) from the Raman measurements \( \sim 1.65 \times 10^{11} \text{ Pa} \) is consistent with \( 1.66 \times 10^{11} \text{ Pa} \) measured by ultrasonic wave propagation.\(^71\) In 2L-MoS\textsubscript{2} two Raman peaks are observed, while two overlapping bands are seen in 3L-MoS\textsubscript{2}. More Raman peaks are observed for thicker MoS\textsubscript{2} flakes.

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### Table I. Symmetry, polarization, and positions of C and LB modes in 5 and 6L-MoS\textsubscript{2}.

<table>
<thead>
<tr>
<th>Layer number</th>
<th>C</th>
<th>LB</th>
</tr>
</thead>
<tbody>
<tr>
<td>5L (Num.) mode</td>
<td>(2)E(_R) (IR)</td>
<td>(2)E(_R) (IR)</td>
</tr>
<tr>
<td>polarization</td>
<td>XX,YY</td>
<td>XX,YY</td>
</tr>
<tr>
<td>exp. (cm(^{-1}))</td>
<td>19,30</td>
<td>17.47</td>
</tr>
<tr>
<td>6L (Num.) mode</td>
<td>(3)E(_g) (IR)</td>
<td>(3)E(_g) (silent)</td>
</tr>
<tr>
<td>polarization</td>
<td>XX,YY</td>
<td></td>
</tr>
<tr>
<td>exp. (cm(^{-1}))</td>
<td>23,32</td>
<td>15.41(XX)</td>
</tr>
</tbody>
</table>
of calculations. The irreducible representation of each mode is also indicated. Solid lines are guides to the eye.

Well those predicted for LBMs, i.e., the \( \alpha \) vibrations: ONL-MoS\(_2\), e.g., the two Raman modes according to group analysis, there should be no Raman active \( \alpha \) vibrations: LBM lattice dynamics, while those parallel to the basal plane, as discussed later, they are included in Fig. 4(c). Since a MoS\(_2\) layer consists of two types of atoms, S and Mo, we implement a diatomic chain model (DCM) to explain the data. Figure 1(a) shows the ball and stick model for 2 and Mo, we implement a diatomic chain model (DCM) to explain the data. Figure 1(a) shows the ball and stick model for 2 and 3L-MoS\(_2\). Only two force constants are needed to describe the vibrations: \( \alpha_{ss} \) and \( \alpha_{sm} \), where \( \alpha_{ss} \) is the force constant per unit area between two nearest S planes in two adjacent layers, and \( \alpha_{sm} \) is force constant per unit area between the nearest S and Mo planes within a MoS\(_2\) layer. Their components perpendicular to the basal plane, \( \alpha_{ss} ^{\perp} \) and \( \alpha_{sm} ^{\perp} \), determine the LBMs lattice dynamics, while those parallel to the basal plane, \( \alpha_{ss} ^{\parallel} \) and \( \alpha_{sm} ^{\parallel} \), determine the C modes dynamics. The reduced mass for one S (Mo) plane, \( m_S \) (\( m_{Mo} \)), is its atomic mass per unit area. In MoS\(_2\), \( m_S = 0.6 \times 10^{-2} \, \text{g/cm}^2 \) and \( m_{Mo} = 1.8 \times 10^{-2} \, \text{g/cm}^2 \), \( \alpha_{ss} ^{\perp} \) and \( \alpha_{sm} ^{\perp} \) can be estimated from the high-frequency \( A_1 \) and \( E' \) modes of 1L-MoS\(_2\). In 1L-MoS\(_2\), \( 9 \times 9 \) dynamical matrices can be constructed and solved analytically. We get \( \omega_{A_1} = (1/2\pi c) \sqrt{2\alpha_{ss} ^{\perp} / \mu} \), with \( \mu = 2m_S \), and \( c \) the speed of light. The atom displacement eigenvectors show that the vibration directions of the two external S atoms are opposite along the \( c \) axis, while the center Mo atom stays still, as shown in Fig. 1(d) for IL-MoS\(_2\), corresponding to a spring connected by two S atoms with a force constant per unit area \( 2\alpha_{sm} ^{\perp} \), since the Mo atom stays still at the spring equilibrium position. We measure \( \omega_{A_1} \sim 403 \, \text{cm}^{-1} \) in 1L-MoS\(_2\). This gives \( \alpha_{ss} ^{\perp} \sim 3.46 \times 10^{21} \, \text{N/m}^3 \). We also get \( \omega_{E'} = (1/2\pi c) \sqrt{2\alpha_{sm} ^{\perp} / \mu} \), where \( 1/\mu = 1/m_{Mo} + 1/(2m_S) \). The atom displacement eigenvectors indicate that the vibration directions of the two S atoms are opposite to the center Mo atom, along the basal plane, as shown in Fig. 1(d) for IL-MoS\(_2\), corresponding to a spring connected by two S atoms and one Mo atom with a force constant per unit area \( 2\alpha_{sm} ^{\perp} \). From the experimental 384 \, \text{cm}^{-1} \), we get \( \alpha_{ss} ^{\parallel} = 1.88 \times 10^{21} \, \text{N/m}^3 \). Note that the weak interaction of the two S planes in the MoS\(_2\) layers is not included because the S-S plane distance is twice the S-Mo one.

To understand the C modes of NL-MoS\(_2\), the layer coupling between two nearest S planes in the two adjacent layers should be included. \( 3N \times 3N \) dynamical matrices can be constructed for NL-MoS\(_2\). By numerically solving the eigenequation for NL-MoS\(_2\), we get the eigenfrequencies and corresponding eigenvectors. By fitting these to our experimental data we get: \( \alpha_{ss} ^{\parallel} = 8.90 \times 10^{19} \, \text{N/m}^3 \) and \( \alpha_{ss} ^{\perp} = 2.82 \times 10^{19} \, \text{N/m}^3 \). Multiplying \( \alpha_{ss} ^{\perp} \) and \( \alpha_{ss} ^{\parallel} \) by the unit cell...
area gives the interlayer force constants, \( k_{s}^{\text{shear}} = 2.5 \, \text{N/m} \) and \( k_{s}^{\text{comp}} = 7.8 \, \text{N/m} \). They agree well with those for bulk samples reported in Ref. 59 \((k_{1}^{\text{shear}} = 2.7 \, \text{N/m} \) and \( k_{1}^{\text{comp}} = 7.4 \, \text{N/m} \)) derived by considering S-Mo-S as a rigid-layer mass unit, and deducing the interlayer force constants from \( \omega = \sqrt{k_{1}/\mu_{1}} \), with \( \omega \) the rigid-layer mode frequency and \( \mu_{1} \) the reduced mass. Multiplying \( \alpha_{1}^{\text{s}} \) by the equilibrium distance between two adjacent MoS\(_2\) layers gives a shear modulus \( \sim 18.9 \, \text{GPa} \), in good agreement with that measured for bulk MoS\(_2\),\(^72\) from phonon dispersion curves determined by neutron scattering, and x-ray measurements of the linear compressibilities.

The eigenvectors of the rigid-layer vibrations in 2 and 3L-MoS\(_2\), derived from the corresponding eigenvalues, are depicted in Figs. 1(b) and 1(c). Applying symmetry analysis to the corresponding NL-MoS\(_2\) eigenvectors, we assign the irreducible representations of the corresponding point group to each mode. The eigenfrequencies of Raman active rigid-layer vibrations for \( E_{g}^{2} \) (C modes in ENL-MoS\(_2\)), \( E' \) (C modes in ONL-MoS\(_2\)), and \( A_{1} \) (LBMs in ONL-MoS\(_2\)) are summarized in Figs. 4(a), 4(b), and 4(d). The eigenfrequencies of the Raman inactive \( B_{2g}^{2} \) (LBMs) in ENL-MoS\(_2\) are also included in Fig. 4(c). The eigenfrequencies of the modes for 1L-, 2L-, and 3L-MoS\(_2\) are also given in Figs. 1(b)–1(d). As illustrated in Fig. 4, the model calculations are in good agreement with experiments, including the Raman inactive \( \omega_{LBM} \) of the \( C \) peak positions in bulk and bilayer graphene (2LG) is \( \sim 28 \, \text{cm}^{-1} \) and \( \sim 115413 \) (2013) in 2L-MoS\(_2\). Each of these splits in two branches with increasing \( N \), and to 32.5 cm\(^{-1}\) in 3L-MoS\(_2\). This suggests that the Raman inactive LBMs \( (B_{2g}^{2}) \) in ENL-MoS\(_2\) might be observed, with polarization behavior identical to the \( A_{1} \) (LBMs) in ONL-MoS\(_2\).

We now consider the evolution of the rigid-layer vibrations with increasing \( N \) based on symmetry analysis. In Figs. 4(a) and 4(c), one \( C \) mode \( (E_{2g}^{2}) \) and one LBM \( (B_{2g}^{2}) \) are observed in 2L-MoS\(_2\). Each splits in two branches with increasing \( N \), one stiffening, the other softening with \( N \). A new mode appears when \( N \) increases up to \( 4N + 2 \). For example, \( \omega_{LBM} \) of the \( \omega_{C} \) mode \( (E') \) [Fig. 4(b)] and LBMs \( (A_{1}') \) [Fig. 4(d)] in ONL-MoS\(_2\) exhibit similar trends with \( N \) as the C modes \( (E_{2g}^{2}) \) [Fig. 4(a)] and LBMs \( (B_{2g}^{2}) \) [Fig. 4(c)] in ENL-MoS\(_2\), but with decreasing frequency for \( E' \) and increasing frequency for \( A_{1}' \). Connecting each branch of the rigid-layer modes with solid lines shows that these form series of cone-like curves, Figs. 4(a)-4(d). The number of LB and shear modes in ONL- and ENL-MoS\(_2\) increases with \( N \). However, in the experiment, no more than three of them are observed. In both ONL- and ENL-MoS\(_2\), most of the observed shear modes are from the upper branch and their frequencies stiffen with increasing \( N \), while most of the LBMs are from the lower branch, and their frequencies soften with increasing \( N \).

Figure 5 plots the positions of all the observed and calculated rigid-layer vibration modes. The shear mode at 22.6 cm\(^{-1}\) \( (E_{2g}^{2}) \) in 2L-MoS\(_2\) blue-shifts to 28 cm\(^{-1}\) \( (E') \) in 3L-MoS\(_2\), and to 32.5 cm\(^{-1}\) \( (E') \) in 19L-MoS\(_2\), reaching \( \sim 32.7 \, \text{cm}^{-1} \) \( (E_{2g}^{2}) \) in bulk MoS\(_2\). In multilayer graphene,\(^40\) with each layer composed of one type of atom, the ratio of \( C \) peak positions in bulk and bilayer graphene (2LG) is \( \omega_{\text{bulk}}/\omega_{2\text{LG}} = \sqrt{2} \). In our MoS\(_2\) measurements, the shear mode exhibits the same trend and we have \( 32.7/22.6 = 1.447 \), very close to \( \sqrt{2} \). On the other hand, the LBMs at 40 cm\(^{-1}\) \( (B_{2g}^{2}) \) in 2L red-shifts to 29 cm\(^{-1}\) \((A_{1}')\) in 3L-MoS\(_2\), and \( 5 \, \text{cm}^{-1} \) \((A_{1}')\) in 19L-MoS\(_2\). The blue-shifted branch reaches \( 56.8 \, \text{cm}^{-1} \) in 19L-MoS\(_2\), close to the LBMs in bulk MoS\(_2\).\(^73\)

For C and LB modes in NL-MoS\(_2\), three atoms of the S-Mo-S layer vibrate along same direction, as shown in Figs. 2(b) and 2(c). Based on our DCM, we find that the relative displacements between Mo and two S atoms are very small. For example, the relative displacement in 2L-MoS\(_2\) is \( \sim 0.6\% \), decreasing with increasing \( N \). Therefore, the relative vibration of \( C \) and LB modes between Mo and two S atoms can be ignored. We can thus further simplify the model collapsing an entire layer in a single ball. So we consider a reduced monatomic chain model (MCM). Taking one layer as a ball with mass \( (m_{Mo} + 2m_{s}) \) and interlayer bonding \( \alpha_{ss}^{\text{Mo-Mo}} \) for LBMs, and \( \alpha_{ss}^{\text{Mo}} \) for modes we get: \( \omega_{LBM} = (1/\sqrt{2\pi c})\sqrt{\alpha_{ss}^{\text{Mo-Mo}}/(m_{Mo} + 2m_{s})} \), \( \omega_{C} = (1/\sqrt{2\pi c})\sqrt{\alpha_{ss}^{\text{Mo}}/(m_{Mo} + 2m_{s})} \) for 2L-MoS\(_2\), with \( \omega_{LBM} \) the LB position, and \( \omega_{C} \) the C peak position. The corresponding \( \omega_{LBM} \) \((40.8 \, \text{cm}^{-1})\) and \( \omega_{C} \) \((23.0 \, \text{cm}^{-1})\) are in good agreement.
with those from the DCM ($\omega_{\text{LBM}} = 40.3 \text{ cm}^{-1}$ and $\omega_{C} = 22.9 \text{ cm}^{-1}$) and the experimental data ($\omega_{\text{LBM}} = 40.2 \text{ cm}^{-1}$ and $\omega_{C} = 22.6 \text{ cm}^{-1}$). We can now solve the eigenequation analytically and find the relation between position and $N$ both for shear and LB modes. These modes can be assigned to several branches, as shown in Fig. 5. A new branch will emerge from each ENL-MoS$_2$, i.e., 2, 4, 6, 8L, ... -MoS$_2$, at about the same position as that of the C mode or LBM in 2L-MoS$_2$, then splitting into two sub-branches, one blue shifting, the other red shifting with increasing $N$. For the branches originating from each ENL-MoS$_2$, the frequency as a function of $N$ is $\omega(N) = \omega(2N_0)\sqrt{T \pm \cos(\pi N)}/\sqrt{1 - \cos(\pi/N)}$ ($N \geq 2N_0$, and $N_0$ an integer: 1, 2, 3, 4, ...), with $+$ for the high-frequency subbranch and $-$ for the low-frequency one. Our calculations show that $\omega(2N_0)$ is almost the same as $\omega(2)$ for C and LB modes. Therefore, the evolution of C and LB modes with increasing $N$ can be further simplified as $\omega(N) = \omega(2)\sqrt{1 - \cos(\pi/N)} \omega(2)$ for the high-frequency one, and $\omega(N) = \omega(2)\sqrt{1 + \cos(\pi/N)} \omega(2)$ for the low-frequency one. These change with number of layers, with different scaling factors as confirmed by polarized Raman spectroscopy.

For NL-MoS$_2$ the observed C modes are usually in the high-frequency subbranch, while the corresponding LBMs are usually in the low-frequency one; these are connected by solid lines in Fig. 5. The appearance of the high-frequency C subbranches and the absence of the high-frequency LB subbranches is consistent with the bulk case, where the C mode $E_{2g}^1$ is Raman-active while the LBMs $A_{1g}$, $E_{1g}$, $E_{2g}$, $B_{2g}$, $B_{1g}$, $B_{3g}$, and $E_{3g}$ are optical-inactive. For the observed high-frequency C subbranch originating from 2L-MoS$_2$, we have $N_0 = 1$, thus $\omega_{C}(N) = \omega_C(2)\sqrt{1 + \cos(\pi/N)} \omega(2)$ for the high-frequency subbranch originating from 2L-MoS$_2$, and $\omega_{C}(N) = \omega_C(2)\sqrt{1 - \cos(\pi/N)} \omega(2)$ for the low-frequency subbranch originating from 10L-MoS$_2$. For the observed LBMs in MoS$_2$, the relation between frequency and $N$ in the low-frequency subbranch originating from 2L-MoS$_2$ is: $\omega_{\text{LBM}}(N) = \omega_{\text{LBM}}(2)\sqrt{1 - \cos(i \pi/N)}$ ($N \geq 2i$), with $i = 1, 3, 5$, where $\omega_{\text{LBM}}(2) = 40.8 \text{ cm}^{-1}$. This well matches with the experiments, Figs. 5(a) and 5(b). Figure 5 also shows another sub-branch for 2L, 6L and 10L-MoS$_2$, both for C and LB modes, as indicated by gray dashed lines. Only one or two modes are experimentally observed for these sub-branches. Their frequency is in good agreement with the theoretical predictions.

Note that any coupling between supported MoS$_2$ and the substrate is not included in our chain models. The agreement between experiments and model predictions means that the coupling between MoS$_2$ and the substrate does not play a major role, the scaling with $N$ being only determined by the interaction between the MoS$_2$ layers. Indeed, for the suspended multilayer graphene in Ref. 40, no coupling was considered, and the C scaling with $N$ was also well described by a MCM.

In principle, our chain model can be extended to predict rigid-layer vibrations in other LMs. The general approach is to calculate the reduced mass for the monolayer of a given material, and then measure C and LBMs in 2L samples. One can then predict the relation between frequency and $N$ for the different branches in any LM. For example, the theoretical positions of the C and LB modes in 2L-hBN are $\sim 38.6 \text{ cm}^{-1}$ and $85.6 \text{ cm}^{-1}$, respectively.

Our model predicts that the C mode generates two branches, $\omega_{C}(N) = 38.6\sqrt{1 + \cos(\pi/N)} \omega(2)$ for the high-frequency one, and $\omega_{C}(N) = 38.6\sqrt{1 - \cos(\pi/N)} \omega(2)$ for the low-frequency one. Similarly, the C mode ($\sim 38.6 \text{ cm}^{-1}$) and LBMs ($\sim 85.6 \text{ cm}^{-1}$) in 4L-hBN, will also generate two branches, and so on. Thus, we can predict all the C and LB modes in NL-hBN.

### III. CONCLUSIONS

We characterized single- and few-layer MoS$_2$ by Raman spectroscopy. We observed rigid-layer vibrations both for shear and layer breathing modes. These were assigned to irreducible representations of the point group that the sample belongs to, as confirmed by polarized Raman spectroscopy. These change with number of layers, with different scaling for odd and even layers. A diatomic chain model, combined with group theory, can account for the observed trends. Furthermore, a reduced monatomic chain model can be used to describe the shear and layer breathing modes in MoS$_2$ and any other layered material with any number of layers.

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