# Raman spectroscopy of shear and layer breathing modes in multilayer $\mathbf{M o S}_{\mathbf{2}}$ 

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#### Abstract

We study by Raman scattering the shear and layer breathing modes in multilayer $\mathrm{MoS}_{2}$. 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. ${ }^{4}$ 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. ${ }^{4}$ For example, $\mathrm{NiTe}_{2}$ and $\mathrm{VSe}_{2}$ are semimetals; ${ }^{4}$ $\mathrm{WS}_{2},{ }^{6} \mathrm{WSe}_{2},{ }^{7} \mathrm{MoS}_{2},{ }^{8} \mathrm{MoSe}_{2}, \mathrm{MoTe}_{2}, \mathrm{TaS}_{2},{ }^{9} \mathrm{RhTe}_{2}$ and $\mathrm{PdTe}_{2}$ are semiconductors; ${ }^{4} \mathrm{~h}-\mathrm{BN}$, and $\mathrm{HfS}_{2}$ are insulators; $\mathrm{NbS}_{2}, \mathrm{NbSe}_{2},{ }^{10} \mathrm{NbTe}_{2}$, and $\mathrm{TaSe}_{2}$ are superconductors; ${ }^{4}$ $\mathrm{Bi}_{2} \mathrm{Se}_{3}{ }^{11}$ and $\mathrm{Bi}_{2} \mathrm{Te}_{3}{ }^{11}$ 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. ${ }^{1,2}$ One could combine conductive, insulating, superconducting and magnetic $2 d$ 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 $\mathrm{LMs}, \mathrm{MoS}_{2}$ 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 $\mathrm{MoS}_{2}$ (1L-MoS $\mathrm{Mo}_{2}$ ) 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 $\mathrm{MoS}_{2}$ 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 $1 \mathrm{~L}-\mathrm{MoS}_{2} .{ }^{13-15,25}$ While bulk $\mathrm{MoS}_{2}$ is a semiconductor with a $1.3-\mathrm{eV}$ indirect band gap, ${ }^{26} 1 \mathrm{~L}-\mathrm{MoS}_{2}$ has a $1.8-\mathrm{eV}$ direct band gap. ${ }^{14,15}$ The absence of interlayer coupling of electronic states at the $\Gamma$ point of the Brillouin zone in $1 \mathrm{~L}-\mathrm{MoS}_{2}{ }^{15,27}$ results in strong absorption and PL bands at $\sim 1.8 \mathrm{eV}(680 \mathrm{~nm}) .{ }^{14,15} 1 \mathrm{~L}-\mathrm{MoS}_{2}$ field effect transistors (FETs) show both unipolar ${ }^{13}$ and ambipolar ${ }^{28}$ transport, with high mobilities and on-off ratios. ${ }^{29,30} 1 \mathrm{~L}-\mathrm{MoS}_{2}$ is also a promising candidate for novel optoelectronic devices, ${ }^{16}$ such as photodetectors ${ }^{31-33}$ and light-emitting devices operating in the visible range. ${ }^{16}$

Raman spectroscopy is the prime nondestructive characterization tool for carbon materials, ${ }^{34,35}$ in particular graphite, ${ }^{35-38}$ single, ${ }^{35,39}$ and multilayer ${ }^{35,39}$ graphene. The Raman spectrum of graphene consists of two fundamentally different sets of peaks. Those, such as $\mathrm{D}, \mathrm{G}, 2 \mathrm{D}$, etc., due to in-plane vibrations, ${ }^{34-36}$ and others, such as the shear (C) ${ }^{40}$ and layer breathing (LB) modes (LBMs), ${ }^{41-43}$ due to relative motions of the planes themselves, either perpendicular or parallel to their normal. Albeit being an in-plane mode, the 2D peak is sensitive to $N$ since the resonant Raman mechanism that gives rise to it is closely linked to the details of the electronic band structure, ${ }^{35,39,44}$ the latter changing with $N,{ }^{45,46}$ and the layers relative orientation. ${ }^{44}$ On the other hand, the C modes and LBMs are a direct probe of $N,{ }^{40-42}$ since the vibrations themselves are out of plane, thus directly sensitive to $N$. The success of Raman scattering in characterizing graphene prompted the community to extend this technique to other LMs, from bulk to monolayer. ${ }^{40,47-52}$ For example, the Raman spectrum of bulk $\mathrm{MoS}_{2}$ consists of two main peaks at $\sim 382$, $407 \mathrm{~cm}^{-1}{ }^{53,54}$ These are assigned to $E_{2 g}^{1}$ (in-plane vibration) and $A_{1 g}$ (out of plane vibration) modes. ${ }^{53,54}$ The $E_{2 g}^{1}$ red shifts, while the $A_{1 g}$ blue shifts with increasing $N .{ }^{49,55}$ The $E_{2 g}^{1}$ and $A_{1 g}$ modes have opposite trends when going from bulk $\mathrm{MoS}_{2}$ to $1 \mathrm{~L}-\mathrm{MoS}_{2}$, so that their difference can be used to monitor $N .{ }^{49}$ The $E_{2 g}^{1}$ shift with $N$ may be attributed to stackinginduced structure changes, or long-range Coulombic interlayer interactions, ${ }^{49,55}$ while the $A_{1 g}$ shift is due to increasing restoring forces as additional layers are added. ${ }^{49,55}$ Further work is still needed to fully clarify and assign these trends.

Our focus here is on the C and LB modes that appear in the low-frequency region in the various LMs. ${ }^{56}$ These have been extensively studied in multilayer graphene. ${ }^{40-42,57}$ Unlike graphite and graphene, most LMs consist of more than one atomic element. For example, each $\mathrm{MoS}_{2}$ layer contains one Mo plane sandwiched by two S planes, while $\mathrm{Bi}_{2} \mathrm{Se}_{3}$ contains two Bi and three Se planes. This makes their lattice dynamics more complex than multilayer graphene, starting from the symmetry and force constants. Even $N L-\mathrm{MoS}_{2}\left(\mathrm{ENL}^{-} \mathrm{MoS}_{2}\right)$ belong to point group $\mathrm{D}_{6 h}$ with inversion symmetry, while odd $N \mathrm{~L}-\mathrm{MoS}_{2}\left(\mathrm{ONL}-\mathrm{MoS}_{2}\right)$ correspond to $\mathrm{D}_{3 h}$ without inversion symmetry. ${ }^{58}$ There are a few reports on C and LBMs in LMs other than graphene. Reference 59 reported them in bulk samples as: $\sim 21.5 \mathrm{~cm}^{-1}$ (C), $32.5 \mathrm{~cm}^{-1}(\mathrm{C}), \sim 50 \mathrm{~cm}^{-1}(\mathrm{LBM})$ for $\mathrm{As}_{2} \mathrm{Se}_{3}$ at 15 K ; $\sim 27 \mathrm{~cm}^{-1}(\mathrm{C}), 38 \mathrm{~cm}^{-1}(\mathrm{C}), \sim 60 \mathrm{~cm}^{-1}(\mathrm{LBM})$ for $\mathrm{As}_{2} \mathrm{~S}_{3}$ at


FIG. 1. (Color online) (a) Lattice structure and linear chain models of 2 and $3 \mathrm{~L}-\mathrm{MoS}_{2}$. Inversion symmetry applies to 2, not $3 \mathrm{~L}-\mathrm{MoS}_{2}$. (b) C modes and (c) LBMs in 2 and $3 \mathrm{~L}-\mathrm{MoS}_{2}$. (d) High-frequency optical vibration modes for 1 and $2 \mathrm{~L}-\mathrm{MoS}_{2}$. The symbol under each mode is its irreducible representation. R or IR indicate if the mode is Raman, or infrared active, or both. The theoretical results based on the diatomic chain model are also indicated.
$15 \mathrm{~K} ; \sim 34 \mathrm{~cm}^{-1}(\mathrm{C}), \sim 56 \mathrm{~cm}^{-1}$ (LBM) for $\mathrm{MoS}_{2} ; \sim 22 \mathrm{~cm}^{-1}$ (C) for $\mathrm{GaS} ; \sim 56 \mathrm{~cm}^{-1}$ (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 $10 \mathrm{~L}-\mathrm{MoS}_{2}$. Reference 52 observed only one set of C and LB modes for 2 to $6 \mathrm{~L}-\mathrm{MoS}_{2}$ and $9 \mathrm{~L}-\mathrm{MoS}_{2}$. Both did not consider the symmetry difference between ONL-MoS ${ }_{2}$ and ENL-MoS 2 , e.g., they assigned the C mode in $\mathrm{ONL} \mathrm{MoS}_{2}$ as $E_{2 g}^{2}$, but, as we show later, this is instead $E^{\prime}$. Reference 51 suggested that the scaling rule of the C mode in multilayer graphene ${ }^{40}$ cannot be extended to few-layer $\mathrm{MoS}_{2}$, 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 $\mathrm{MoS}_{2}$.

Here we report the shear and layer breathing modes for $N \mathrm{~L}-$ $\mathrm{MoS}_{2}$ up to $19 \mathrm{~L}-\mathrm{MoS}_{2}$, and bulk $\mathrm{MoS}_{2}$. We identify several groups of modes with frequencies dependent on $N$. ONL-MoS ${ }_{2}$ and $\mathrm{ENL}-\mathrm{MoS}_{2}$ 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

$\mathrm{NL}-\mathrm{MoS}_{2}$ samples are produced from bulk $\mathrm{MoS}_{2}$ (SPI Supplies) by mechanical exfoliation, following a similar procedure to that used for graphene samples. ${ }^{2,61} \mathrm{NL}-\mathrm{MoS}_{2}$ are supported on a Si wafer with $93-\mathrm{nm} \mathrm{SiO}_{2}$, 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. ${ }^{55}$ 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 $\sim 0.23 \mathrm{~mW}$ is used to avoid sample heating. The laser plasma lines are removed using a BragGrate 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 BragGrate notch filters with an optical density 3 and a spectral bandwidth $\sim 5-10 \mathrm{~cm}^{-1}$. This configuration is similar to that used in Ref. 40 for multilayer graphene. The spectral resolution is $\sim 0.6 \mathrm{~cm}^{-1}$, as estimated from the full width at half maximum (FWHM) of the Rayleigh peak.

Bulk $\mathrm{MoS}_{2}$ and $2 \mathrm{~L}-\mathrm{MoS}_{2}$ belong to the space group $\mathrm{P}_{3} / \mathrm{mmc}$ (point group $\mathrm{D}_{6 h}$ ), ${ }^{63}$ with unit cell consisting of two Mo atoms in sites with point group $\mathrm{D}_{3 h}$, and four S atoms in sites with point group $\mathrm{C}_{3 v},{ }^{53}$ as shown in Fig. 1(a). There are 18 normal vibration modes. ${ }^{63}$ The factor group of bulk and $2 \mathrm{~L}-\mathrm{MoS}_{2}$ at $\Gamma$ is $\mathrm{D}_{6 h}$, 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 $\mathrm{D}_{3 h}, \mathrm{~S}$ site group $\mathrm{C}_{3 v}$, and factor group $\mathrm{D}_{6 h}$ allows one to derive the following irreducible representations for the 18 normal vibration modes at $\Gamma:{ }^{53,65}$ $\Gamma=A_{1 g}+2 A_{2 u}+2 B_{2 g}+B_{1 u}+E_{1 g}+2 E_{1 u}+2 E_{2 g}+E_{2 u}$, with $A_{2 u}$ and $E_{1 u}$ translational acoustic modes, $A_{1 g}, E_{1 g}$, and $E_{2 g}$ Raman active, $A_{2 u}$ and $E_{1 u}$ infrared (IR) active. The $E_{1 g}$ and $A_{1 g}$ modes and one of the doubly degenerate $E_{2 g}$ modes, $E_{2 g}^{1}$, as shown in Fig. 1(d) for 2 L and bulk $\mathrm{MoS}_{2}$, give rise to Raman modes above $200 \mathrm{~cm}^{-1} .^{49}$ Only $A_{1 g}\left(\sim 408 \mathrm{~cm}^{-1}\right.$ in bulk and $\sim 405 \mathrm{~cm}^{-1}$ in $\left.2 \mathrm{~L}-\mathrm{MoS}_{2}\right)$ and $E_{2 g}^{1}\left(\sim 382 \mathrm{~cm}^{-1}\right.$ in bulk and $\sim 383 \mathrm{~cm}^{-1}$ in $2 \mathrm{~L}-\mathrm{MoS}_{2}$ ) can be observed when the laser excitation is normal to the sample basal plane. ${ }^{49}$ The other doubly degenerate $E_{2 g}$ mode, $E_{2 g}^{2}$, and one $B_{2 g}$ mode, $B_{2 g}^{2}$, are shear and LB modes. ${ }^{53,54,66} E_{2 g}^{2}$ corresponds to a rigid-layer displacement perpendicular to the $c$ axis (C mode), while $B_{2 g}^{2}$ corresponds to rigid-layer displacements parallel to the $c$ axis (LBM), as shown in Figs. 1(b) and 1(c) for $2 \mathrm{~L}-\mathrm{MoS}_{2}$.
$1 \mathrm{~L}-\mathrm{MoS}_{2}$ has $D_{3 h}$ symmetry, with three atoms per unit cell. ${ }^{63}$ The $\Gamma$ phonons can be expressed by the irreducible


FIG. 2. (Color online) (a) Raman spectra of 5, 6 L , and bulk $\mathrm{MoS}_{2}$. (b) Raman spectra of 5 and $6 \mathrm{~L}-\mathrm{MoS}_{2}$ measured for $X X$ (red) and $Y X$ (blue) polarizations. The irreducible representation of each mode is indicated.
representation of $D_{3 h}:{ }^{63,65} \Gamma=2 A_{2}^{\prime \prime}+A_{1}^{\prime}+2 E^{\prime}+E^{\prime \prime}$, where $A_{2}^{\prime \prime}$ and $E^{\prime}$ are acoustic modes, $A_{2}^{\prime \prime}$ is IR active, $A_{1}^{\prime}$ and $E^{\prime \prime}$ are Raman active, and another $E^{\prime}$ is both Raman and IR active. The $E^{\prime}$ and $A_{1}^{\prime}$ modes, Fig. 1(d), were previously detected in the Raman spectra of $1 \mathrm{~L}-\mathrm{MoS}_{2}$ at $\sim 384$ and $\sim 403 \mathrm{~cm}^{-1} .49$ Of course, no rigid-layer vibrations can exist in $1 \mathrm{~L}-\mathrm{MoS}_{2}$.
$3 \mathrm{~L}-\mathrm{MoS}_{2}$ has the same point group $\left(D_{3 h}\right)$ as $1 \mathrm{~L}-\mathrm{MoS}_{2}$, with $A_{1}^{\prime}$ and $A_{2}^{\prime \prime}$ corresponding to LBMs, and $E^{\prime}$ and $E^{\prime \prime}$ being C modes, Figs. 1(b) and 1(c). ENL-MoS ${ }_{2}$ belongs to point group $\mathrm{D}_{6 h}$ (with inversion symmetry), while ONL-MoS $\mathrm{S}_{2}$ corresponds to $\mathrm{D}_{3 h}$ (without inversion symmetry). ${ }^{58}$ Therefore, it is convenient to denote each mode of $\mathrm{NL}-\mathrm{MoS}_{2}$ by the corresponding irreducible representation according to the their point group, and then determine if they are Raman or IR active, or inactive.
$N L-\mathrm{MoS}_{2}$ 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 $N-1$ LBMs along the $c$ axis, and $N-1$ doubly degenerate shear modes perpendicular to it. When $N$ is even, there are 0 Raman active LBMs and $\frac{N}{2}$ doubly degenerate Raman active shear modes. When $N$ is odd, $\frac{N-1}{2}$ LBMs and $N-1$ doubly degenerate shear modes are Raman active. The interlayer distance in LMs is much larger than the in-plane bond length, e.g., in $\mathrm{MoS}_{2}$ the interlayer distance is $\sim 6.7 \AA$, while the in-plane bond length is $\sim 3.2 \AA .{ }^{67}$ 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 $\mathrm{MoS}_{2}$. In the high-frequency region above $200 \mathrm{~cm}^{-1}$, the $E_{2 g}^{1}\left(\sim 384 \mathrm{~cm}^{-1}\right), A_{1 g}\left(\sim 409 \mathrm{~cm}^{-1}\right), 2 \mathrm{LA}(\mathrm{M})\left(\sim 453 \mathrm{~cm}^{-1}\right)$,
and $A_{2 u}\left(\sim 463 \mathrm{~cm}^{-1}\right)$ modes are detected both in bulk and $6 \mathrm{~L}-\mathrm{MoS}_{2}$. Although the notation in $5 \mathrm{~L}-\mathrm{MoS}_{2}$ is different from 6 L and bulk $\mathrm{MoS}_{2}$ because of the different crystal symmetry, the modes $\left(E^{\prime}, A_{1}^{\prime}\right)$ are observed in $5 \mathrm{~L}-\mathrm{MoS}_{2}$. The line shape and peak positions in the high-frequency region for 5 L and 6 L $\mathrm{MoS}_{2}$ are almost identical, both being similar to bulk $\mathrm{MoS}_{2}$. In the low-frequency region below $100 \mathrm{~cm}^{-1}$, there is only one Raman peak $\sim 33 \mathrm{~cm}^{-1}$, i.e., $E_{2 g}^{2}$, in bulk $\operatorname{MoS}_{2}$. However, as discussed above, there should exist six Raman active modes for 5 L and three for $6 \mathrm{~L}-\mathrm{MoS}_{2}$. Of these, four and three shear modes should be doubly degenerate for 5 L and $6 \mathrm{~L}-\mathrm{MoS}_{2}$, respectively. Experimentally, we observe three modes below $60 \mathrm{~cm}^{-1}$ in 5L and four modes in $6 \mathrm{~L}-\mathrm{MoS}_{2}$, as for Fig. 2(a).

The LB $\left(A_{1}^{\prime}\right)$ and $\mathrm{C}\left(E^{\prime}, E^{\prime \prime}\right)$ Raman tensors in ONL-MoS ${ }_{2}$, and $\mathrm{C}\left(E_{2 g}^{2}\right)$ Raman tensor in ENL-MoS 2 are ${ }^{68,69}$

$$
\begin{aligned}
A_{1}^{\prime}(\mathrm{LB}, \mathrm{ONL}): & {\left[\begin{array}{lll}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & b
\end{array}\right], } \\
E^{\prime}(\mathrm{C}, \mathrm{ONL}): & :\left[\begin{array}{lll}
0 & d & 0 \\
d & 0 & 0 \\
0 & 0 & 0
\end{array}\right],\left[\begin{array}{ccc}
d & 0 & 0 \\
0 & -d & 0 \\
0 & 0 & 0
\end{array}\right], \\
E^{\prime \prime}(\mathrm{C}, \mathrm{ONL}): & :\left[\begin{array}{lll}
0 & 0 & 0 \\
0 & 0 & c \\
0 & c & 0
\end{array}\right],\left[\begin{array}{ccc}
0 & 0 & -c \\
0 & 0 & 0 \\
-c & 0 & 0
\end{array}\right], \\
E_{2 g}^{2}(\mathrm{C}, \mathrm{ENL}): & {\left[\begin{array}{lll}
0 & d & 0 \\
d & 0 & 0 \\
0 & 0 & 0
\end{array}\right],\left[\begin{array}{ccc}
d & 0 & 0 \\
0 & -d & 0 \\
0 & 0 & 0
\end{array}\right] }
\end{aligned}
$$



FIG. 3. (Color online) (a) Stokes and anti-Stokes Raman spectra of ONL-MoS ${ }_{2}$ in the low-frequency range. (b) Stokes and anti-Stokes Raman spectra of $E N L-\mathrm{MoS}_{2}$. The spectrum of bulk $\mathrm{MoS}_{2}$ 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 $N$. (d) FWHM of C and LBM as a function of $N$. Solid lines in (c), (d) are guides to the eye.

We do not discuss the $\mathrm{LBM}\left(B_{2 g}^{2}\right)$ in $\mathrm{ENL}-\mathrm{MoS}_{2}$ since it is Raman inactive. These tensors show that, in backscattering, the $A_{1}^{\prime}$ modes in $5 \mathrm{~L}-\mathrm{MoS}_{2}$ should appear only under unpolarized $X X$ configuration, and $E^{\prime}$ should exist under both unpolarized $X X$ and polarized $Y X$ configurations, while $E^{\prime \prime}$ should not appear for either $X X$ or $Y X$. Here $Y X$ indicates two mutually perpendicular axes within the basal plane of $N \mathrm{~L}-\mathrm{MoS}_{2}$, the first being the polarization direction of the incident laser, the second the analyzer's polarization. For $6 \mathrm{~L}-\mathrm{MoS}_{2}$ under backscattering, the $E_{2 g}^{2}$ modes exist for both $X X$ and $Y X$ configurations.

In Fig. 2(b) two sharp peaks are observed under both $X X$ and $Y X$ configurations at $\sim 19$ and $\sim 30 \mathrm{~cm}^{-1}$ for 5 L , and $\sim 23$ and $\sim 32 \mathrm{~cm}^{-1}$ for $6 \mathrm{~L}-\mathrm{MoS}_{2}$. According to the symmetry analysis discussed above, we assign these to $E^{\prime}$ in 5 L and $E_{2 g}^{2}$ in $6 \mathrm{~L}-\mathrm{MoS}_{2}$. Two broad peaks are observed for $X X$ measurements at $\sim 17$ and $47 \mathrm{~cm}^{-1}$ for $5 \mathrm{~L}-\mathrm{MoS}_{2}$, which we assign to $A_{1}^{\prime}$. Note that the lower $E^{\prime}$ mode of $5 \mathrm{~L}-\mathrm{MoS}_{2}$ at $\sim 19 \mathrm{~cm}^{-1}$ cannot be fully resolved for $X X$ measurements due to the presence of the broad $A_{1}^{\prime}$ mode at $\sim 17 \mathrm{~cm}^{-1}$. We also detect two Raman modes at $\sim 15$ and $41 \mathrm{~cm}^{-1}$ in $6 \mathrm{~L}-\mathrm{MoS}_{2}$. These are consistent with what should be optically silent $B_{2 g}^{2}$ LBMs, as discussed later. The symmetry, polarization, and mode frequency are summarized in Table I for the C and LB modes of 5 and $6 \mathrm{~L}-\mathrm{MoS}_{2}$. Although the in-plane modes in 5 and $6 \mathrm{~L}-\mathrm{MoS}_{2}$ above $200 \mathrm{~cm}^{-1}$ are almost identical, the C and LB mode positions below $100 \mathrm{~cm}^{-1}$ are different. The frequencies of all $5 \mathrm{~L}-\mathrm{MoS}_{2} \mathrm{LBMs}$ are higher than in $6 \mathrm{~L}-\mathrm{MoS}_{2}$, while all C modes are lower than in $6 \mathrm{~L}-\mathrm{MoS}_{2}$.

Figures 3(a) and 3(b) show the low-frequency Raman measurements for $N \mathrm{~L}-\mathrm{MoS}_{2}$, with $N=1-19$, as well as bulk $\mathrm{MoS}_{2}$. Since the point group of ONL-MoS $2_{2}\left(\mathrm{D}_{3 h}\right)$ is different from ENL-MoS ${ }_{2}\left(\mathrm{D}_{6 h}\right)$, we plot the Raman spectra of $\mathrm{ONL}^{-\mathrm{MoS}_{2}}$ [Fig. 3(a)] and ENL-MoS 2 [Fig. 3(b)] in two panels. Bulk $\mathrm{MoS}_{2}$ is included both in $\mathrm{ONL}-\mathrm{MoS}_{2}$ and

ENL-MoS $2_{2}$ panels because we cannot distinguish its parity in a (noninfinite) bulk sample. Of course, there are no LB or C modes in 1L-MoS 2 , as confirmed in Fig. 3(a). The two spikes $\sim 4.55 \mathrm{~cm}^{-1}$, 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 $\mathrm{C}_{11}$ from $\mathrm{C}_{11}=\rho \nu^{2} \pi^{2} / \mathrm{k}_{0}^{2}\left(\eta^{2}+\kappa^{2}\right)$, where $\rho$ is the Si density, $v$ is the LA mode frequency, $k_{0}=2 \pi / \lambda_{0}, \lambda_{0}$ is the incident light wavelength, and $(\eta+\mathrm{i} \kappa)$ is the Si complex refractive index. The $\mathrm{C}_{11}$ determined from our Raman measurements $\left(\sim 1.65 \times 10^{11} \mathrm{~Pa}\right)$ is consistent with $1.66 \times 10^{11} \mathrm{~Pa}$ measured by ultrasonic wave propagation. ${ }^{71}$ In $2 \mathrm{~L}-\mathrm{MoS}_{2}$ two Raman peaks are observed, while two overlapping bands are seen in 3L-MoS ${ }_{2}$. More Raman peaks are observed for thicker $\mathrm{MoS}_{2}$ 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 $\sim 22.6 \mathrm{~cm}^{-1}$ in 2 L to $32.5 \mathrm{~cm}^{-1}$ in $19 \mathrm{~L}-\mathrm{MoS}_{2}$, while one LBM softens from $\sim 40.1 \mathrm{~cm}^{-1}$ in 2 L to $4.7 \mathrm{~cm}^{-1}$ in 19L-MoS 2 , Fig. 3(c). The two sets of modes have different FWHM, Fig. 3(d). In 2L-MoS 2 , FWHM

TABLE I. Symmetry, polarization, and positions of C and LB modes in 5 and $6 \mathrm{~L}-\mathrm{MoS}_{2}$. The number (Num.) of each mode is indicated in the bracket before the mode.

|  | C |  | LBM |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 5L (Num.) mode | $(2) E^{\prime}(\mathrm{R}, \mathrm{IR})$ | $(2) E^{\prime \prime}(\mathrm{R})$ | $(2) A_{1}^{\prime}(\mathrm{R})$ | $(2) A_{2}^{\prime \prime}(\mathrm{IR})$ |
| polarization | $X X, Y X$ | $X Z, Y Z$ | $X X$ | - |
| exp. $\left(\mathrm{cm}^{-1}\right)$ | 19,30 | - | 17,47 | - |
| 6L (Num.) mode | $(3) E_{2 g}^{2}(\mathrm{R})$ | $(2) E_{1 u}(\mathrm{IR})$ | $(3) B_{2 g}^{2}($ silent $)$ | $(2) A_{2 u}(\mathrm{IR})$ |
| polarization | $X X, Y X$ | - | - | - |
| exp. $\left(\mathrm{cm}^{-1}\right)$ | 23,32 | - | $15,41(X X)$ | - |



FIG. 4. (Color online) Position of C modes as a function of $N$ for (a) $\mathrm{ENL}_{\mathrm{MoS}}^{2}$ and (b) $\mathrm{ONL}^{\left(\mathrm{MoS}_{2} \text {. Position of LBMs as a function }\right.}$ of $N$ for (c) $\mathrm{ENL}-\mathrm{MoS}_{2}$ and (d) $\mathrm{ONL}-\mathrm{MoS}_{2}$. The blue open circles are the experiment data. The red crosses are the diatomic chain model calculations. The irreducible representation of each mode is also indicated. Solid lines are guides to the eye.
(LBM $\sim 40.1 \mathrm{~cm}^{-1}$ ) is $\sim 9.6 \mathrm{~cm}^{-1}$, much larger than that $\left(\sim 0.8 \mathrm{~cm}^{-1}\right)$ of the C mode at $22.6 \mathrm{~cm}^{-1}$. All data for ENL- and ONL-MoS ${ }_{2}$ are summarized in Figs. 4(a)-4(d). According to group analysis, there should be no Raman active LBMs in ENL-MoS 2 . However, a set of peaks are observed in ENL- $\mathrm{MoS}_{2}$, with the same polarization behavior as LBMs in ONL-MoS 2 , e.g., the two Raman modes $\sim 15$ and $41 \mathrm{~cm}^{-1}$ in $6 \mathrm{~L}-\mathrm{MoS}_{2}$ in Fig. 2(b). Because their measured positions match well those predicted for LBMs, i.e., the $B_{2 g}^{2}$ modes in ENLs as discussed later, they are included in Fig. 4(c).

Since a $\mathrm{MoS}_{2}$ 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 $3 \mathrm{~L}-\mathrm{MoS}_{2}$. Only two force constants are needed to describe the vibrations: $\alpha_{\mathrm{ss}}$ and $\alpha_{\mathrm{sm}}$, where $\alpha_{\mathrm{ss}}$ is the force constant per unit area between two nearest $S$ planes in two adjacent layers, and $\alpha_{\mathrm{sm}}$ is force constant per unit area between the nearest S and Mo planes within a $\mathrm{MoS}_{2}$ layer. Their components perpendicular to the basal plane, $\alpha_{\mathrm{ss}}^{\perp}$ and $\alpha_{\mathrm{sm}}^{\perp}$, determine the LBMs lattice dynamics, while those parallel to the basal plane, $\alpha_{\mathrm{ss}}^{\|}$and $\alpha_{\mathrm{sm}}^{\|}$, determine the C modes dynamics. The reduced mass for one $\mathrm{S}(\mathrm{Mo})$ plane, $m_{\mathrm{S}}\left(m_{\mathrm{Mo}}\right)$, is its atomic mass per unit area. In $\mathrm{MoS}_{2}, m_{\mathrm{S}}=0.6 \times 10^{-7} \mathrm{~g} / \mathrm{cm}^{2}$ and $m_{\mathrm{Mo}}=$ $1.8 \times 10^{-7} \mathrm{~g} / \mathrm{cm}^{2} . \alpha_{\mathrm{sm}}^{\perp}$ and $\alpha_{\mathrm{sm}}^{\|}$can be estimated from the highfrequency $A_{1}^{\prime}$ and $E^{\prime}$ modes of $1 \mathrm{~L}-\mathrm{MoS}_{2}$. In $1 \mathrm{~L}-\mathrm{MoS}_{2}, 9 \times 9$ dynamical matrices can be constructed and solved analytically.

We get $\omega_{A_{1}^{\prime}}=(1 / 2 \pi c) \sqrt{2 \alpha_{\mathrm{sm}}^{\perp} / \mu}$, with $\mu=2 m_{\mathrm{S}}$, 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 $1 \mathrm{~L}-\mathrm{MoS}_{2}$, corresponding to a spring connected by two S atoms with a force constant per unit area $2 \alpha_{\mathrm{sm}}^{\perp}$, since the Mo atom stays still at the spring equilibrium position. We measure $\omega_{A_{1}^{\prime}} \sim 403 \mathrm{~cm}^{-1}$ in $1 \mathrm{~L}-\mathrm{MoS}_{2}$. This gives $\alpha_{\mathrm{sm}}^{\perp}=$ $3.46 \times 10^{21} \mathrm{~N} / \mathrm{m}^{3}$. We also get $\omega_{E^{\prime}}=(1 / 2 \pi c) \sqrt{2 \alpha_{\mathrm{sm}}^{\|} / \mu}$, where $1 / \mu=1 / m_{M_{0}}+1 /\left(2 m_{\mathrm{S}}\right)$. 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 $1 \mathrm{~L}-\mathrm{MoS}_{2}$, corresponding to a spring connected by two S atoms and one Mo atom with a force constant per unit area $2 \alpha_{\mathrm{sm}}^{\|}$. From the experimental $384 \mathrm{~cm}^{-1}$, we get $\alpha_{\mathrm{sm}}^{\|}=1.88 \times 10^{21} \mathrm{~N} / \mathrm{m}^{3}$. Note that the weak interaction of the two S planes in the $\mathrm{MoS}_{2}$ layers is not included because the S-S plane distance is twice the S-Mo one.

To understand the C modes of $\mathrm{NL}-\mathrm{MoS}_{2}$, the layer coupling between two nearest $S$ planes in the two adjacent layers should be included. $3 N \times 3 N$ dynamical matrices can be constructed for $N \mathrm{~L}-\mathrm{MoS}_{2}$. By numerically solving the eigenequation for $\mathrm{NL}-\mathrm{MoS}_{2}$, we get the eigenfrequencies and corresponding eigenvectors. By fitting these to our experimental data we get: $\alpha_{\mathrm{ss}}^{\perp}=8.90 \times 10^{19} \mathrm{~N} / \mathrm{m}^{3}$ and $\alpha_{\mathrm{ss}}^{\|}=$ $2.82 \times 10^{19} \mathrm{~N} / \mathrm{m}^{3}$. Multiplying $\alpha_{\mathrm{ss}}^{\perp}$ and $\alpha_{\mathrm{SS}}^{\|}$by the unit cell
area gives the interlayer force constants, $k_{\mathrm{ss}}^{\text {shear }}=2.5 \mathrm{~N} / \mathrm{m}$ and $k_{\mathrm{ss}}^{\mathrm{LBM}}=7.8 \mathrm{~N} / \mathrm{m}$. They agree well with those for bulk samples reported in Ref. $59\left(k_{1}^{\text {shear }}=2.7 \mathrm{~N} / \mathrm{m}\right.$ and $\left.k_{1}^{\text {comp }}=7.4 \mathrm{~N} / \mathrm{m}\right)$, 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 $\alpha_{\mathrm{ss}}^{\|}$by the equilibrium distance between two adjacent $\mathrm{MoS}_{2}$ layers gives a shear modulus $\sim 18.9 \mathrm{GPa}$, in good agreement with that measured for bulk $\mathrm{MoS}_{2},{ }^{72}$ 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 $3 \mathrm{~L}-\mathrm{MoS}_{2}$, derived from the corresponding eigenequations, are depicted in Figs. 1(b) and 1(c). Applying symmetry analysis to the corresponding $\mathrm{NL}-\mathrm{MoS}_{2}$ eigenvectors, we assign the irreducible representations of the corresponding point group to each mode. The eigenfrequencies of Raman active rigid-layer vibrations for $E_{2 g}^{2}\left(\mathrm{C}\right.$ modes in $\left.\mathrm{ENL}-\mathrm{MoS}_{2}\right), E^{\prime}(\mathrm{C}$ modes in $\mathrm{ONL}-\mathrm{MoS}_{2}$ ), and $A_{1}{ }^{\prime}\left(\mathrm{LBMs}\right.$ in $\left.\mathrm{ONL}-\mathrm{MoS}_{2}\right)$ are summarized in Figs. 4(a), 4(b), and 4(d). The eigenfrequencies of the Raman inactive $B_{2 g}^{2}$ (LBMs) in ENL-MoS 2 are also included in Fig. 4(c). The eigenfrequencies of the modes for $1 \mathrm{~L}-, 2 \mathrm{~L}-$, and $3 \mathrm{~L}-\mathrm{MoS}_{2}$ 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 $B_{2 g}^{2}$. This suggests that the Raman inactive LBMs $\left(B_{2 g}^{2}\right)$ in ENL-MoS 2 might be observed, with polarization behavior identical to the $A_{1}^{\prime}$ (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 ( $E_{2 g}^{2}$ ) and one $\operatorname{LBM}\left(B_{2 g}^{2}\right)$ are observed in $2 \mathrm{~L}-\mathrm{MoS}_{2}$. Each splits in two branches with increasing $N$, one stiffening, the other softening with $N$. A new mode appears when $N$ increases up to $4 N+2, N=1,2,3, \ldots$, and splits into two branches again for higher $N$. The C modes ( $E^{\prime}$ ) [Fig. 4(b)] and LBMs ( $A_{1}^{\prime}$ ) [Fig. 4(d)] in ONL-MoS 2 exhibit similar trends with $N$ as the C modes ( $E_{2 g}^{2}$ ) [Fig. 4(a)] and LBMs $\left(B_{2 g}^{2}\right)$ [Fig. 4(c)] in $\mathrm{ENL}^{-} \mathrm{MoS}_{2}$, but with decreasing frequency for $E^{\prime}$ and increasing frequency for $A_{1}^{\prime}$. 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 $2_{2}$, 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 $22.6 \mathrm{~cm}^{-1}\left(E_{2 g}^{2}\right)$ in $2 \mathrm{~L}-\mathrm{MoS}_{2}$ blue-shifts to $28 \mathrm{~cm}^{-1}\left(E^{\prime}\right)$ in $3 \mathrm{~L}-\mathrm{MoS}_{2}$, and to $32.5 \mathrm{~cm}^{-1}\left(E^{\prime}\right)$ in $19 \mathrm{~L}-\mathrm{MoS}_{2}$, reaching $\sim 32.7 \mathrm{~cm}^{-1}\left(E_{2 g}^{2}\right)$ in bulk $\mathrm{MoS}_{2}$. 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 $\omega_{\text {bulk }} / \omega_{2 \mathrm{LG}}=\sqrt{2}$. In our $\mathrm{MoS}_{2}$ 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 LBM at $40 \mathrm{~cm}^{-1}\left(B_{2 g}^{2}\right)$ in


FIG. 5. (Color online) Position of (a) $C$ modes and (b) LBMs as a function of $N$. The blue open circles are the experimental data. The diameter of the circles represents the Raman intensity of each mode. The red crosses are calculations based on the diatomic chain model (DCM). The black solid lines in (a) and (b) are, respectively, fitted by $\omega_{C}(N)=\omega_{C}(2) \sqrt{1+\cos \left(N_{0} \pi / N\right)}(N \geqslant$ $\left.2 N_{0}\right)$ and $\omega_{\text {LBM }}(N)=\omega_{\mathrm{LBM}}(2) \sqrt{1-\cos \left(N_{0} \pi / N\right)}\left(N \geqslant 2 N_{0}\right)$ for the phonon branches originating from $2 \mathrm{~L}-\left(N_{0}=1\right)$, $6 \mathrm{~L}-\left(N_{0}=3\right)$ and $10 \mathrm{~L}\left(N_{0}=5\right)-\mathrm{MoS}_{2}$ based on the monatomic chain model (MCM). The gray dashed lines are another set of the C and LB modes based on the MCM.

2 L red-shifts to $29 \mathrm{~cm}^{-1}\left(A_{1}^{\prime}\right)$ in $3 \mathrm{~L}-\mathrm{MoS}_{2}$, and $5 \mathrm{~cm}^{-1}\left(A_{1}^{\prime}\right)$ in $19 \mathrm{~L}-\mathrm{MoS}_{2}$. The blue-shifted branch reaches $56.8 \mathrm{~cm}^{-1}$ in $19 \mathrm{~L}-\mathrm{MoS}_{2}$, close to the LBM value in bulk $\mathrm{MoS}_{2} .{ }^{73}$

For C and LB modes in $N \mathrm{~L}-\mathrm{MoS}_{2}$, 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 $2 \mathrm{~L}-$ $\mathrm{MoS}_{2}$ 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 ( $m_{\mathrm{Mo}}+$ $2 m_{s}$ ) and interlayer bonding $\alpha_{\mathrm{ss}}^{\perp}$ for LBMs, and $\alpha_{\mathrm{ss}}^{\|}$for C modes, we get: $\omega_{\mathrm{LBM}}=(1 / \sqrt{2} \pi c) \sqrt{\alpha_{\mathrm{ss}}^{\perp} /\left(m_{\mathrm{Mo}}+2 m_{s}\right)}, \omega_{C}=$ $(1 / \sqrt{2} \pi c) \sqrt{\alpha_{\mathrm{ss}} /\left(m_{\mathrm{Mo}}+2 m_{s}\right)}$ for $2 \mathrm{~L}-\mathrm{MoS}_{2}$, with $\omega_{\mathrm{LBM}}$ the LBM position, and $\omega_{C}$ the C peak position. The corresponding $\omega_{\text {LBM }}\left(40.8 \mathrm{~cm}^{-1}\right)$ and $\omega_{C}\left(23.0 \mathrm{~cm}^{-1}\right)$ are in good agreement
with those from the DCM ( $\omega_{\text {LBM }}=40.3 \mathrm{~cm}^{-1}$ and $\omega_{C}=$ $22.9 \mathrm{~cm}^{-1}$ ) and the experimental data ( $\omega_{\text {LBM }}=40.2 \mathrm{~cm}^{-1}$ and $\omega_{C}=22.6 \mathrm{~cm}^{-1}$ ). 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 $\mathrm{ENL}^{-\mathrm{MoS}_{2}}$, i.e., $2,4,6,8 \mathrm{~L}, \ldots-\mathrm{MoS}_{2}$, at about the same position as that of the C mode or LBM in $2 \mathrm{~L}-\mathrm{MoS}_{2}$, 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 $\omega(N)=\omega\left(2 N_{0}\right) \sqrt{1 \pm \cos \left(N_{0} \pi / N\right)}\left(N \geqslant 2 N_{0}\right.$, and $N_{0}$ an integer: $1,2,3,4 \ldots$ ), with + for the high-frequency subbranch and - for the low-frequency one. Our calculations show that $\omega\left(2 N_{0}\right)$ is almost the same as $\omega(2)$ both for C and LB modes. Therefore, the evolution of C and LB modes with increasing $N$ can be further simplified as $\omega(N)=\omega(2) \sqrt{1 \pm \cos \left(N_{0} \pi / N\right)}$ ( $N \geqslant 2 N_{0}$, and $N_{0}$ an integer: $1,2,3,4 \ldots$ ).

For $N \mathrm{~L}-\mathrm{MoS}_{2}$ 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 LBM subbranches is consistent with the bulk case, where the C mode $E_{2 g}^{2}$ is Raman-active while the LBM $B_{2 g}^{2}$ is optical-inactive. For the observed high-frequency C subbranch originating from 2 L $\operatorname{MoS}_{2}$, we have $N_{0}=1$, thus $\omega_{C}(N)=\omega_{C}(2) \sqrt{1+\cos (\pi / N)}$ $(N \geqslant 2)$, where $\omega_{C}(2)=23.0 \mathrm{~cm}^{-1}$. If we replace $\omega_{C}(2) \sim 23.0 \mathrm{~cm}^{-1}$ in $\mathrm{MoS}_{2}$ with $\omega_{C}(2) \sim 31 \mathrm{~cm}^{-1}$, this relation describes the C peaks in multilayer graphene. ${ }^{40}$ Similarly, $\quad \omega_{C}(N)=\omega_{C}(2) \sqrt{1+\cos (3 \pi / N)} \quad(N \geqslant 6)$ for the high-frequency subbranch originating from $6 \mathrm{~L}-\mathrm{MoS}_{2}$, and $\omega_{C}(N)=\omega_{C}(2) \sqrt{1+\cos (5 \pi / N)} \quad(N \geqslant 10)$ for the high-frequency subbranch originating from $10 \mathrm{~L}-\mathrm{MoS}_{2}$. For the observed LBMs in $\mathrm{MoS}_{2}$, the relation between frequency and $N$ in the low-frequency subbranch originating from 2,6 and $10 \mathrm{~L}-\mathrm{MoS}_{2}$ is: $\omega_{\mathrm{LBM}}(N)=\omega_{\mathrm{LBM}}(2) \sqrt{1-\cos (i * \pi / N)}$ $(N \geqslant 2 * i), i=1,3,5$, where $\omega_{\text {LBM }}(2)=40.8 \mathrm{~cm}^{-1}$. This well matches with the experiments, Figs. 5(a) and 5(b). Figure 5 also shows another sub-branch for 2, 6, and $10 \mathrm{~L}-\mathrm{MoS}_{2}$, 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 prediction.

Note that any coupling between supported $\mathrm{MoS}_{2}$ and the substrate is not included in our chain models. The agreement
between experiments and model predictions means that the coupling between $\mathrm{MoS}_{2}$ and the substrate does not play a major role, the scaling with $N$ being only determined by the interaction between the $\mathrm{MoS}_{2}$ 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 2 L 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 $\sim 38.6 \mathrm{~cm}^{-1}$ and $85.6 \mathrm{~cm}^{-1}$, respectively. ${ }^{57}$ Our model predicts that the C mode generates two branches, $\omega_{C}(N)=38.6 \sqrt{1+\cos (\pi / N)}(N \geqslant$ 2) at higher frequency, and $\omega_{C}(N)=38.6 \sqrt{1-\cos (\pi / N)}$ $(N \geqslant 2)$ at lower. The LBM also generates two branches, $\omega_{\text {LBM }}(N)=85.6 \sqrt{1+\cos (\pi / N)} \quad(N \geqslant 2)$ at higher frequency, and $\omega_{\text {LBM }}(N)=85.6 \sqrt{1-\cos (\pi / N)}(N \geqslant 2)$ at lower. Similarly, the C mode $\left(\sim 38.6 \mathrm{~cm}^{-1}\right)$ and LBM $\left(\sim 85.6 \mathrm{~cm}^{-1}\right)$ in $4 \mathrm{~L}-\mathrm{hBN}$, will also generate two branches, and so on. Thus, we can predict all the C and LB modes in $N$ L-hBN.

## III. CONCLUSIONS

We characterized single- and few-layer $\mathrm{MoS}_{2}$ 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 $\mathrm{MoS}_{2}$ and any other layered material with any number of layers.

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