Molybdenum disulfide (MoS$_2$) is systematically studied using Raman spectroscopy with ultraviolet and visible laser lines. It is shown that only the Raman frequencies of $E_{2g}$ and $A_{1g}$ peaks vary monotonously with the layer number of ultrathin MoS$_2$ flakes, while intensities or widths of the peaks vary arbitrarily. The coupling between electronic transitions and phonons are found to become weaker when the layer number of MoS$_2$ decreases, attributed to the increased electronic transition energies or elongated intralayer atomic bonds in ultrathin MoS$_2$. The asymmetric Raman peak at 454 cm$^{-1}$, which has been regarded as the overtone of longitudinal optical M phonons in bulk MoS$_2$, is actually a combination band involving a longitudinal acoustic mode (LA(M)) and an optical mode ($A_{mn}$). Our findings suggest a clear evolution of the coupling between electronic transition and phonon when MoS$_2$ is scaled down from three- to two-dimensional geometry.

1. Introduction

Molybdenum disulfide (MoS$_2$) has a layered structure of hexagons that consist of covalently bonded Mo and S atoms. A plane of Mo atoms is sandwiched covalently between two planes of S atoms in a trigonal prismatic arrangement. Bulk MoS$_2$ is built up of S-Mo-S layers attached to each other through Van der Waals forces, and it is a good semiconducting material that can be employed for photovoltaic and photocatalyst applications.$^{[1-3]}$

In the past a few years, ultrathin MoS$_2$ flakes have been successfully obtained using the Scotch-tape method.$^{[4]}$ Field-effect transistors (FETs) based on monolayer MoS$_2$ have shown a larger current on/off ratio ($\sim 10^8$).$^{[5]}$ Theoretically, MoS$_2$ transistors could have even a second-order process involving the longitudinal phonons in ultrathin MoS$_2$ flakes are addressed. With resonance, four first-order Raman active modes at $32 \text{ cm}^{-1}$ ($E_{1g}$), $286 \text{ cm}^{-1}$ ($E_{2g}$), $383 \text{ cm}^{-1}$ ($E_{1g}$), and $408 \text{ cm}^{-1}$ ($A_{1g}$) in bulk MoS$_2$ can be observed. The $E_{1g}$ mode is forbidden in back-scattering experiment on a basal plane. The in-plane $E_{1g}$ mode results from opposite vibration of two S atoms with respect to the Mo atom while the $A_{1g}$ mode is associated with the out-of-plane vibration of only S atoms in opposite directions.$^{[14]}$ On resonance, more Raman peaks are observed in bulk MoS$_2$ due to strong electron–phonon couplings. The most prominent mode around 460 cm$^{-1}$ arises from a second-order process involving the longitudinal acoustic phonons at M point (LA(M)). Most of the new peaks are typically assigned to multiphonon bands involving LA(M) and other phonons at M point.$^{[10,13]}$ Very recently, Lee et al. reported on the layer thickness dependent $E_{1g}$ and $A_{1g}$ peak frequencies, intensities and widths in ultrathin MoS$_2$ flakes.$^{[15]}$ In contrast, we find that the Raman frequencies of $E_{1g}$ and $A_{1g}$ peaks, instead of the intensities and widths of the peaks, vary monotonously with the layer number of ultrathin MoS$_2$ flakes and can be used as reliable features to identify the layer number. In this paper, we present systematic Raman study of ultrathin MoS$_2$ flakes using various laser lines. With resonance Raman spectroscopy, the couplings between the electronic structure and phonons in ultrathin MoS$_2$ flakes are addressed.

2. Results and Discussion

MoS$_2$ flakes were mechanically exfoliated from a piece of commercially available nature crystalline MoS$_2$ sample (SPI Supplies) with Scotch tape.$^{[16]}$ Figure 1a shows the optical image of a MoS$_2$ flake (sample S1) consisting of monolayer (1 L), bilayer...
MoS$_2$. The very different PL spectra between mono layer and multilayer MoS$_2$ is consistent with the theoretical prediction that a monolayer MoS$_2$ is a direct bandgap material, while a multilayer MoS$_2$ is an indirect material.

Figure 2a shows the Raman spectra of sample S1 excited by 488 nm line in air ambient environment. $E_{12g}$ ($\sim 383$ cm$^{-1}$ for bulk MoS$_2$) and $A_{1g}$ ($\sim 408$ cm$^{-1}$ for bulk MoS$_2$) modes are observed in both ultrathin and bulk MoS$_2$. (The $E_{22g}$ mode is not detectable due to the constrain of our Rayleigh line rejection filter ($>100$ cm$^{-1}$)). It is found that the frequency of $E_{12g}$ peak decreases while that of the $A_{1g}$ peak increases with increasing layer number. When the layer number increases, the interlayer Van der Waals force in MoS$_2$ suppresses atom vibration, resulting in higher force constants. Thus, both $E_{12g}$ and $A_{1g}$ modes are supposed to stiffen (blue-shift). The observed blue-shift of $A_{1g}$ peak with increasing layer number is consistent with the predicted stiffening. On the contrary, $E_{12g}$ peak shows a red-shift, instead of a blue-shift, suggesting that the increased interlayer Van der Waals force plays a minor role while stacking-induced structure changes or long-range Coulombic interlayer interactions in multilayer MoS$_2$ may dominate the change of atomic vibration. Such thickness-dependent Raman spectra are found in more than a dozen of MoS$_2$ flakes with different layer numbers (see Figure S1 and S2a of the Supporting Information). Figure 2b shows the Raman mapping image with $E_{12g}$ peak intensity using 488 nm laser line. It is noted that the contrast of the image with $E_{12g}$ peak intensity is not uniform.

Figure 1. Optical image, AFM image and photoluminescence spectra of sample S1. a) Optical image of sample S1 placed on the surface of a heavily doped silicon wafer capped by 285-nm-thick silicon dioxide. The number of layers (1 L, 2 L, 3 L, 4 L and bulk) are labeled. b) AFM height image of the region inside the green square in (a). Inset: color bar of height signal. c) Height profile along the dashed line in (b). Inset: 3D plot of the AFM height signal. d) Photoluminescence and Raman spectra of sample S1. "1 L", "2 L", "3 L", and "4 L" indicate monolayer, bilayer, trilayer, and quadrilayer, respectively.

(2 L), trilayer (3 L), quadrilayer (4 L), and bulk (indicates thick layer) MoS$_2$ on a heavily doped p-type silicon wafer capped by a 285-nm-thick thermally grown silicon dioxide (SiO$_2$) layer. The number of the layers can be easily identified through the different optical contrasts, as shown in Figure 1a (the layer numbers are labeled). The height image obtained from a tapping-mode atomic force microscopy (AFM) measurement of the square region in Figure 1a (solid green lines) is shown in Figure 1b. A height profile along the dashed line in Figure 1b is depicted in Figure 1c, where the three-dimensional AFM height image is inserted. It is noted that the height of a monolayer MoS$_2$ on SiO$_2$ substrate is about 0.8–1.0 nm while that of a monolayer on MoS$_2$ flake is only 0.5–0.7 nm, consistent with the theoretical thickness of 6.15 Å. The deviation could imply that the monolayer MoS$_2$ on SiO$_2$ substrate has absorbents on its surface so that it is thicker than the theoretical thickness.

Figure 1d depicts the photoluminescence (PL) and Raman spectra of sample S1 excited by 532 nm line at room temperature. One can see that the strongest PL signal is associated with monolayer MoS$_2$, while the bulk MoS$_2$ shows a negligible PL signal. The two PL peaks around 670 and 630 nm correspond to the A1 and B1 direct excitonic transitions at 1.85 and 1.97 eV, respectively. It is worth noting that the PL signals of bilayer, trilayer, and quadrilayer MoS$_2$ are significantly weaker than that of monolayer MoS$_2$. The stronger PL emission in monolayer MoS$_2$ was attributed to much slower electronic relaxation arising from the unique electronic structure of monolayer MoS$_2$. The very different PL spectra between monolayer and multilayer MoS$_2$ is consistent with the theoretical prediction that a monolayer MoS$_2$ is a direct bandgap material, while a multilayer MoS$_2$ is an indirect material.
even in a region of a given thickness. It is even more difficult to differentiate layer numbers with \( E_{1\text{g}}^{2\text{g}} \) peak width mapping (see Figure S2b of the Supporting Information). In addition, we were not able to distinguish layer numbers with \( A_{1\text{g}} \) peak intensity or width.

Figure 2c depicts the frequency mapping of \( E_{1\text{g}}^{2\text{g}} \) peak (recorded simultaneously with those Raman images shown in Figure 2b), where the brighter color represents the blue-shift of \( E_{1\text{g}}^{2\text{g}} \) peak. One can see that uniform color contrast in each region precisely corresponds to different thicknesses. It is noted that the brighter the color, the thinner the MoS\(_2\) layer. The Raman frequency mapping of \( A_{1\text{g}} \) peak is shown in Figure 2d, where the darker color indicates the red-shift of \( A_{1\text{g}} \) peak. Figure 2e shows the frequency profiles of \( E_{1\text{g}}^{2\text{g}} \) and \( A_{1\text{g}} \) peaks along the lines a–b and A–B drawn in Figures 2c and 2d. One can see that the frequency variation corresponds to the change in the layer number very well. The results are consistent with the aforementioned optical, AFM, and PL measurements.
Most importantly, the peak frequencies are uniform for a given thickness. These observations show that the \( E_{1g} \) and \( A_{1g} \) peak frequencies can be used to identify the layer number of an ultrathin MoS\(_2\) flake with much higher accuracy than the intensities and widths of the peaks.

Figure 3a displays the Raman spectra of sample S1 excited by 325 nm line. The evident peak broadening could be caused by the low spectral resolution of the Raman spectroscopy with 325 nm laser. The frequencies of \( E_{1g} \) and \( A_{1g} \) peaks excited by 325, 488 and 532 nm laser lines are displayed in Figure 3b for comparison. Similar dependences of the peak frequencies on the layer number are observed (see Figure S2 for Raman spectra from more MoS\(_2\) flakes). In obvious contrast, the Raman spectra excited by 632.8 nm line have more Raman peaks, as depicted in Figure 3c. On the spectrum of bulk MoS\(_2\), the peaks around 180, 454, and 634 cm\(^{-1}\) are observed (besides the \( E_{1g} \) \((382\ \text{cm}^{-1})\) and \( A_{1g} \) \((407\ \text{cm}^{-1})\) peaks) owing to the resonance Raman (RR) scattering, because the 632.8 nm line is in resonance with the direct band gap \((1.96\ \text{eV})\) at the K point. The assignment of the asymmetric peak centered at 454 cm\(^{-1}\) in bulk MoS\(_2\) is an open question. It was previously assigned to the double frequency of the LA(M) mode \((227\ \text{cm}^{-1})\). Nevertheless, Frey et al. argue that it consists of two peaks, i.e., a second-order zone-edge phonon peak \(2\text{LA(M)}\) and a first-order optical phonon peak \( A_{1u}\). A closer look in Figure 3d reveals that the asymmetric feature splits into three peaks around 440, 450, and 459 cm\(^{-1}\) in ultrathin MoS\(_2\), providing a supportive evidence for Frey et al.’s argument. The Raman peak \((D)\) at 440 cm\(^{-1}\) can be ascribed to Mo-S vibrations for oxysulfide species. Oxygen may attack Mo-S-Mo bonds, especially at the edge of the flake, because of the existing dangling bonds. The oxygen-related peak appears only in ultrathin MoS\(_2\) implies that oxygen is able to attack only surface layers. This finding indicates that passivation of monolayer/few-layer MoS\(_2\) based optoelectronic devices is necessary to prevent oxygen from influencing device performances. Upon fitting, we obtain a LA(M) peak frequency of 226 cm\(^{-1}\) and \( A_{1u}\) peak frequency of 462 cm\(^{-1}\) (see Figure 3d). The peaks centered at 180 and 634 cm\(^{-1}\) are then assigned to \( A_{1g}(M) - \text{LA(M)} \) and \( A_{1g}(M) + \text{LA(M)} \) Raman modes, respectively. Thus, the \( A_{1g}(M) \) peak frequency is estimated as \(407 \pm 1\ \text{cm}^{-1}\), close to the \( A_{1g}(\Gamma) \) peak frequency, consistent with the fact that the dispersion of \( A_{1g} \) mode in the \( \Gamma - M \) direction is small.

The intensity of \( A_{1g} \) peak is comparable with that of \( E_{1g} \) peak on the off-resonance spectra of sample S1 (see Figure 2a), whereas the intensity of \( A_{1g} \) peak is greatly enhanced with respect to that of \( E_{1g} \) peak under the resonance condition. The final state of direct electronic transition (K point) is mainly related to \( d_{x^2-y^2} \) orbitals of Mo atoms that are aligned along the same direction (\( c \) axis) as the atomic displacements involved.
in $A_{1g}$ mode. Thus, a strong electron-phonon coupling along $c$ axis is expected in RR scattering, resulting in the enhanced $A_{1g}$ peak. However, such an enhancement almost disappears in ultrathin MoS$_2$, indicating a weaker coupling between electronic transition at K point with $A_{1g}$ phonon in ultrathin MoS$_2$ flakes. The weakened coupling could be ascribed to the increased transition energy at K point due to quantum confinement along the $c$ axis or elongated intralayer bonds in ultrathin MoS$_2$. The shoulder of $A_{1g}$ peak in bulk MoS$_2$ evolves into an individual peak at 415 cm$^{-1}$ in ultrathin MoS$_2$. This peak has been interpreted through a Raman-inactive mode ($B_{1u}$) due to a two-phonon scattering process involving a longitudinal quasi-acoustic phonon and a transverse optical phonon. Both theoretical and experimental results suggest that the peak frequency of 415 cm$^{-1}$ corresponds to an energy difference $\Delta E$ of 0.1 eV between the excitation laser energy ($E_l$) and that of $A_1$ excitons ($E_{11}$). Thus, $E_{11}$ can be obtained as $E_l - \Delta E = 1.86$ eV, giving $E_{11}$ of 1.96 eV (632.8 nm). This estimation result agrees very well with $A_1$ exciton energy of 1.85 eV obtained from PL measurement (see Figure 1d). Moreover, the deduced value of $E_{11}$ is comparable with 1.83 eV obtained by other group, suggesting the validity of our assignment. The $B_{1u}$ peak that forms a Davydov pair with $A_{1g}$ peak appears due to the resonant effect. The small frequency difference (7 cm$^{-1}$) between $A_{1g}$ and $B_{1u}$ peak indicates the weak interlayer interaction. Similar observations are found in different MoS$_2$ flakes, as shown in Figure S3 of the Supporting Information.

The Raman spectra of sample S2 (see inset for the optical image) excited by 532 nm laser line are depicted in Figure 4a. In comparison with sample S1, sample S2 is so small that it is difficult to resolve the different thicknesses using optical microscopy with the 100x objective. Interestingly, the Raman mapping images give a higher resolution than the optical images, as shown in Figures 4b and c. Regions with different layer numbers are unambiguously distinguished by clear boundaries. The $E_{1g}$ and $A_{1g}$ peak frequencies measured using different laser lines are summarized in Table 1. As the layer number increases, two notable features can be seen: 1) a red-shift about 2.2 cm$^{-1}$ (standard deviation of 0.7) is associated with the $E_{1g}$ peak, and 2) a blue-shift of 4.1 cm$^{-1}$ (standard deviation of 1.0) is observed for the $A_{1g}$ peak. Moreover, the $E_{1g}$ and $A_{1g}$ peak frequencies of 384.6 cm$^{-1}$ (standard deviation of 0.3) and 403.4 cm$^{-1}$ (standard deviation of 0.5) are obtained for monolayer MoS$_2$. The small deviation values imply that Raman spectroscopy could serve as a reliable tool for identifying monolayer MoS$_2$.

3. Conclusions

Ultrathin MoS$_2$ flakes have been investigated systematically using Raman and resonance Raman spectroscopy. The frequencies, widths and intensities of the Raman $E_{1g}$ and $A_{1g}$ peaks are strongly influenced by the thicknesses of the ultrathin flakes. However, only the frequencies of $E_{1g}$ and $A_{1g}$ peaks can be used as key features to identify the layer number of a MoS$_2$ flake (≤4 layers). The layer number identification using $E_{1g}$ or $A_{1g}$ peaks frequency are consistent with optical, AFM and PL characterization. Resonance Raman spectra show that the coupling between electronic transition at K point and $A_{1g}$ phonon is weakened in ultrathin MoS$_2$ in comparison with that in bulk MoS$_2$, which is ascribed to the increased transition energy at K point due to the perpendicular quantum confinement or elongated intralayer atomic bonds. We confirm that
the asymmetric Raman feature centered at 454 cm\(^{-1}\) in bulk MoS\(_2\) is actually a combinational band involving LA(M) and \(A_{2g}\) modes. The consistent \(E_{2g}\) and \(A_{2g}\) peak frequencies of monolayer MoS\(_2\) using various laser lines show that Raman spectroscopy is a reliable diagnostic tool to identify monolayer MoS\(_2\).

### 4. Experimental Section

MoS\(_2\) flakes were mechanically exfoliated from a piece of commercially available nature crystalline MoS\(_2\) sample (SPI Supplies) with Scotch tape. The Raman measurements with the excitation laser lines of 488, 532 and 632.8 nm were performed using a WITEC alpha300 R Confocal Raman system in air ambient environment. The Raman measurements with the excitation laser line of 325 nm were performed using a Renishaw Raman spectroscopy integrated with a Kimmon IK5751-G UV laser. The powers of the excitation laser lines are kept well below 1 mW to avoid heating effect. The Raman emission was collected by an Olympus 100x objective (N.A. = 0.8) and dispersed by 600 (for PL measurement in Figure 3c and d), 1800 (for Raman measurement in Figure 2 and 4) and 2400 (Figure 3a) lines mm\(^{-1}\) gratings. The Renishaw Raman spectroscopy with 325 nm line and 2400 lines mm\(^{-1}\) grating has a step size of 3–4 cm\(^{-1}\). The WITEC Raman spectroscopy with 600 lines mm\(^{-1}\) grating has a spectral resolution around 2 cm\(^{-1}\) while that with 1800 lines mm\(^{-1}\) grating has a spectral resolution better than 1 cm\(^{-1}\).

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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