Anisotropic electron–photon–phonon coupling in layered MoS₂

Deepu Kumar¹,³, Birender Singh¹, Rahul Kumar², Mahesh Kumar² and Pradeep Kumar¹,³

¹ School of Basic Sciences, Indian Institute of Technology Mandi, Mandi-175005, India
² Department of Electrical Engineering, Indian Institute of Technology Jodhpur, Jodhpur-342037, India
E-mail: deepu7727@gmail.com and pkumar@iitmandi.ac.in

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Abstract
Transition metal dichalcogenide, MoS₂ has attracted a lot of attention recently owing to its tunable visible range band gap, and anisotropic electronic and transport properties. Here, we report comprehensive inelastic light scattering measurements on both chemical vapor deposition grown (horizontally and vertically aligned) flakes, and mechanically exfoliated flakes of single crystal MoS₂. We probe the anisotropic optical response by studying the polarization dependence intensity of the Raman active phonon modes as a function of different incident photon energy and flake thickness. Our polarization dependent Raman studies reveal strong anisotropic behavior reflected in the anomalous renormalization of the modes intensity as a function of flake thickness, phonons and photon energy. Our observations reflect the strong anisotropic light–matter interaction in this high crystalline symmetric layered MoS₂ system, especially for the in-plane vibrations, crucial for understanding as well as future applications of these materials.

Keywords: Raman scattering, phonon, lattice-dynamics

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction

The journey of two-dimensional (2D) nano materials begins with the discovery of graphene [1], the first 2D material that defied the Mermin–Wagner theorem. Since the discovery in 2004, these materials have been intensively probed both experimentally as well as theoretically owing to their extraordinary properties and rich physics [2]. Recently, they have been joined by another large class of newly discovered 2D materials, namely 2D transition metal dichalcogenides (TMDCs). In the bulk form, TMDCs had been probed for decades [3, 4], however the current interest lies in their atomically thin 2D form. Although TMDCs have the properties which are complementary to those of graphene, such as graphene being a zero gap semiconductor, it cannot be switched off and as a result is not good for the semiconductor industry. TMDCs provide a tunable band gap that helps in overcoming the bottleneck faced by graphene, and are thus promising materials for the next generation electronic and optoelectronic applications. In these systems, one may tune their properties as a function of layer thickness providing great leverage against the conventional 3D bulk systems [5]. Additionally, numerous properties of TMDCs such as electrical mobility, photoluminescence, photo-responsivity and thermoelectric figure of merit show strong dependence on the in-plane crystalline orientation [6–9] as well as layer thickness. Interestingly, all these properties may be linked with the underlying behavior of the electrons, phonons and their coupling with the photons, which may be investigated using light–matter interaction such as Raman spectroscopy. In these systems, reduced dielectric screening and significant quantum confinement also lead to strong Coulomb interactions between electrons and holes, giving rise to tightly bound excitons with a large binding energy.
MoS\(_2\) is one of first 2D TMDC systems being explored as an alternative to replace silicon in the semiconductor industry owing to the tunable band gap, from \(\sim 1.2\) eV in bulk to 1.9 eV in its monolayer [11]. In addition to the finite spin–orbit coupling, broken inversion symmetry in MoS\(_2\) provides optical access to the valley degrees of freedom suggesting its potential in future spintronic and valleytronic devices. Light–matter interaction in these 2D materials provides a deep insight into the underlying interaction mechanism as photons may easily interact with electrons and phonons, which control their electrical and thermal properties. The underlying mechanism responsible for the stark difference in physical properties when one moves from bulk to the monolayer may be linked with the behavior of quasi-particles and coupling between them such as anisotropic coupling between electrons and phonons/photons [12–15]. This anisotropy may be gauged via an indirect probe by an external perturbation such as probing by light, in particular Raman scattering. Raman scattering has proved to be a very powerful technique to understand intricate coupling between different quasi-particles in both nano systems and bulk via coupling of electrons and phonons with the incoming and outgoing photons [16–23]. An anisotropy in the thermal conductivity was reported for the case of MoS\(_2\), where in-plane conductivity is reported to be \(\sim 5–6\) times more than the out-of-plane conductivity [24] suggesting the more dominant role of the in-plane lattice vibrations such as \(E_{1g}\) phonon mode as phonons coupling controls the thermal behavior of a material.

Phonon modes in TMDC are sensitive to the thickness of these materials. In case of MoS\(_2\), as one moves from bulk to the monolayer, the out-of-plane phonon mode (\(A_{1g}\)) involving the vibration of S atom is red-shifted; on the other hand, \(E_{2g}\) mode involving the in-plane displacement of Mo and S atoms shows blue-shift attributed to the dielectric screening of long-range coulombic interaction [20]. Interestingly in 2D materials, phonon modes may be tuned by varying the incident photon energies if they fall within the resonance range of optical transition [25]. In fact, close to the resonance condition, one may get additional modes including the forbidden one owing to the broken symmetry, and/or resonance effect which eases the momentum conservation rule. In case of MoS\(_2\), excitation with 633 nm (1.96 eV) laser, which is close to \(A\) exciton energy, gives rise to many multiphonon modes [26, 27]. These multimodes provide very rich information about phonons in the entire Brillouin zone (BZ) as opposed to the conventional Raman process where observed phonon modes are confined only at the \(\Gamma\) point in the BZ. A detailed study focusing on the polarization dependence of phonon modes as a function of incident photon energy and layer thickness was lacking for high symmetric MoS\(_2\). Focusing on the polarization dependence of the phonon modes, here, we have undertaken such a study and report comprehensive results in vertically and horizontally chemical vapor deposition (CVD) grown MoS\(_2\) as well as mechanically exfoliated flakes from MoS\(_2\) bulk single crystal as a function of flake thickness and different incident photon energies. We show how the electron–photon and electron–phonon interactions in MoS\(_2\) are related to its thickness reflecting via the different polarization dependence behavior of the phonon modes, as a function of layer thickness as well as phonons and incident photon energy.

2. Experimental techniques

Vertically and horizontally aligned MoS\(_2\) was synthesized using CVD method as described in reference [28]. Single crystal flakes were obtained using scotch tape method from the bulk single crystal of MoS\(_2\) (2D semiconductors, USA) on 300 nm SiO\(_2\)/Si substrate, see figure S5(f) in the supplementary information (http://stacks.iop.org/JPCM/32/415702/mmedia) for the steps used for exfoliation method. Polarization dependent measurements using Raman spectroscopy may be done using different configurations based on the polarization of incident, scattered light and rotation of the sample. In one possibility, polarization of the incident laser light is varied while the analyzer is fixed. Second possibility is by keeping the polarization of the incident beam fixed, while the polarization of the scattered light is varied using an analyzer. It is also possible to combine the previous two configurations and control the polarization of the incident and scattered lights simultaneously. Another possibility is that by keeping the polarization of incident and scattered light fixed and only rotating the sample around the laser beam. Here we followed the second configuration i.e. by fixing the direction of polarization of the incident beam and the rotation of the sample, we made use of the scattered light polarization direction using analyzer (see figure 1 for the exp. geometry); and all the measurements were done in backsckattering geometry using 532 nm and 633 nm laser. The spectra were collected using a 100 x long working distance objective and Peltier cooled charge couple device detector. The laser power was kept very low (\(\sim 500\) \(\mu\)W) to avoid any heating.

3. Result and discussions

3.1. Raman scattering and polarization dependence

TMDCs have chemical formula MX\(_2\), where two nearest layers of X (chalcogen atom) are separated by a layer of M (transition metal), which means the monolayer of MX\(_2\) system is composed of a trilayer i.e. X–M–X. For bulk MoS\(_2\) (point group \(D_{3h}^1\)), Mo is sandwiched between two S atom layers forming a hexagonal plane, and is connected with S via a trigonal prismatic coordination in 2H phase, where H stands for the hexagonal symmetry and prefix 2 for the number of layers in each stacking order i.e. after two layer the pattern is repeated [3]. As one moves from bulk to finite number of layers, then symmetry reduces owing to a lack of translational symmetry in Z direction; 24 symmetry operation in bulk reduced to 12 in a few layers, and as a result, space group is different for the few layered TMDC systems (see table S1). Monolayer/odd number of layers of MoS\(_2\) belong to \(D_{1h}^1\) point group \(P6m2\), \#187, on the other hand bilayer/even number of layers belongs to \(D_{3h}^3\) (\(P3m1\), \#164) [29–31]. Details of the character
whereas $X$ with respect to $\hbar$, respectively; and effect. From the frequency difference ($\Delta \omega$) to the higher-order overtone modes owing to the resonance, few other modes for 633 nm incident photon energy attributed to the higher-order overtone modes owing to the resonance effect. From the frequency difference ($\Delta \omega = \omega_{A1g} - \omega_{E1g}$) of mode $A1g$ and $E1g$, one may estimate the number of layers in these flakes [35, 36]. For monolayer, the frequency difference ($\Delta \omega$) is $\sim$18 cm$^{-1}$ for mechanically exfoliated one and $\sim$20 cm$^{-1}$ for CVD grown sample, and difference increases by $\sim$2–3 cm$^{-1}$ in the case of bilayer, and with further addition of layers it increases by $\sim$1 cm$^{-1}$ per layer till six–seven layers [35, 36]. We also measured thickness of the mechanically exfoliated layers of single crystal MoS$_2$ using an AFM and using Raman compared the corresponding frequency difference in each layer (see figures S3 and S5 in supplementary information), the observed frequency difference is found to be commensurate with the measured thickness as stated above.

To understand the anisotropic coupling between electrons, photons and phonons, compressive polarized Raman scattering measurements were carried out on CVD grown horizontally aligned MoS$_2$ flakes. Figure 3 shows the polarization dependence of $A1g$ and $E1g$ modes for both 532 and 633 nm laser as a function of increasing thickness of horizontally aligned flakes of MoS$_2$. For flake 1 (532 nm laser), the intensity of $E1g$ mode remains invariant with respect to the rotation of the analyzer, however the intensity of $A1g$ mode shows a two-fold symmetric nature i.e. it has maximum intensity at both 0$^\circ$ and 180$^\circ$. One may understand the observed variation in intensity as a function of polar angle within the semi-classical approach. As incident polarized light lies in the $XY$ plane, polarized vector ($\hat{e}_i$) of the incident beam may be decomposed as (cos $\alpha$, sin $\alpha$, 0), where $\alpha$ is an arbitrary angle from the $x$-axis (see figure 1(d)). We have fixed the direction of $\hat{e}_i$ and rotated the analyzer at an interval of 10$^\circ$, polarization vector ($\hat{e}_s$) for the scattered light also lies within the $XY$ plane with decomposition (cos($\theta + \alpha$), sin($\theta + \alpha$), 0), where $\theta = 0^\circ$ to 360$^\circ$. Within the semi-classical approach, Raman scattering intensity is given as $I_{int} = |\langle \hat{e}'_s, R | \hat{e}_i \rangle|^2$, where $t$ denotes the transpose of $\hat{e}_s$ and $R$ represents the Raman tensor [37]. Using the above expression, the intensity of the $A1g$ and $E1g$ modes for our experimental setup is given as $I_{A1g} = a^2 \cos^2 \theta$, $I_{E1g} = b^2 (\cos^2 \theta + \sin^2 \theta)$, respectively. $I_{A1g}$ decreases to zero when $\hat{e}_i$ and $\hat{e}_s$ are parallel; on the other hand $I_{E1g}$ remains constant. Solid lines in figure 3 (flake 1, 532 nm) are the fitted curves using the above functions, and the fitting is in a very good agreement with the theoretical prediction.

As we changed the energy of the incident photon to 633 nm, and considering the data on the same flake and the same spot (see figure 3, 633 nm, flake 1), remarkably, the intensity of the $E1g$ mode is no longer invariant under rotation and shows that the intensity is maximum around 0$^\circ$ and 180$^\circ$, similar to that of $I_{A1g}$. As we moved to the other flakes (flakes 2, 3 and 4) for 532 and 633 nm laser, intensity pattern of the $A1g$ mode remained constant. Interestingly for 532 nm laser, isotropic nature of $E1g$ changes slightly with increasing thickness i.e. the constant intensity shows the signature of minima around 90$^\circ$ and 270$^\circ$; on the other hand, as we changed the laser to 633 nm, the intensity pattern for $E1g$ mode shows remarkable changes and becomes two-fold symmetric similar to that of $A1g$ mode. For 532 nm, as we move from flake 2 to flake 4 the point of maxima for $E1g$ mode showed a small variation; for
Figure 2. Raman spectra for four different flakes of horizontally aligned CVD grown MoS_2 under two different (a) 532 nm and (b) 633 nm laser excitation energies. The solid red line shows the total sum of Lorentzian fit and thin blue lines show the individual fit of the phonon modes. Flake numbering (from 1 to 4) is done in the increasing order of flakes thickness. Single layer thickness is ∼0.8–0.9 nm. Number of layers and flake thickness mentioned in the left panel is estimated based on the frequency difference between A_1g and E_{1g} phonon modes. Inset shows optical image of the region where Raman spectra were measured. Δω corresponds to the frequency difference between A_1g and E_{1g} mode.

example, point of maxima for flake 4 is not at zero but slightly above it. These features clearly reflect the anisotropic nature of these phonon modes with respects to the layer thickness and incident photon energy. For these flakes (#2, 3 and 4) we also notice that intensity of the E_{1g} mode at zero and 360° is not exactly same suggesting slight loss of periodicity in intensity at these angles. Solid lines for A_{1g} (both 532 and 633 nm) and E_{1g} mode (for 633 nm) are fitted with the functions a^2 cos^2 θ and the fitting is very good. For E_{1g} mode for 532 nm, where the intensity pattern is deviating from constant value and forming a semi-lobes kind of structure, we have fitted using the combined functions i.e., (a^2 + a^2 cos^2 θ + d^2 sin^2 θ), overall fitting is modest. Figure 4 shows the intensity ratio (I_{E_{1g}}/I_{A_{1g}}), which diverges as one moves closer to 90° (see figure 4(a), for 532 nm) on the expected lines within the theoretical prediction. The intensity pattern is governed mainly by the intensity of A_{1g}(I_{A_{1g}} ∝ cos^2 θ) hence the ratio is expected to show divergence as the angle closes to 90°. On the other hand, for 632 nm (see figure 4(b)) intensity ratio no longer show any divergence rather it is constant with respect to the rotation of the analyzer, completely in opposition to that observed for 532 nm (see figure 4(a)). This constant intensity ratio observed for 632 nm photon energy clearly reveal that both A_{1g} and E_{1g} modes have same dependence on the polarization angle in stark contrast to that predicted by the theory. This diametrically opposite behavior observed for E_{1g} mode intensity under different photon energy again point the anisotropic nature of these phonon modes.

Figure 5 shows the polarization dependence data for A_{1g} and E_{1g} modes for both 532 and 633 nm laser as a function of increasing thickness for four different flakes of vertically aligned MoS_2. The intensity of the out of plane vibrational mode (A_{1g} mode) shows consistent behavior irrespective of the incident photon energy and layer thickness, except some minor changes in the lobes sizes; for example, lobe size in the 2nd–3rd quadrant is more expanded for flake 1 and 4 (for 532 nm). On the other hand, the intensity of the in-plane vibrational mode (E_{1g} mode) changes drastically as we vary the incident photon energy as well as layer thickness, similar to what we observed for the horizontally aligned MoS_2 discussed above. For example, for flake 1 intensity of the E_{1g} mode is not invariant under rotation instead it shows maxima around 0° and 180° but without any nodes at 90° and 270°. As we changed the incident photon energy to 633 nm (see flake #1), intensity of the E_{1g} mode changes significantly and show two nodes at 90° and 270° similar to those of A_{1g} mode. Analogous behavior is also observed for other flakes as well. The observed asymmetry reflected in the in-plane vibrational mode (E_{1g}) clearly
Figure 3. Intensity polar plots for the Raman active phonon modes $E_{2g}^1$ and $A_{1g}$ with two different laser excitation energies (532 and 633 nm) in horizontally aligned CVD grown flakes of MoS$_2$. Black spheres are the experimental data points for different polarization angles from $\theta = 0^\circ$ to $360^\circ$ and solid blue lines show fitted curves as described in the text. In plane vibrational mode $E_{2g}^1$ shows remarkable anisotropic response when the incident photon energy is changed from 532 to 633 nm. Number of layers and flake thickness mentioned in the left panel is estimated based on the frequency difference between $A_{1g}$ and $E_{2g}^1$ phonon modes. 

suggests strong anisotropic nature of the phonon modes in MoS$_2$, and weaker polarization dependence of out-of-plane vibrational mode ($A_{1g}$) as compared to the in-plane vibrational mode ($E_{2g}^1$), suggesting that out-of-plane vibrations couple less anisotropically with the electronic states as compared to the in-plane vibrations. Intensity ratio (see figure S1 for the Raman spectra as a function of flake thickness and figure S2 for the intensity ratio) also shows similar changes as observed in the horizontally aligned MoS$_2$ discussed above. To probe this anisotropic coupling further, we also did similar measurements using single crystal flakes of MoS$_2$ on five different flakes starting from monolayer of MoS$_2$ (see figure 6). Interestingly, single crystals flakes also show similar polarization-dependent behavior as that observed for the horizontally and vertically aligned flakes i.e. the intensity of the $A_{1g}$ mode shows two fold symmetric nature irrespective of the incident photon energy and layer thickness; while intensity of $E_{2g}^1$ changes as a function of layer thickness as well as incident photon energy. For example (see flake #1, 532 nm) intensity of the $E_{2g}^1$ is showing quasi-isotropic nature with maxima around $0^\circ$ and $180^\circ$ and lowering of intensity around is observed around $90^\circ$ and $270^\circ$. As soon as we changed the laser to 633 nm (see flake #1), intensity of the $E_{2g}^1$ mode changes significantly and shows two nodes at $90^\circ$ and $270^\circ$ similar to those of $A_{1g}$ mode. Intensity ratio (i.e., $I_{E_{2g}^1}/I_{A_{1g}}$) also shows similar behavior as for horizontally and vertically aligned MoS$_2$ (see figure S3 for the Raman spectra as a function of flake thickness and figure S4 for the intensity ratio). The results shown in figures 3, 5 and 6 clearly suggest strong anisotropic optical response in this high crystalline symmetric layered MoS$_2$ and its intricate dependence on the incident photon energy, phonon energy as well as flake thickness.

### 3.2. Discussion

Our observations on these three different forms of MoS$_2$ as a function of layer thickness as well as incident photon energies evidently reflect the anisotropic nature of the phonons. They also make clear that the semi-classical approach cannot capture the complete picture with respect to the observed anisotropies especially for the case of in-plane vibrations. For example, within this semi-classical approach, a phonon mode with the same symmetry would have the same polarization
dependence irrespective of the incident photon energy; what we observed for $E_{2g}$ mode (see figures 3, 5 and 6) is completely different from this prediction. This failure of semi-classical approach to explain the polarization dependence as a function of layer thickness and incident photon energy ($E_L$) may be understood from the fact that the intensity of a Raman active mode within this approach is independent of the $E_L$ as well as the thickness of the materials. This independence of the intensity from $E_L$ and thickness comes from the fact that the optical dipole selection rule for the absorption and emission of a photon is not included in this semi-classical theory. All optical dipole selection rule for the absorption and emission mode within this approach is independent of the $E_L$ as well.

Figure 4. Intensity ratio of $E_{1g}$ with respect to $A_{1g}$ in horizontally aligned CVD grown flakes of MoS$_2$ under two different (a) 532 nm (b) 633 nm laser excitation energies. Solid blue lines are a guide to the eye.

(c) Finally, the electron comes back to the initial state and combines with the hole and emits the photon (electron–photon interaction; $H_{op}$).

From this Raman scattering process, one may easily gauge that Raman process can play a pivotal role in deciphering the intricate coupling between photons, phonons and electrons. The first-order Raman scattering process involves three steps, as described above, and quantum mechanical expression for the Raman intensity, which uses the dipole selection rule for the optical transition, is given as [37, 38]:

$$\text{Int.} = \left| \sum_{g,i} \langle \langle g | H_{op} | i \rangle \langle \langle i | H_{el-ph} | g \rangle \rangle (E_L - \Delta E_{g})(E_L - \hbar \omega_{ph} - \Delta E'_{g}) \right|^2$$  \hspace{2cm} (1)

where, $\Delta E_{ig} = (E_i - E_g + \gamma)$ and $\Delta E'_{ig} = (E_i - E_g + \gamma')$, $|g\rangle$ is the ground state, $|i\rangle$ and $|i'\rangle$ are the intermediate states (eigen or non-eigen ones), $H_{op}$ and $H_{el-ph}$ are the electron–photon and electron–phonon interactions, respectively. $E_L$ is the incident photon energy and $E_g$, $E_i$ and $E_{i'}$ are the energies of the corresponding electronic states, and $\gamma$ is the broadening factor which is introduced phenomenologically for the finite lifetime of the absorption/emission. Matrix elements $\langle \langle g | H_{op} | g \rangle \rangle$ and $\langle \langle i | H_{op} | i \rangle \rangle$ represent the process of optical absorption and emission, respectively and $\langle \langle i | H_{el-ph} | i \rangle \rangle$ is the electron–phonon matrix element. Treating the electron–photon interaction within the dipole approximation i.e. by neglecting higher order multipole or non-linear effects, the electron–phonon matrix element $\langle \langle i | H_{op} | g \rangle \rangle$ is given as $\langle \langle i | H_{op} | g \rangle \rangle = \langle \langle i | H_{op} | g \rangle \rangle \propto \hat{e}_i \vec{D}_{eg}$, where $\hat{e}_i$ is the polarization vector of the incident light and dipole vector $\vec{D}_{eg} = \langle \langle g | \nabla | i \rangle \rangle$ [39, 40]. From this expression, it is clear that to have a non-zero contribution of electron–photon, the matrix element $\vec{D}_{eg}$ should have a finite component along the direction of light polarization $\hat{e}_i$. This may also explain which two states ($|i\rangle$, $|g\rangle$) from the energy bands be involved in this transition of an electron for a given $E_L$ and direction of $\hat{e}_i$, and the different possible values of the matrix element $\langle \langle i | H_{op} | g \rangle \rangle$ for varying incident light polarization direction and incident photon energies. As there are three matrix components involved (see equation (1) above), to get the finite intensity for a mode each component should be non-zero and should be allowed by the symmetry. For example, to obtain non-vanishing electron–photon matrix elements for the optical transition from ground state to the intermediate state $|\vec{r}\rangle$, it should satisfy $\Gamma_g \otimes \Gamma_D \subset \Gamma_i$, where $\Gamma_D$, $\Gamma_g$ and $\Gamma_i$ are the irreducible representations of $\vec{D}$ (i.e., the parallel component of $\vec{D}_{eg}$ with respect to $\hat{e}_i$), $\langle \langle g | \nabla | i \rangle \rangle$ and $\langle \langle i | \nabla | g \rangle \rangle$, respectively. Similarly, $\langle \langle g | \nabla | i \rangle \rangle \propto \hat{e}_i \vec{D}_{gi}$, where $\hat{e}_i$ is the polarization vector of the scattered light and $\vec{D}_{gi} = \langle \langle g | \nabla | i \rangle \rangle$. Comparing quantum expression (equation (1)) with the semi-classical approach, one may write the XY component of Raman tensor, say for $E_{2g}$ mode, as $d \propto \langle \langle g | \nabla | i \rangle \rangle \langle \langle i | H_{el-ph} | g \rangle \rangle | \langle \langle g | \nabla | i \rangle \rangle | (E_L - \Delta E_{gi})(E_L - \hbar \omega_{ph} - \Delta E_{gi}) \hat{e}_i \hat{e}_X \hat{e}_{gY}$. This suggests that XY and similarly YY component of the Raman tensor changes with the change in $E_L$ and this may give rise to a change in a different polar dependence of the intensity. Also, electron–phonon matrix element $\langle \langle i | H_{el-ph} | g \rangle \rangle$ may also change.
Figure 5. Intensity polar plots for the Raman active phonon modes $E_{2g}$ and $A_{1g}$ with two different laser excitation energies (532 and 633 nm) in vertically aligned CVD grown flakes of MoS$_2$. Black spheres are experimental data points for different polarization angles from $\theta = 0^\circ$ to $360^\circ$ and solid blue lines show fitted curves as described in the text. Number of layers and flake thickness mentioned in the left panel is estimated based on the frequency difference between $A_{1g}$ and $E_{2g}$ phonon modes.

When the energy of the incident photon changes, the intermediate states $|i\rangle$, $|i'\rangle$ change to new states $|low\rangle$, which may also change the denominator. In case of TMDCs, this renormalization of the intermediate states may happen easily because of the existence of many energy bands with different symmetries within a short range of energy. Importantly, as one moves from bulk to single layer in TMDCs, band topology near the valance band and the bottom of the conduction band changes drastically, which may also give different polar plots for given Raman active phonon modes simply by changing the thickness. We note that similar anisotropic phonon modes as a function of layer thickness and different $E_1$ have been reported in other class of 2D materials with low crystalline symmetry such as black phosphorus, GaTe, ReSe$_2$, ReS$_2$ [41–45].

Our observation of anisotropic polarization dependence for three different forms of MoS$_2$ flakes as a function of thickness and incident photon energy is attributed to the selection rule for optical transition, which can be expressed in quantum theory of Raman scattering via electron–photon–phonon matrix elements as $\langle i|\nabla|g\rangle$, $\langle g|H_{op}|i'\rangle$ and $\langle i'|H_{el–ph}|i\rangle$. Layered TMDCs have a large number of conduction bands with different symmetries at the $\Gamma$ point in BZ. When incident photon energy or layer thickness is changed, the intermediate states get modified and is reflected in the renormalized electron–photon matrix elements. To get the finite contribution for Raman intensity, both electron–photon matrix elements in equation (1) should be finite, which constraints that symmetries of $|i\rangle$, $|i'\rangle$ be linked with $|g\rangle$ state. Based on the group theory, one can find the allowed symmetries of the intermediate electronic states $|i\rangle$ and $|i'\rangle$. A detailed list of the intermediate states for a given polarization direction and phonon mode is given in tables S2 and S3 (see supplementary information). Our observations, clearly reveal the strong in-plane anisotropic behavior in high symmetric MoS$_2$. It has been observed that for many low-symmetry 2D systems [41–45], Raman active phonon modes do show polarization dependence on the crystalline orientation. However, it was suggested that polarization dependence as well as anisotropic transport properties such as mobility, are also coupled to the underlying electronic symmetry along with the crystalline symmetry of the material [41–46].
Figure 6. Intensity polar plots for the Raman active phonon modes $E_{2g}$ and $A_{1g}$ with two different laser excitation energies (532 and 633 nm) in mechanically exfoliated flakes of MoS$_2$. Black spheres are experimental data points for different polarization angles from $\theta = 0^\circ$ to $360^\circ$ and solid blue lines show fitted curves as described in the text. Number of layers and flake thickness mentioned in the left panel is as per the thickness measured using AFM method (also see figure S5 in supplementary information) and it corroborate well with the thickness estimated using the frequency difference between $A_{1g}$ and $E_{2g}$ phonon modes.

4. Summary and conclusions

In summary, we performed comprehensive Raman scattering studies on three different forms of layered MoS$_2$, probing the anisotropic behavior of the Raman active phonon modes revealing strong anisotropic electron–photon–phonon coupling. The observed anisotropy in the Raman intensity depends strongly on the incident photon energy, phonon energy as well as laser energy and flake thickness. This suggests that more theoretical as well experimental studies are required for the high crystalline symmetric 2D materials for an understanding of their underlying properties for potential future applications.
as the thickness of MoS$_2$ for all the three different forms studied here. Our work cast a crucial light on understanding the anisotropic strong light–matter interactions in high symmetric MoS$_2$, especially for the in-plane vibrations, and we hope our studies also pave the way for the applications of this system in electronic and optoelectronic devices. We believe that our experimental findings will motivate other groups to develop a comprehensive theoretical model for a quantitative understanding.

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ORCID iDs

Deepu Kumar  
https://orcid.org/0000-0002-7900-6311

Birender Singh  
https://orcid.org/0000-0002-9640-0070

Mahesh Kumar  
https://orcid.org/0000-0002-5357-7300

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