Raman Spectroscopy of Shear Modes in a Few-Layer MoS₂

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1. Introduction

Atomically thin layered transition metal dichalcogenide compounds (TMD) MX₂, where M = transition metal, X = S, Se, Te, are of considerable interest due to their unique physical and optical properties [1]. Strong ion-covalent bonds within planes of hexagonally arranged X and M atoms and weak out-of-plane of the der Waals interactions between the planes make their properties very strongly dependent on the number of layers which form the structure. In particular the transition from the indirect bandgap in bulk TMDs to the direct bandgap in their two-dimensional form [2] can be exploited in several optoelectronic applications [3]. Possible applications and interesting physics justify investigation of basic properties of a few layer TMDs and in particular studies of their lattice dynamics. Phonons are important for several physical processes as e.g. carrier scattering [4], heat propagation [5], and mechanical strength of the crystal [6]. Mechanical properties of TMDs are determined by force constants resulting from interlayer interactions. Following several recent contributions [7–10] we study the Raman scattering spectroscopy in a low-energy range in which the rigid layer modes can be observed. We identify the shear mode and we follow its dependence on the number of layers. We show that the energy evolution of the mode with the increasing number of layers is well described using a linear chain model with only nearest neighbor interactions. The in-plane shear force constant is determined.

2. Experimental

The sample was prepared by thinning down MoS₂ crystal by exfoliation with a high-quality backgrinding tape. An all-dry, non-deterministic, polydimethylsiloxan-based stamping technique was employed to transfer the sample onto a Si/90 nm SiO\textsubscript{2} substrate. Optical spectroscopic measurements were performed in a backscattering geometry using \( \lambda = 532 \text{ nm} \) (2.33 eV). The He–Ne laser with \( \lambda = 632.8 \text{ nm} \) (1.96 eV) excitation was also used for comparative studies. At room temperature the laser light power on the sample was equal to \( \approx 190 \mu \text{W} \). An Olympus MPlan N microscope 100/0.90 objective was used to both excite the sample and to collect the emitted light. The collected spectra were dispersed by a Horiba-Yobin T64000 Series II \( \mu \text{-Raman} \) system, equipped with a multichannel high-resolution Si-charge coupled device. The spectrometer was set to a tri-grid measuring mode (with a grating of 1800 l/mm).

3. Results and discussion

In our study we focus on the low-energy features observed at the energies below 60 cm\textsuperscript{-1}. One expects two families of interlayer modes in the low-energy range, which correspond to the rigid vibrations of MoS₂ layers. These are shear modes related to rigid layer displacements perpendicular to the \( c \) axis and breathing modes which correspond to rigid layer displacements along the \( c \) axis [10–12]. The modes evolve into the Raman active \( E_{2g}^c \) and optically inactive \( B_{2g}^c \) in bulk, respectively. The evolution of the low-energy Raman spectrum with changing number of layers (\( N \)) is presented in Fig. 1. It can be seen that the spectrum critically depends on the number of layers.

There are no interlayer modes in monolayer MoS₂, which explains the lack of any features in the corresponding spectrum. Starting from bilayer (2ML) there is just one clearly observed peak in the spectrum and its frequency increases with \( N \). Eventually, in bulk the peak corresponds to \( E_{2g}^c \) Raman active mode. This suggests that the peaks represent the interlayer shear modes. Beyond the model, another peak is present (denoted in Fig. 1 with a star) in the Raman spectrum from hexalayer (\( N = 6 \)), its possible origin is discussed later in the text.

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In our analysis of the evolution of the Raman peaks due to the shear modes we employ the linear chain model of the crystal lattice vibrations. Whole layers of atoms are represented in the model by a single point of mass which represents the surface mass density of the atoms, composing the layer. Only the interaction between the adjacent layers is retained which is described by a single force constant $K$. $K_x$ and $K_z$ correspond to the shearing and compression strength, respectively. The approach has recently proved to describe reasonably the rigid modes in MoS$_2$ and WSe$_2$ [10, 12].

The evolution of the mode energies (in cm$^{-1}$) as a function of $N$-layers can be represented within the model by

$$\omega_{i,\alpha} = \sqrt{\frac{K_i}{2\mu\pi^2c^2}} \left[1 - \cos \left(\frac{(\alpha - 1)\pi}{N}\right)\right] = \sqrt{\frac{1 - \cos \left(\frac{(\alpha - 1)\pi}{N}\right)}{\mu}}$$

with $\alpha = 2, 3, ..., N$. The reduced mass $\mu = 3 \times 10^{-6}$ kg/m$^2$ is the rigid layer mass per unit area ($\mu = 2m_S + m_{Mo}$, where $m_S = 0.6 \times 10^{-6}$ kg/m$^2$ for S atoms and $m_{Mo} = 1.8 \times 10^{-6}$ kg/m$^2$ for Mo, and $c$ is the speed of light in cm$^{-1}$.

There are two sets of subbranches expected for shear (breathing) modes. The Raman active shear (breathing) modes belong to the higher-energy (lower-energy) branches of the corresponding set.

We start our analysis with the mode $E_{2g}^2$ which can be observed in bulk at 31.9 cm$^{-1}$. Assuming that the force constant $K_x$ does not change significantly as $N$ changes from 2 to $N \rightarrow \infty$ [13] one can predict the value of $\omega_x = 22.6$ cm$^{-1}$. The energy of the shear mode in bilayer predicted by the model corresponds to the energy of one of the modes observed in our experiment at 22.5 cm$^{-1}$. Using the value one can model the evolution of the shear modes with $\alpha = N$ and $N - 1$, which are denoted in Fig. 2 with continuous and dashed line, respectively. It can be seen that the subbranch modelled with $\alpha = N$ reproduces well the observed evolution of the main modes, which stiffen with increasing number of layers. The $\omega_{x,N}$ subbranch corresponds to previously observed S1 shear mode in MoS$_2$ and WSe$_2$ [10] which is also referred to as $C_2$ [14]. Using the value of $\omega_x = 22.6$ cm$^{-1}$ one can also find the in-plane (shear) force constant $K_x = 2.7 \times 10^{19}$ N/m$^3$ which perfectly matches the previously reported value [10] and which is smaller than the value for WSe$_2$ ($3.1 \times 10^{19}$ N/m$^3$) [13].

The most intriguing property of the observed Raman spectrum is the peak at 27.5 cm$^{-1}$ observed in 6 ML sample (see Fig. 2). As it can be seen in Fig. 2 the mode coincides with the expected energy of a shear mode, which belongs to $\alpha = N - 1$ subbranch, and which is not normally observed in the Raman spectrum. In our opinion the brightening of the mode must be due to the strain or defects present in 6 ML flake. The same effect must be also responsible for the unexpected lineshape of the out-of-plane mode ($A_{1g}$) in the spectrum excited resonantly with $\lambda = 632$ nm (see Fig. 3). The additional line corresponds most likely to $A_{2u}$ IR-active mode in 6 ML MoS$_2$ however the mechanism of its brightening is also not clear at the moment.
4. Conclusions

We have studied low frequency vibrational modes in atomically thin MoS$_2$ by means of the Raman scattering spectroscopy. A shear mode related to rigid interlayer vibrations has been identified. Its energy evolution with the increasing number of layers has been described using a linear chain model with only nearest neighbor interactions. The resulting force constant ($K_x = 2.7 \times 10^{19}$ N/m$^3$) has been found to correspond well to the previously published data.

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