Low-frequency interlayer vibration modes in two-dimensional layered materials

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Abstract

Two-dimensional (2D) layered materials have been attracted tremendous research interest because of their novel photoelectric properties. If a single atomic layer instead of individual atoms is taken as a rigid motion object, two unique interlayer vibrations, i.e. compression/breathing and shear motions, at ultra-low frequencies can be expected and actually have been observed in many layered materials. The vibrations stem from the interlayer van der Waals interaction and can be well described by a conventional linear-chain model in most cases. The vibration frequencies strongly depend on layer thickness, which enables an accurate determination of layer numbers. A quick and nondestructive determination of flake thickness is particularly important for the materials, since the physical properties can be dramatically changed in the cases of several atomic layers. As a measure of interlayer coupling, the low-frequency modes are also sensitive to the stacking methods of atomic layers and the overlapping of different kinds of 2D materials. This allows the modes to play a key role in the applications like van der Waals heterojunctions. In this paper, we will give a brief review on the experimental observations and theoretical understanding of the interlayer modes in several typical 2D systems, as well as their actual and potential applications.

Keywords: Layered materials, Raman scattering, interlayer coupling, low-frequency interlayer mode, linear chain model

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Contents

I. Introduction

- 1.1 Several typical 2D layered systems
- 1.2 Simple classification of low-frequency interlayer modes
- 1.3 Linear chain model

II. Layer-number dependence of low-frequency interlayer modes

- 2.1 Graphene
- 2.2 Transition metal dichalcogenides
- 2.3 Black phosphorus
- 2.4 Other layered systems

III. Effect of stacking method on low-frequency modes

IV. Low-frequency modes in twisted multilayer materials

V. Summary and outlook

I. Introduction

1.1 Several typical 2D layered systems

The successive discovery of fullerene C₆₀ and carbon nanotubes [1,2], stimulated great interest to explore the possibility of two-dimensional carbon materials. It had been predicted that 2D material does not exist in nature due to its thermal instability [3]. Until 2004, the emergence of graphene invalidated the theoretical prediction and opened the door to two-dimensional materials [4]. The sp² hybridization and covalent in-plane σ -bonding between neighboring carbon atoms in graphene (Fig. 1a and b), provide a mechanical strength stronger than that of steel by two orders of magnitude [5-7]. Graphene only absorbs 2.3% of the incident light intensities [8,9]. It has a very high Young's modulus [10] and a thermal conductivity as high as 5300W/m·K [11]. Its electron mobility at room temperature reaches up to 200,000cm²/V·s [12]. These outstanding properties make graphene the most promising semiconducting material after silicon. There are two principal phonon modes in graphene, named as G and 2D bands. G band at ~1580 cm⁻¹ originates from in-plane vibrations of sp²-hybridized carbon atoms and has the symmetry of E_{2g}. 2D band at 2650 cm⁻¹ has an almost doubled frequency of D band, which is a second-order resonance process and identified as an inter-valley scattering assisted by optical phonons and defects [13]. Therefore, 2D band is related to defects while G band is not. The lineshapes and widths of G and 2D bands depend on flake thickness, which makes the two modes as an indicator of layer number and flake quality.

Besides graphene, many other materials such as the members of graphene family (h-BN) [14], transition metal sulfides [15], transition metal oxides [16], topological insulators and some mixed phases, etc., have been prepared in 2D form [17-22]. Transition metal dichalcogenides (TMDs) refer to one hexagonal M metal atomic layer sandwiched between two hexagonal X chalcogenide atomic layers (MoS₂, for example shown in Fig. 1c and d). More than 40 graphene-like TMD layered materials can be formed through the combination of X (= S, Se and Te) and M (= Mo, W, Nb, Re, Ni and V) elements. For the 2D layered materials, a common feature is the

coexistence of strong in-plane M-X-M covalent bonding and weak interlayer van der Waals force interaction (Fig. 1c and d). There are four Raman-active modes in bulk MoS₂. E_{2g}¹ mode at 385 cm⁻¹ and A_{1g} mode at 410 cm⁻¹ correspond to the in-plane vibrations of Mo-S bond and the out-of-plane vibrations of Mo atoms with S atoms fixed, respectively. In few-layer cases, the frequencies of the two modes exhibit an opposite evolution with flake thickness. The frequency difference between the two modes is ~19 cm⁻¹ in monolayer case and gradually becomes indistinguishable in five or more layer cases. This is attributed to the increasing dielectric screening and the modifications of intralayer and interlayer coupling [23]. The other TMD compounds have the similar behaviors/properties. Atomically thin TMD flakes have many outstanding advantages, like the very high on/off current ratio up to 10⁶ [22]. But the relatively low mobility (~200cm²/V·s) limits its industrial applications at present [24].

Recently layered black phosphorus (BP) has invoked enormous interest. Like other 2D materials, black phosphorus has a folded hexagonal honeycomb structure (as shown in Fig. 1e and f), with in-plane covalent bonding of phosphorus atoms and weak interlayer van der Waals force [25-27]. The main Raman modes in bulk BP are A_g¹, A_g² and B_{2g} [28]. A_g¹ mode at ~366 cm⁻¹ refers to the out-of-plane vibrations of sulfur atoms while A_g² (~440 cm⁻¹) and B_{2g} (~466 cm⁻¹) modes are the in-plane vibrations of sulfur atoms. A_g¹ and B_{2g} modes have little change in peak position with decreasing thickness, but the frequencies of A_g² mode clearly depend on layer number. BP has an adjustable direct band gap ranging from 0.33 eV in bulk form to 2.0 eV in monolayer case [29-32]. BP exhibits a large anisotropy in Young's modulus [33,34], Poisson's ratio [35], electron mobility [36], thermal conductivity [37] etc., strongly depending on zigzag or armchair direction [38]. And its mobility in a ~10nm flake can reach 1000 cm²/V·s at room temperature [39], which seems promising in semiconducting applications, despite its easy degrade in air[40-44].

1.2 Simple classification of low-frequency interlayer modes

Raman scattering is an effective and nondestructive technique to probe electronic properties and lattice vibrations, and has been widely used in the research on

low-dimensional materials [45]. Through monitoring the subtle change of lattice vibrations, Raman scattering can reflect the influence from the degrees of freedom of charge, spin and lattice [46]. Here we take graphene as an example to demonstrate symmetry considerations of interlayer modes. Bulk graphite has a hexagonal lattice structure with D_{6h}^4 symmetry. There are four atoms in each primitive cell, which gives 12 vibration modes at Γ points, i.e., $2E_{1u}+2A_{2u}+2E_{2g}+2B_{2g}$ [47,48]. Among the modes, two E_{2g} modes are Raman-active and correspond to in-plane optical mode and the rigid-layer shear mode (in-plane relative vibration parallel to layers) respectively. The two B_{2g} modes are Raman-inactive and correspond to the out-of-plane optical mode and the rigid-layer compression/breathing mode (out-of-plane relative vibration perpendicular to layers) [47]. The symmetry changes with the reduction of flake thickness. The point group with even/odd number of layers is D_{3d}/D_{3h} , and the compression and shear modes are Raman-active in both cases [49,50]. The rigid-layer compression mode (C_N or LBM) and shear mode (S_N) is used to be called low-frequency modes due to their low vibration frequencies ($<100\text{cm}^{-1}$) [51].

The shear mode E_g locates at 44 cm^{-1} in graphite, and moves to 42.7 cm^{-1} in 11-layer graphene, further to 31 cm^{-1} in bi-layer graphene [52]. Therefore, layer number can be accurately determined by shear mode, particularly at few-layer case. By contrast, the frequency changes of G and 2D peaks are very small with layer thickness [52,53]. Similarly, high-frequency A_g^2 mode in black phosphorus indicates a change of only 3 cm^{-1} from monolayer to bulk, while its low-frequency mode has a variation of 19 cm^{-1} [28,54,55]. So the low-frequency mode can be taken as a precise tool for determining the thickness of 2D materials. Furthermore, the shear and compression modes are a good measure of interlayer coupling, and the shear and compression modulus can be extracted by fitting the experimental data [51,54,56]. In addition, the interlayer modes are very sensitive to the stacking styles of atomic layers, the interface and the rotation angle [57-60]. This may be very helpful to the fabrication and characterization of van der Waals heterojunction. So the study of low-frequency modes has become one of the most fundamental issues in 2D layered materials in recent years.

1.3 Linear chain model:

For layered materials, intra-layer covalent bonding is much stronger than the interlayer van der Waals interaction. The low-frequency shear and compression modes arise from the relative vibrations between layers. By taking a rigid atomic layer as one “atom” with large mass, a layered system can be simplified to a one-dimensional monatomic chain with free ends, and only the interaction between the nearest neighboring layers is considered in this chain model. The linear chain model has been well examined in the layered materials grown by epitaxial method [61]. For N-layer materials, totally there are 3(N-1) rigid-plane optical modes in the center of Brillouin zone, including N-1 compression modes along the c axis and N-1 degenerate shear modes. The characteristic displacement vector of the phonon modes are as follows:

$$\mu_j^i \propto \cos \left[\frac{(i-1)(2j-1)\pi}{2N} \right] \quad (1)$$

where i is the mode index (i = 2, ..., N), and j is the location index of each atom. So the frequency of the i-th vibration mode is obtained:

$$\omega_i^2 = \frac{\alpha}{2\pi^2 c^2 \mu} \left\{ 1 - \cos \left[\frac{(i-1)\pi}{N} \right] \right\} \quad (2)$$

where μ is the mass per unit area of a single atomic layer, c is the speed of light and α is the interlayer force constant per unit area associated with interlayer coupling. For the modes with the highest frequency (i = N),

$$\omega_N = \sqrt{\frac{\alpha}{2\pi^2 c^2 \mu} \left[1 + \cos \left(\frac{\pi}{N} \right) \right]} \quad (3)$$

when $N \rightarrow \infty$, it goes to a bulk case, and $\omega_\infty = \sqrt{\frac{\alpha}{\pi^2 c^2 \mu}}$, which is $\sqrt{2}$ times larger than that of two layers. Formula (2) tells one that there are two opposite trends in the relationship of ω and N. One is that the frequency increases with increasing layer number, while the other is that the frequency decreases with increasing layer number. Therefore, equation (2) can be resolved to the following form,

$$\omega_n = \sqrt{1 \pm \cos\left(\frac{n\pi}{N}\right)} \quad (4)$$

wherein n is the mode index, $N \geq 2n$ and $n = 1, 2, 3, \dots$. The formula with “+” applies to the upper branch which frequency increases with number layer, while the formula with “-” applies to the lower branch which has an opposite evolution with layer number. The relation between frequency and layer number based on linear chain model, has been extensively applied to graphene [52,62,63], MoS₂ [23,64-64], MoSe₂ [59,68], NbSe₂ [69], MoTe₂ [70] and black phosphorus [54,55,71], etc., and in each case the experimental results are fitted perfectly.

II. Layer-number dependence of low-frequency interlayer modes

2.1 Graphene

The study on low-frequency modes in graphene was firstly focused on the shear mode E_g [52]. P.H. Tan *et al.* made the symmetry analysis and calculated the frequencies of the shear mode by density functional theory (DFT). As shown in Fig. 2a, there are $N-1$ shear modes for the N -layer sample. As mentioned above, the sample with even/odd layers has a point group D_{3d}/D_{3h} . Therefore in even-numbered layer the shear mode has the symmetries of E_g and E_u , while in odd layer it is E' and E'' . One can see that both the highest and the lowest branches are Raman-active. But only the upper branch of the shear mode, which frequency increases with layer number, is visible in graphene, since only the upper branch is symmetry-allowed for the AB stacking of layered materials (we will discuss this later) (Fig. 2b). Experimentally, it was found that the intensity of the shear mode measured on mechanically exfoliated graphene with the support of SiO₂/Si substrate, is very weak (far less than the characteristic G peak), almost invisible in bi-layer case [51]. On the other hand, in the free-standing graphene obtained by drilling on a silicon wafer, the shear mode can be clearly seen. For graphene with 2 to 11 layers and the bulk graphite (Fig. 2b), the uppermost branch of shear mode is clearly visible, and its frequency substantially increases with layer number, while G peak remains almost unchanged. The calculated frequencies are perfectly consistent with the experimental

values. And the linear chain model provides a perfect fitting curve (Fig. 2c). Equation (3) gives $\omega_2 = \sqrt{\frac{\alpha}{2\pi^2 c^2 \mu}}$ where the quantity α , which is about $12.8 \times 10^{18} \text{ Nm}^{-3}$ in this case, can be determined by the ω_2 formula. This indicates that the hardening of the shear mode with increasing layer number in the AB stacked graphene, is caused by the increase of overall restoring force rather than the change of interlayer coupling [52]. The shear modulus of 4.3 GPa can be calculated by the use of $C_{44} = \alpha t$ (where t is the interlayer spacing). The value is consistent with the result given by inelastic X-ray scattering [52,72].

It is hard to observe a compression/breathing mode with first-order Raman measurements. The compression mode (LBM or ZO') located at about 100 cm^{-1} has been studied in bulk graphite [62]. C. Lui *et al.* measured the double overtone $2\text{ZO}'$ of ZO' mode in few-layer graphene utilizing double-resonance Raman technique. As seen in Fig. 3c, there are two conduction bands (c1, c2) and two valence bands (v1, v2) in 2-layer graphene. This provides four possible resonance processes, i.e. P11, P12, P21, P22 for intra-valley double-phonon scattering. Only the two processes P11 and P22 which correspond to $2\text{ZO}'^-$ and $2\text{ZO}'^+$, are allowed, since P12, P21 is restricted in the high-symmetry points of the Brillouin zone center. It can be seen from Fig. 3a that there are two peaks in the vicinity of 180 cm^{-1} in 2-layer sample. They are similar to the high-order 2D peak. For N-layer sample, there are N-1 branches of compression mode from $2\text{ZO}_N'^{(1)}$ to $2\text{ZO}_N'^{(N-1)}$. For each compression mode, its frequency increases with increasing layer number and decreases with increasing mode index. The thickness dependence of ZO' mode frequency is given by $2\text{ZO}'$ central peak and can be well described with the theoretical model (Fig. 3b).

2.2 Transition metal dichalcogenides

MoS_2 has a structure of AB stacking (D_{6h}^4 , P63/mmc) in which one Mo atomic layer is sandwiched between two layers of S atoms [73-76]. Its primitive cell contains six atoms. So it has 18 branches of phonons at Γ point, namely $\Gamma_{\text{bulk}} = A_{1g} + 2B_{2g} + E_{1g} + 2E_{2g} + 2A_{2u} + B_{1u} + 2E_{1u} + E_{2u}$ [66,74-76], where A_{1g} mode at $\sim 408 \text{ cm}^{-1}$

and E_{2g}^1 mode at $\sim 382\text{cm}^{-1}$ correspond to the out-of-plane vibrations of S atoms and in-plane vibrations of Mo and S atoms, respectively. The frequencies of both modes change with layer number and the difference in frequency between the two modes increases from 19 cm^{-1} to 26 cm^{-1} with the thickness variation from monolayer to bulk [23,77]. The low-frequency E_{2g}^2 and B_{2g}^2 modes correspond to the shear mode and compression vibrations, respectively (Fig. 4a). B_{2g}^2 mode is invisible in bulk since it is a Raman inactive in this case. The point group of few-layer MoS_2 is D_{3d} in even-layer sample and D_{3h} in odd-layer sample, and the compression mode becomes Raman-active. The frequency difference of shear mode E_g in bilayer and bulk samples can reach up to 10 cm^{-1} as shown in Fig. 4b. The compression mode A_{1g} exhibits an even larger frequency variation (41cm^{-1} for bilayers and 12 cm^{-1} for 7 layers). Its width is significantly reduced with increasing layer number and the peak eventually disappears in bulk sample. Therefore, the layer number of few-layer MoS_2 can be accurately determined with the two low-frequency modes. Both modes well follow the simple one-dimensional monoatomic chain model and the experimental data can be fitted perfectly (Fig. 4c and d) using formula (4). The fitting gives the interlayer force constant per unit area $\alpha_S = 2.9 \times 10^{19}\text{ N m}^{-3}$ and $\alpha_C = 8.6 \times 10^{19}\text{ N m}^{-3}$ with $C_{44} \sim 17.9\text{ GPa}$ and $C_{33} \sim 52.0\text{ GPa}$ [59,66]. The ratio of the in-plane shear force constant to the interlayer one, can be estimated to be about 100 [56] using a simple relationship $\omega^2 \sim K/M$, where K is the force constant and M the atomic mass [56,78]. For the compression force constant, we have approximately the same ratio. Similar to graphene, in principle there are $N-1$ branches of degenerate shear modes and $N-1$ branches of compression modes for N -layer MoS_2 . Besides the shear mode with the highest frequency and the compression mode with the lowest frequency, the interlayer modes for $n=3, 5$ are also observed [64]. The fitting difference between the diatomic and monatomic chain models, is almost negligible.

Other TMD compounds with AB stacking have the similar hexagonal lattice structure as that of MoS_2 . The in-plane strong M-X-M bonding and the weak van der Waals interlayer coupling coexist in MX_2 . The interlayer vibration modes have also been observed in other TMD materials such as MoSe_2 , WSe_2 , MoTe_2 and ReS_2 at low

frequencies [59,66,68,70,79,80]. The low-frequency mode of MoSe₂ under parallel polarization is shown in Fig. 5a, in which no peak is seen in monolayer case but it emerges in the samples with more than two layers. The shear modes have the highest, the third highest and the fifth highest frequencies respectively, which reduce rapidly with increasing layer number. It locates at about 19 cm⁻¹ in bilayer case, slightly less than that of MoS₂. Fig. 5b indicates the two low-frequency modes in WSe₂ under parallel polarization. The compression mode is symmetry-prohibited under cross polarization. The upper branch of the shear mode (S₁, S₂) and the lower branch of the compression mode (B₁, B₂), are observed under parallel polarization. The two branches have an opposite evolution with layer number, i.e. blue shift for S₁, S₂ and red shift for B₁, B₂. The low-frequency modes in the two TMDs also satisfy linear chain model exactly and the fitting gives C₄₄ = 18.6 GPa and C₃₃ = 52.1 GPa in WSe₂. Both values are slightly larger than those of MoS₂ [66].

In bulk/bilayer MoTe₂, both the shear mode (B_{2g}/A_{1g}) and the compression mode (E_{2g}/E_g) are Raman-active [70]. Fig. 5c shows the Stokes and anti-Stokes Raman spectra under XX and XY polarization configurations in N-layer (N= 1 to 12) and bulk MoTe₂. Only A_{1g} compression mode is visible in the parallel-polarization (XX) channel, while both modes are observed in the cross polarization (XY) channel. And the intensity of compression mode in XX channel is one order of magnitude larger than that in XY channel. The shear (compression) mode exhibits a gradual softening (hardening) with increasing layer number. The evolution well follows linear chain model and hence can be taken as an accurate way of determining layer number, as seen in other layered TMD materials.

ReS₂ is a 2D layered semiconductor with novel electronic properties and the stable phase in monolayer case has a distorted 1T structure [79,80]. The anisotropy in ReS₂ allows two non-degenerate interlayer shear mode (S_{||} and S_⊥) and one compression mode, all of which are observed in the Raman spectra below 50 cm⁻¹ (Fig. 5d). Compared to the theoretical calculations, they are assigned to S_{||} (13 cm⁻¹), S_⊥ (16.5 cm⁻¹) and B modes (28 cm⁻¹), respectively. Actually it is hard to distinguish the shear modes from other low-frequency modes due to their weak intensities (Fig.

5b). The compression mode (B) shifts to lower frequencies with increasing thickness. B_1 mode locates at $\sim 8 \text{ cm}^{-1}$ in 10-layer case, while it has a large frequency change of $\sim 20 \text{ cm}^{-1}$ from 2- to 10-layer cases. The higher-order compression modes (B_2 , B_3 , B_4) are also visible in the spectra, and all the observed compression modes can be fit by linear chain model.

2.3 Black phosphorus

Black phosphorus has attracted more and more attention recently because of its unique structure and electronic/optical properties. Black phosphorus has an orthogonal structure (D_{2h}^{18}) [81,82]. One phosphorus atom is covalently bonded with its three nearest neighbors. And it is generally believed that the interlayer coupling also arises from weak van der Waals interaction. There are four atoms in a primitive cell, which allows 12 phonon modes, namely $\Gamma_{\text{bulk}}=2A_g+B_{1g}+B_{2g}+2B_{3g}+A_{2u}+2B_{1u}+2B_{2u}+B_{3u}$, wherein $2A_g$ 、 B_{1g} 、 B_{2g} 、 $2B_{3g}$ modes are Raman-active and refer to in-plane relative vibrations [81]. The D_{2h} symmetry remain unchanged in few-layer black phosphorus. But different from bulk, the point group is D_{2h}^7 (pmna) for odd layers and D_{2h}^{11} (pbca) for even layers [82]. In few-layer case, the classification of vibration modes is changed to $\Gamma_{\text{n-layer}}=n(2A_g+B_{1g}+B_{2g}+2B_{3g}+A_{2u}+2B_{1u}+2B_{2u}+B_{3u})$, where the Raman-active A_g , B_{1g} and B_{2g} modes are the out-of-plane compression mode and the shear mode along zigzag and armchair directions, respectively [55].

Due to Raman selection rules, only the A_g mode can be observed under $z(xx)z$ configuration. Raman measurements on a large number of BP flakes indicate that two branches of low-frequency modes exhibit a significant evolution with layer number (Fig. 6a), while no low-frequency peak is seen in monolayer and bulk samples[54]. It means that the modes appearing at low frequencies are interlayer vibrations. And only the compression mode is allowed according to the symmetry analysis on few-layer black phosphorus. The mode near 80 cm^{-1} can be well fitted by linear chain model, and is further identified as a conventional interlayer compression/breathing vibration perpendicular to sulphur planes (Fig. 6b and d). The modes at relatively high frequencies are determined to be the second and fourth compression ones.

The mode around 30 cm^{-1} is of particular interest. Its redshift with layer number can be well described by $1/\sqrt{N}$ rather than $\omega_q = \sqrt{1 \pm \cos\left(\frac{n\pi}{N}\right)}$ or $1/N$ [54].

This suggests that the vibration represents a collective compression motion relative to substrate by combining all the layers as a whole rather than a single layer (Fig. 6c and e). This mode is called as collective compression mode (CCM). It means that the interlayer coupling is quite strong to bind the individual layers together. The mode has also been observed in KBr films epitaxially grown on a NaCl substrate [83]. The layer-number dependence of the mode frequency is quadratic and its intensity has a weak dependence on the polarization of incident light, which is consistent with the conclusion mentioned above (Fig. 6f and g). The ratio of intralayer to interlayer force constants can be estimated through the ratio of the intralayer vibration mode A_g^1 ($\sim 366 \text{ cm}^{-1}$) to the compression mode A_g (71 cm^{-1}) in bilayer BP. The ratio is about 26, much smaller than that of MoS_2 [54]. The ratio of intra- and interlayer force constants are the interlayer binding energy per unit are listed in Table 1, compared to those of MoS_2 and graphene. The values in BP are significantly larger than those of the other two samples. This evidences that the interlayer coupling in few-layer BP is different from the case of MoS_2 and may play an important role in understanding the structural and electronic properties of few-layer BP and its applications. The strong interlayer coupling is considered to arise from the electron hybridization of lone pair of electrons besides van der Waals interlayer interaction [84].

The low-frequency modes in multi-layer BP can also be used to effectively determine the flake thickness. The high-frequency modes A_g^1 and B_{2g} have little frequency shift with varying the layer number, and A_g^2 mode only has a shift of $\sim 3 \text{ cm}^{-1}$ from monolayer to five-layer and is not effective for the determination of layer number, particularly in few-layer case. On the other hand, the CCM and interlayer compression mode exhibit a large shift in frequency with flake thickness. From bilayer to bulk, the frequency change of CCM and the compression mode are 32 cm^{-1} and 19 cm^{-1} respectively[54]. Furthermore, both modes are still very sensitive to the thickness even in the thicker samples with ten or more layers. So they can provide an

accurate and effective way to determine the layer number of few-layer BP. This is particularly helpful for the studies of BP, since the easy degradation in air makes it difficult to determine BP flake thickness with conventional techniques like optical imaging.

Table I Comparison of the interlayer coupling in BP, MoS₂ and graphene. Here is the experimental per unit area interlayer force constant α , $K_{\text{intra}}/K_{\text{inter}}$ (intralayer/interlayer spring force constant) and interlayer binding energy per unit area E_B which is calculated by density functional Optb88-vdW, DFT-D2, and Optb86-vdW.

	a (α 10^{18} N/m^3)	$K_{\text{intra}}/K_{\text{inter}}$	E_B (meV/Å²)		
			Optb88-vdW	DFT-D2	Optb86-vdW
black P	127	26	31	23	35
MoS₂	29	100	26	18	27
graphene	12.8	/	26	21	26

2.4 Other layered systems

Distinguished from graphene, TMD and BP layered materials discussed above, the V-VI compounds Bi₂Te₃ and Bi₂Se₃ are well-known topological insulators [85]. The layered Bi₂X₃ (X=Te, Se) is structured by the tight stacking of hexagonal atomic layers along c axis. Each few-quintuple-layer (QL) is composed of five ABC-stacked atomic layers which are covalently bonded through X-Bi-X-Bi-X chains (Fig. 7c&d). The neighboring QL layers are coupled through van der Waals interaction. It has a rhombohedral lattice with point group D_{3d}^5 (R-3m) in bulk, which gives 15 branches of optical phonon modes, i.e., $\Gamma_{\text{bulk}}=2A_{1g}+2E_g+3A_{2u}+3E_u$ [86]. The symmetry changes to D_{3d}^3 (R-3m1) with a hexagonal lattice in few-layer cases, and the primitive cell of N-QL system contains 5N atoms. The optical modes are $\Gamma_{\text{odd}}=(5N-1)/2(A_{1g}+E_g) + (5N+1)/2(A_{2u}+E_u)$ for odd-QL systems and $\Gamma_{\text{even}}=5N/2(A_{1g}+E_g+A_{2u}+E_u)$ for even-QL systems, where A_{1g} and E_g are Raman-active shear and

compression/breathing modes, respectively. According to the Raman tensors, both A_{1g} and E_g modes are visible in parallel polarization configuration while only E_g mode can be seen in the cross polarization channel.

The low-frequency Raman spectra of few-layer Bi_2Te_3 and Bi_2Se_3 under $-Z(XX)Z$ backscattering configuration are shown in Fig. 7a&b. The redshifts of the shear mode (S1) and compression mode (B1) with thickness are observed in both materials, and the frequency evolution still well follows linear chain mode (Fig. 7c). Interestingly, there appears a particular mode in 2/3-layer Bi_2Te_3 , which is out of the classification of the optical modes at Γ points and cannot be described simply by linear chain model. The experimental results are in good agreement with the theoretical values of the effect of substrate is taken into account. The acoustic mode changes to optical interface mode (I) in this case (Fig. 7d). It can be understood as the vibration of the whole atomic layers relative to substrate, which is similar to the CCM in multilayer BP and indicates a relatively strong interlayer coupling.

III. Effect of stacking method on low-frequency modes

The usual stacking methods are ABA and ABC in 2D layered materials. They demonstrate considerable differences in electronic structures, manipulation of energy band gap, quantum Hall effect, infrared absorption and other aspects [87-92]. In principle, the impact of stacking on interlayer phonon modes is very small (Fig. 8b), since it stems from the weak van der Waals interlayer coupling. However, the symmetries of ABA- and ABC-stacking are significantly different [58]. For three-layer graphene, ABA stacking corresponds to point group D_{3h} with 18 branches of standard phonon modes at Γ points, namely $2A_1' + 4E' + 4A_2' + 2E''$. E' and E'' modes are the uppermost and lowest branches of shear mode, and A_1' is the lowest branch of compression mode. As shown in Fig. 8a, all the three low-frequency branches are Raman active. But for ABC stacking, the point group becomes D_{3d} with inversion center. It gives 18 branches of phonon modes at Γ points as $3A_1^1 + 3E_g + 3A_u + 3E_u$. In this case, E_g and A_1^1 modes are the lowest branch of shear mode and the lowest

branch of compression mode, respectively. And the rest of the modes are infrared-active vibrations. Fig. 8c shows Raman measurements on three-layer ABA- and ABC-stacking graphene. The identified compression mode appears at 57cm^{-1} in both ABA- and ABC-stacking graphene. This is because the nearest-neighboring interlayer coupling is the same for ABA and ABC stacking and the next nearest neighbor interaction is so small that it can be negligible. However, the effect of stacking on low-frequency modes is clear in a lower frequency region. By comparison with the theoretical values, one can see that the uppermost branch of C appears in ABA stacking graphene while the lowest branch of C' occurs in ABC stacking graphene. ABA stacking has mirror symmetry and ABC stacking has antisymmetry. That is why they are obviously distinct in Raman activity and phonon intensity [58].

The dependence of low-frequency mode on stacking methods has also been well verified in other 2D materials. For example, the upper branch of shear mode was also observed in the mechanically exfoliated AB stacking MoS_2 and WSe_2 [63,64-66], while the lowest shear mode appears in ABC stacking Bi_2Se_3 and Bi_2Te_3 [57,86]. Two kinds of stacking methods, i.e. AB and ABC, are available in the epitaxially grown MoSe_2 . Therefore, not only the upper branch but also the lower branch has been observed [59,68]. It seems that the stacking effect are generally applicable to the interlayer modes of many 2D systems, since it comes from symmetry rather than materials.

IV. Low-frequency modes in twisted multilayer materials

The twisted multilayer flakes formed by the overlapping of few-layer ones have many promising applications in electronic devices and optoelectronic fields. The low-frequency modes of such multiplayer systems contain some key information on interlayer coupling. For $m+n$ layers of graphene [$t(m+n)\text{LG}$, $m \neq n$], the symmetry is C_3 with $\Gamma_{\text{Raman}} = A + E$, where the compression mode has A symmetry and the shear mode E symmetry. According to the Raman tensors, A and E modes can be observed in parallel polarization, while E mode is prohibited in cross polarization channel [93].

Fig. 9 shows Raman spectra of six twisted graphene samples $t(1+2)\text{LG}$,

t(1+1+1)LG, t(1+3)LG, t(2+2)LG, t(2+3)LG, t(5+5)L. The peak at $\sim 109.9 \text{ cm}^{-1}$ in t(1+2)LG and the peak at 108.8 cm^{-1} in t(1+1+1)LG h are close to the calculated $\text{pos}(\text{LBM}_{31}) = 110.8 \text{ cm}^{-1}$ but quite far away from $\text{pos}(\text{LBM}_{21}) = 90.5 \text{ cm}^{-1}$. The mode is assigned as the compression/breathing vibration of tri-layer graphene. Similarly, in t(1+3)LG and t(2+2)LG the two compression modes are almost identical and consistent with the calculated values of 4-layer graphene. This suggests that the compression mode in m+n layer twisted graphene is little affected by interface distortion. The interlayer compression coupling is almost constant and the frequency only depends on the total number of layers N. On the other hand, it is very different for shear mode. The two peaks C_{31} and C_{32} in t(1+3)LG and C_{21} were identified as shear modes. And the three peaks were also found in t(2+3)LG, while C_{51} , C_{53} and C_{54} are visible in t(5+5)LG. It indicates that the shear modes in (m+n)-layer graphene seem to come from the separate mLG and nLG. This is due to the fact that the periodic mismatch between the twisted layers reduces interlayer coupling force and the mode frequency.

The shear mode in Bernal stacking graphene can be observed only in free-standing form on silicon and no sign of compression mode is seen [52]. The low-frequency modes can be observed very easily in the twisted overlapped graphene and their intensities are also much enhanced. In the overlapped multilayer systems made of different kinds of few-layer 2D materials, such as $\text{MoS}_2/\text{MoSe}_2$ and $\text{MoS}_2/\text{WSe}_2$, low-frequency modes are also sensitive to the composition of flakes, the contact surface condition and the overlapping angle etc. [60]. The studies of low-frequency modes for overlapped layered materials is a fundamental issue and substantially contributes to the understanding and development of 2D van der Waals heterojunctions.

V. Summary and outlook

The low-frequency modes originating from relative vibrations between layers, are particularly meaningful for the study of 2D layered materials. They can not only accurately determine the layer number of few-layer samples, but also provides a good

measure of the strength of interlayer interaction. By determining α with mode frequencies, the interlayer shear and compression modulus can be conveniently extracted [23,54,64-66]. This offers a simple but effective and non-destructive way compared to other methods of modulus measurement.

A key application of low-frequency modes is to monitor the interlayer coupling of van der Waals heterojunction, in which the intrinsic electronic properties of two individual layers are modified due to the weak interlayer coupling at contact surface. The atomic-layer stacking of different kinds of 2D layered materials, will output new features and applications in optics, electronics and other aspects [94-99]. For instance, the photoluminescence (PL) of MoSe₂ is strongly suppressed in MoSe₂/graphene heterojunction, which indicates that there exists a very fast charge transfer of photo-generated carriers between MoSe₂ and graphene [98]. And the interlayer coupling can be adjusted by inserting dielectric layer into heterojunction. The PL peaks are changed when monolayer h-BN is inserted in WSe₂/MoS₂ heterojunction. If the heterojunction contains tri-layer h-BN, the PL peaks seems consistent with those of monolayer MoS₂ and monolayer WSe₂, suggesting that the interlayer coupling between two different atomic layers can be ignored in this case. PL peaks of WSe₂/MoS₂ heterojunction without dielectric layer are weaker than those of monolayer WSe₂ and MoS₂, due to the strong coupling of interlayer charge carriers. Because the direct absorption and indirect emission exists in heterojunction, about 100meV of stokes-like shift appears in PL peaks and the lowest energy absorption peaks [99]. In addition, there are many unique properties of van der Waals heterojunction in spintronics, excitons etc. [100-102]. The frequencies of low-frequency modes reflect not only the basic information on thickness or layer number of the heterostructure but also some key factors like coupling strength and condition of its contact surface. This suggests low frequency modes may play a key role in the research of van der Waals heterojunction.

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Figure captions

Fig. 1. (a), (c) and (e) are the side views of graphene, MoS₂ and black phosphorus lattice structures. And (b), (d) and (f) are the corresponding top views, respectively.

Fig. 2. (a) DFT calculations of the symmetry and frequencies of C mode. (b) Frequency evolution of C mode with the number of layers. (c) Linear chain fitting of C mode [52].

Fig. 3. (a) 2ZO' Raman spectra of 2- to 20-layer graphene and graphite. (b) Frequency evolution of compression mode ZO' obtained from (a) and fitting results using linear chain model. (c) Electronic scattering processes for double phonon resonance Raman of 2ZO' mode in bi-layer graphene [62].

Fig. 4. (a) Vibration patterns of Raman-active modes in MoS₂. (b) Shear and compression modes in the Raman spectra of few-layer MoS₂. (c) & (d) Fitting results for shear and compression modes using linear chain model, respectively [23].

Fig. 5. (a) Shear modes in few-layer MoSe₂ under parallel polarization configuration (xx) [59]. (b) Evolution of low-frequency interlayer modes with thickness in few-layer WSe₂ [66]. (c) Low-frequency Raman spectra of MoTe₂ from monolayer to bulk [70]. (d) Low-frequency Raman modes of 2- to 10-layer ReS₂ [80].

Fig. 6. (a) Low-frequency Raman spectra of multilayer and bulk black phosphorus. (b) and (c) are frequency dependence of C and CCM modes on layer number and the corresponding linear chain fitting. (d) and (e) are the vibration patterns of the modes. (f)&(g) Evolution of low-frequency Raman modes with polarization of incident light [54].

Fig. 7. (a)&(b) Low-frequency Raman spectra of multilayer and bulk Bi₂Se₃ and Bi₂Te₃ under parallel polarization (xx) configuration, respectively. (c)&(d) Linear chain model with and without a substrate [86].

Fig. 8. (a) Lattice structure and symmetry of trilayer graphene with ABA and ABC stacking and vibration patterns of interlayer modes in trilayer graphene. (b) Phonon dispersions of low frequency modes in trilayer graphene with ABA and ABC stacking. (c) Low frequency Raman spectra for the two kinds of stacking methods [58].

Fig. 9. Shear and compression modes observed in the Stokes and anti-Stokes Raman

spectra of twisted multilayer graphene [93].

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9