Large Frequency Change with Thickness in Interlayer Breathing Mode—Significant Interlayer Interactions in Few Layer Black Phosphorus

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Supporting Information

ABSTRACT: Bulk black phosphorus (BP) consists of puckered layers of phosphorus atoms. Few-layer BP, obtained from bulk BP by exfoliation, is an emerging candidate as a channel material in post-silicon electronics. A deep understanding of its physical properties and its full range of applications are still being uncovered. In this paper, we present a theoretical and experimental investigation of phonon properties in few-layer BP, focusing on the low-frequency regime corresponding to interlayer vibrational modes. We show that the interlayer breathing mode \( A_3^{\text{g}} \) shows a large redshift with increasing thickness; the experimental and theoretical results agree well. This thickness dependence is two times larger than that in the chalcogenide materials, such as few-layer MoS\(_2\) and WSe\(_2\), because of the significantly larger interlayer force constant and smaller atomic mass in BP. The derived interlayer out-of-plane force constant is about 50% larger than that of graphene and MoS\(_2\). We show that this large interlayer force constant arises from the sizable covalent interaction between phosphorus atoms in adjacent layers and that interlayer interactions are not merely of the weak van der Waals type. These significant interlayer interactions are consistent with the known surface reactivity of BP and have been shown to be important for electric-field induced formation of Dirac cones in thin film BP.

KEYWORDS: Few layer black phosphorus, Raman spectroscopy, interlayer vibration, van der Waals solids, density functional theory

Two dimensional (2D) layered materials have received much attention in recent years due to their unique properties and potential applications in nanoelectronics, nano-optoelectronics, and nanoelectromechanical systems. Starting with graphene, the range of 2D materials has expanded to include 2D transition metal dichalcogenides, such as MoS\(_2\), and most recently to the newly discovered 2D black phosphorus (BP). Single-layer BP (phosphorene) has been investigated as a potential candidate in post-silicon electronics due to its semiconducting nature and high hole mobility. However, the full extent of the properties and applications of 2D BP is still being uncovered. One common feature of all 2D materials is that single layers stack up to form layers in the bulk and in thin films. The interlayer interactions are commonly thought to be of the nonlocal weak van der Waals type. However, it has been found that interlayer interactions beyond the weak van der Waals type are important in MoS\(_2\). In particular, the well-known direct to indirect band gap transition, as the thickness of MoS\(_2\) increases from monolayer to multilayer, arises from Coulombic repulsion between sulfur atoms in adjacent layers. Coulombic attraction between S and Mo atoms in adjacent layers of bulk MoS\(_2\) is also responsible for the Davydov splitting in the \((E_1^{\text{p}}, E_2^{\text{p}})\) conjugate modes, while short-range interlayer interactions, possibly of covalent nature, result in enhanced surface forces that give rise to anomalous frequency trends in 2D MoS\(_2\) and WSe\(_2\). Unlike the transition metal dichalcogenides, graphene and phosphorene are mono-
typic materials, so no Coulombic interactions are expected. However, in this work, we find that sizable covalent interaction exist between phosphorene layers, larger than that in graphene and MoS$_2$, resulting in significantly larger interlayer force constants and a large change in the interlayer breathing mode as the thickness of 2D BP increases. Our results show that interlayer interactions in layered BP are not simply of the weak van der Waals type and indicate the need for renewed effort to understand the implications of interlayer interactions on the properties of 2D BP.

Interlayer force constants in 2D layered materials can be theoretically computed and experimentally determined from low frequency Raman spectra, as has previously been seen in multilayer graphene and dichalcogenide materials.$^8,9$ We present first-principles, density functional perturbation theory (DFPT) (see Methods for details) calculations for phonons and nonresonant Raman intensities in few-layer BP, focusing on the low frequency regime for interlayer modes. A linear chain model, which fits well to the DFPT results, is used to predict phonon frequencies for samples thicker than seven layers. These results are compared with experimental data from Raman spectroscopy, which clearly show a low frequency interlayer breathing mode, $A_{3g}$, and is not accessible in the previous Raman experiments on few-layer BP.

We begin our discussion with a description of the lattice and symmetries of bulk and few-layer BP to understand the Raman selection rules of this system. Bulk BP, the most thermodynamically stable form of phosphorus at room temperature and pressure, is a narrow bandgap semiconductor with a direct bandgap of 0.3 eV.$^{10,11}$ The bulk structure belongs to the orthorhombic lattice and consists of puckered layers of atoms, as shown in Figure 1.

Table 1 summarizes the fully optimized lattice constants and internal coordinates obtained using different exchange-correlation functionals together with the experimental data.$^{12}$ LDA stands for the local density approximation to the exchange-correlation functional, PBE is a gradient-corrected approximation,$^{13}$ while vdW stands for the nonlocal vdW-DF2-c09 functional.$^{14,15}$ In general, the interlayer distances in van der Waals layered solids are quite well predicted using LDA (for fortuitous reasons) and vdW-DF2-c09 functionals,$^{8,9,16}$ while PBE overestimates these distances, as can be seen also in Table 1. PBE-D2 adds the dispersion energy to the PBE functional with optimized dispersion coefficients in the empirical pairwise force field expression.$^{17}$ By comparing the lattice parameters in phosphorene and bulk BP, we find that the lattice constant $a$ (in the zigzag direction) is smaller than bulk, while the lattice constant $b$ (in the armchair direction) is larger. Among the different functionals, the PBE-D2 and vdW functionals best describe the experimental bulk BP lattice parameters, while LDA also performs reasonably well.$^{12}$ On the other hand, as we shall see later, the interlayer phonon frequencies are best described using LDA. This is similar to the case for transition metal dichalcogenides$^8$ and indicates that while the vdW functionals are well-optimized to give the structural parameters, they do not perform as well as the LDA for interlayer vibrational properties. Henceforth, we report the LDA results unless otherwise stated.

The symmetry of the bulk BP crystal can be described by the $C_{mca}$ space group ($D_{2h}^{18}$), and the irreducible representation of the phonon modes at the center of the Brillouin zone is $\Gamma_{\text{bulk}} = \Gamma_{1}$.
Among the 12 vibration modes, there are six Raman-active modes ($A_g$, $B_{1g}$, $B_{2g}$, $B_{1u}$, $B_{2u}$, $A_u$), five infrared-active modes ($B_{1u}$, $B_{2u}$, $B_{3u}$, $A_{1g}$, $A_{1u}$), and one optically inactive mode $A_u$. When the system goes from 3D to 2D, the translational symmetry along the $z$-axis is absent. As a result, thin films with an odd and even number of layers belong to the space groups $Pmna (D_{2h}^{17})$ and $Pbcm (D_{2h}^{13})$, respectively. Consequently, the thin film’s irreducible representation of phonon modes at the Gamma point is $\Gamma_{n\text{-layers}} = n(2A_g + 2B_{1u} + 2B_{2u} + A_u + B_{1g} + B_{2g} + B_{1u})$. Since the thin film and bulk BP have the same $D_{2h}$ point group with inversion symmetry, they share the same character table. According to group theory, the Raman tensors of the Raman active $A_g$, $B_{1g}$, $B_{2g}$, and $B_{1u}$ modes are

$$
\begin{pmatrix}
A_g \\
B_{1g} \\
B_{2g} \\
B_{1u}
\end{pmatrix}
= \begin{pmatrix}
0 & 0 & 0 \\
0 & a & 0 \\
0 & 0 & 0 \\
0 & 0 & a
\end{pmatrix}
\begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
0 & 0 & a \\
0 & 0 & 0 \\
a & 0 & 0 \\
0 & a & 0
\end{pmatrix}
\begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
$$

Therefore, the $A_g$, $B_{1g}$, $B_{2g}$, and $B_{1u}$ modes can be detected using Raman spectroscopy under the $\varepsilon(xx)z$, $\varepsilon(xy)z$, $\varepsilon(xz)z$, and $\varepsilon(yz)$
z polarization configurations, respectively. The notation of $\vec{z}(xy)$ $z$ means that the incident light with polarization parallel to the $x$ axis propagates along the $z$ axis, and the scattered light polarized parallel to the $y$ axis propagates along the $z$ axis.

Previous Raman studies of BP have focused on the high frequency intralayer vibrations such as the $A_{1g}$, $A_{2g}$, and $B_{2g}$ modes, while the interlayer vibration modes are still largely unknown. From our LDA calculations, we found that there are several branches of interlayer modes in the low frequency range. Their frequencies and Raman activities are summarized in Table 2. The interlayer vibrational modes in few-layer BP are derived from the acoustic mode of phosphorene, and there will be $N-1$ interlayer breathing modes, the Raman active breathing (out-of-plane) modes are the acoustic mode of phosphorene, and there will be $N-1$ interlayer breathing modes. The $A_{1g}$ mode can be found in N-layer BP ($N \geq 2$), with the lowest frequency in all derived breathing modes. Besides the $A_{1g}$ mode, there are still other trends of breathing modes $A_g$ which will appear when the layer thickness is $\geq 4$ layers but with much smaller Raman intensity. Similar to the other layered materials, there are also interlayer shear modes in few-layer BP, as shown in Table 2. In contrast to the degenerate shear modes in few-layer graphene and MoS$_2$, the degeneracy is broken in few-layer BP, which results in two different sets of shear modes. The shear mode with atomic displacement along the armchair direction is represented as the $B_{3g}$ mode, which can be observed in the $\vec{z}(xy)$ polarization configuration. The shear mode with atomic displacements along the zigzag edge is the $B_{2g}$ mode, which can be detected in the $\vec{z}(xz)$ polarization configuration. We use the notation $B_{3g}$ and $B_{2g}$ to label the highest intensity interlayer shear modes in the armchair and zigzag directions, respectively.

Figure 2 shows the atomic displacements of the $A_{1g}$, $B_{3g}$, $B_{2g}$ and other Raman-active interlayer modes. Since the whole layer is moving as a unit, the arrow indicates the movement of that particular layer. Although the atomic displacements of the three interlayer modes are along different directions, they have similar patterns and all exhibit red shifts with increasing thickness. These red shifts can be understood from the atomic displacements (Figure 2); the total relative change in atomic displacement between adjacent layers decreases with increasing thickness, so the total accumulated force and therefore the frequency also decreases. From the calculated Raman intensities listed in Table 2, we note that the Raman intensities of the $B_{3g}$ and $B_{2g}$ mode are much smaller than the $A_{1g}$ mode, which makes it more difficult to detect these modes.

In our calculations, the Raman intensity of the $A_{1g}$ mode is comparable in value to the high frequency intralayer $A_{1g}$ and $A_{2g}$ modes. Thus, we expect that the $A_{1g}$ mode can also be observed in experiment. We therefore focus on this mode and show in Figure 3a, the predicted ultralow frequency Raman spectra of 1–7 layer and bulk BP under the $\vec{z}(xx)z$ configuration. As expected, this low frequency breathing mode $A_{1g}$ is absent in the single layer due to its interlayer vibrational feature. On the other hand, the bulk limit of the $A_{1g}$ mode is not Raman active due to the cancelation of accumulated bond polarizability under the periodic conditions. Interestingly, we find that the frequency of the $A_{1g}$ mode changes significantly with thickness, much more than that in the previously reported $A_{2g}$ mode for few layer BP, which makes it possible to determine the BP film thickness using the $A_{1g}$ mode frequency determined by Raman spectroscopy.

Inspired by the above theoretical predictions, we performed Raman scattering experiments to detect the ultralow frequency vibrational modes. The sample thickness is determined using a combination of atomic force microscopy (AFM) and optical contrast imaging. An example of the thickness determination using AFM is shown in Figure 4c,d. Although our theoretical thickness for single-layer graphene is 0.52 nm, we use 0.6 nm for calibrating the AFM measurements; this calibration is consistent with previous studies. Figure 4d shows an 11-layer BP sample, and the rough surface is due to possible adsorbates from the environment. For thinner samples, the rough surface makes it difficult to ascertain the sample thickness accurately. On the other hand, the band gap is very sensitive to thickness for thinner samples. We therefore relied on optical contrast to determine the sample thickness more accurately. The Raman spectra are excited by the 633 nm laser in a back scattering configuration with the incident light polarized along the $x$ axis. Experimental results are shown in Figure 4 (and Figure 3b). We show only the spectra acquired with nonpolarized light, as the signal-to-noise ratio is much poorer when polarization configurations are considered. The spectra for different polarization configurations were also acquired and are shown in Figure S1 of the Supporting Information. Samples down to 2–3 layers thin were prepared. However, we were only able to obtain Raman spectra for samples thicker than three layers. This is because even a laser power of 3.5 $\mu$W will cause damage to the three-layer BP sample, as shown in Figure S2. Typically, a laser power of 0.35 mW is used to detect the interlayer modes, while in the four-layer BP sample, laser power had to be reduced to 90 $\mu$W.

There are three frequency trends below 100 cm$^{-1}$ in Figure 4a; the lowest frequency modes guided by the red dashed line is the $A_{2g}$ breathing mode predicted in our calculation, which shows a large red shift with increasing thickness. The frequencies of this observed lowest frequency modes are in good agreement with our LDA predicted $A_{2g}$ breathing mode, as shown in Figure 3b, with direct comparison between experiment and LDA for 4–7 layer BP. The Raman-active breathing mode with the second lowest frequency (we call this $A_{3g}$) corresponds well to the highest frequency peak highlighted for five-layer BP (LDA, 83.7 cm$^{-1}$; experimental peak position, 85 cm$^{-1}$), but according to our calculations, this mode shifts as the thickness increases, to 65.4 cm$^{-1}$ for seven-layer (LDA), and 73.5 cm$^{-1}$ for 13-layer (linear chain model), in contrast to the measured trends, which blue shift with increasing thickness in the 70–90 cm$^{-1}$ range for 5–13 layers. Interestingly, however, a peak at 38 cm$^{-1}$ is

Figure 3. (a) DFT–LDA calculated Raman spectra of few-layer BP in the ultralow frequency range, with the black dashed lines guiding the Raman-active interlayer breathing mode. Note that the peaks are broadened artificially by Lorentzians. (b) Frequency evolution of DFT calculated and measured interlayer breathing mode as a function of the number of layers.
Letter with highlighted trends in the 70–90 cm⁻¹ range are still largely unknown. With decreasing thickness, the full width at half-maximum of the A₃⁺ breathing mode becomes larger. This trend is commonly observed in other materials and can be explained by increased boundary and impurity scattering in thinner samples as well as the commonly accepted RWL phonon confinement effects. We note that in several (but not all) of our spectra, there is an asymmetric broadening of the A₃⁺ breathing mode. By performing multi-Lorentzian fitting on the asymmetric peaks (Figure 4e), we find that the asymmetry is due to an extra peak X₁, which shows a red shift with increasing thickness, changing from 20.2 to 16.4 cm⁻¹ when the thickness increases from six to eight layers. The X₁ peak may come from the second lowest frequency interlayer breathing mode. Furthermore, from the linear-chain model, its thickness-dependent frequency can be simply described by

\[ \omega_n = \omega_0 \sqrt{2} \sin \left( \frac{\pi n}{2N} \right) \]  

(1) where \( \omega_0 \) corresponds to the frequency of the interlayer breathing mode in two-layer BP, that is, 75.0 cm⁻¹ in our calculation. The curve of eq 1 shown as the red line in Figure 3b fits both the LDA and experimentally measured frequency well. The good fitting suggests that the interlayer interactions are dominated by the interactions between nearest-neighbor layers. Similar to few-layer graphene and MoS₂ adsorbates or substrate effects seem to have negligible influence on the frequencies of the interlayer breathing modes. In Figure 3b, we show also the vdW-calculated frequencies, which do not follow the linear chain model well, in contrast to the experimental and LDA results. By using the above expression with the \( \omega_0 \) obtained from DFT–LDA, the thickness of the thin-film BP can be rapidly determined from the low frequency breathing mode. Furthermore, from the linear-chain model, \( \omega_0 \) can be expressed as \( \omega_0 = 1/[(\sqrt{2} \pi c)(k_c/\mu)^{1/2}] \), where \( \mu \) is the mass per unit area of the few-layer BP, \( c \) is the speed of light in cm/s, and \( k_c \) is the out-of-plane interlayer force constant. The thus derived out-of-plane force constant \( k_c \) (14.1 × 10¹⁹ N/m³) is related with the elastic modulus of few-layer BP by \( E_{33} = k_c l \) with \( l \) being the distance between the centers of mass for adjacent puckered layers. As a result, the calculated elastic modulus of \( C_{33} \) is around 73.9 GPa, consistent with calculated values for the bulk. The interlayer out-of-plane force constant \( k_c \) is significantly larger than those derived in the same way for other layered materials (\( k_c \) is 6.11 × 10¹⁹, 9.6 × 10¹⁹, and 9.3 × 10¹⁹ N/m² for Bi₂Te₃, graphite, and MoS₂, respectively). Similarly, if we fit the linear chain model to our experimental
data, we obtain $k_z$ of $12.3 \times 10^{19}$ N/m$^3$, larger than $k_z$ obtained by fitting the experimental frequencies of other layered materials. The larger force constants contribute to a larger $\omega_0$ factor in eq 1 and thus a larger thickness dependence for the $A_{3g}$ frequency. Specifically, the $A_{3g}$ frequency changes by 54 cm$^{-1}$ from two-layer to eight-layer BP, two times more than that in the transition metal dichalcogenides such as few-layer MoS$_2$ (31 cm$^{-1}$ from two-layer to eight-layer) and WSe$_2$ (20 cm$^{-1}$ from two-layer to eight-layer). The above analysis can also be applied to the shear modes $B_{3g}$ and $B_{2g}$, and we can get a shear elastic modulus of 8.9 and 20.4 GPa along the armchair and zigzag directions, respectively. The difference in the shear elastic moduli along the two in-plane directions reflects the strong anisotropic elastic properties of BP.

The larger force constant in BP suggests that the interlayer bonding may be different from that in the other well-studied layered materials like MoS$_2$ and graphite. Previously, it has already been shown that Coulombic interaction can affect the phonon frequencies in thin-film MoS$_2$ while covalent interlayer interactions are also likely to explain the larger surface force constants and resulting anomalous frequency trends in the same material. BP is a monotypic material, where all phosphorus atoms are in principle in the same local environment (not considering surface effects). We therefore do not expect a significant Coulombic interlayer interaction in BP. To ascertain the strength and nature of the interlayer interactions, we use the vdW functional to compute the difference between the charge density of bilayer BP and the sum of the phosphorene components (Figure S5a–c). As shown in Figure S5c, we find a clear covalent character in the interlayer interaction between adjacent layers, that is, the electrons are shared in the bonds between interlayers, with the largest electron density in the region between the nearest neighboring atoms in adjacent layers. Interestingly, while there is a clear directional character as described, the accumulated electron charge density is also slightly delocalized along the zigzag direction of the phosphorene lattice, which gives rise to the strong anisotropic in-plane elastic modulus. This interlayer covalent interaction is significantly larger than that in MoS$_2$ and graphene, as shown in Figure 6. Furthermore, compared with bilayer MoS$_2$ and graphene, the binding energy of bilayer BP is two times larger in both LDA and vdW calculations (Figure 5e). Since the interlayer force is proportional to the curvature of the binding energy versus distance, we also plot the derivative of the binding energy as a function of the separation distance in Figure 5f, which shows a larger curvature in bilayer BP compared with bilayer MoS$_2$ and graphene.

The large interlayer covalent character is in hindsight not surprising given that the phosphorene atoms each have an electron lone pair sticking into the interlayer vacuum region (phosphorus has five valence electrons, only three of which are involved in forming covalent intra-layer bonds). Furthermore, this sizable interlayer covalent interaction is consistent with the known surface reactivity of BP as well as the large interlayer band dispersion and small excitonic effects in bulk BP. On the other hand, it has also recently been predicted that electric fields applied perpendicularly to the BP thin films can result in a topological phase transition involving the formation of Dirac cone in the band structure. We have explained this phenomenon using a tight-binding model and have shown that
the interlayer interactions are a necessary condition for the formation of the Dirac cone. Similarly, we suggest that the formation of topological phases in bulk BP under pressure may also be related to the large covalent interlayer interactions, which is a topic worthy of further investigation.

In conclusion, we have theoretically predicted and experimentally measured the Raman spectra of interlayer modes in few-layer BP to gain insights into the interlayer force constants and interlayer interactions in BP. We demonstrate that the interlayer breathing modes have a large red shift in frequency with increasing thickness, corresponding to an unusually large interlayer force constant. We show that the interlayer force constants arise from sizable interlayer covalent interactions in BP. We have discussed a few known implications of this large interlayer interaction and suggest that this unusual interlayer interaction presents a playground for further new discoveries.

Methods. First-Principles Calculations. First-principles calculations of vibrational Raman spectra are performed within DFT as implemented in the plane-wave pseudopotential code QUANTUM-ESPRESSO. The LDA to the exchange-correlation functional is employed in the norm-conserving (NC) pseudopotential throughout the Raman spectra calculation. For the purpose of comparison, a van der Waals functional (vdW-DF2) with the Cooper’s gradient correction on the exchange and a PBE functional with dispersion correction in Grimme’s scheme (PBE-D2) are also performed to calculate the lattice parameters. To get converged results, plane-wave kinetic energy cutoff of 75 Ry is used for the wave functions. The slabs are separated by 16 Å of vacuum to prevent interactions between slabs (this value has been tested for convergence of phonon frequencies). Monkhorst–Pack k-point meshes of 19 × 15 × 1 and 11 × 11 × 13 are used to sample the Brillouin Zones for the thin films and bulk systems, respectively. In the self-consistent calculation, the convergence threshold for energy is set to 10⁻⁹ eV. All the atomic coordinates and lattice constants are optimized with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm. The structures are considered as relaxed when the maximum component of the Hellmann–Feynman force acting on each ion is less than 0.003 eV/Å. With the optimized structures and self-consistent wave functions, the phonon spectra and Raman intensities are calculated within DFPT as introduced by Lazzeri and Mauri. For the DFPT self-consistent iteration, we used a mixing factor of 0.1 and a high convergence threshold of 10⁻¹⁸ eV. In our DFPT calculations, we compute the static limit of the dielectric response self-consistently (including local field effects). We ignore the frequency dependence of the dielectric matrix as well as the ionic contribution to the dielectric response. These approximations have been found to work very well in practice and are particularly justified in our case given the very small phonon frequencies that are of interest here.

Synthesis. The samples of few-layer BP are mechanically exfoliated from bulk crystals (purchased from Smart Elements) onto a Si substrate covered with thermally grown 300 nm of SiO₂. Prior to exfoliation, the substrate surface is cleaned and activated with O₂ plasma to enhance the yield. An optical microscope is utilized to locate the position of few-layer BP. The thickness of as-prepared samples is determined by both optical contrast and AFM measurements.

Raman Spectroscopy. Raman scattering spectroscopy measurements are carried out at room temperature using a micro-Raman spectrometer (Horiba JY-T64000) in a backscattering configuration. A helium–neon laser (λ = 633 nm) was used to excite the samples. The backscattered signal was...
collected through a 100X objective and dispersed by a 1800 g/mm grating under a triple subtractive mode; this setting can achieve a spectral resolution of ~1 cm⁻¹. To avoid the laser heating effect on the sample, laser power at the sample surface was less than 0.4 mW.

**ASSOCIATED CONTENT**

**Supporting Information**

Polarization-dependent measurement of few-layer BP and Raman measurement on three-layer BP samples. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b00775.

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**Notes**

The authors declare no competing financial interest.

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