Thermodynamic stability and vibrational anharmonicity of black phosphorene—beyond quasi-harmonic analysis

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Abstract
Thermodynamic stability and vibrational anharmonicity of single layer black phosphorene (SLBP) are studied using a spectral energy density (SED) method. At finite temperatures, SLBP sheet undergoes structural deformation due to the formation of thermally excited ripples. Thermal stability of deformed SLBP sheet is analyzed by computing finite temperature phonon dispersion, which shows that SLBP sheet is thermodynamically stable and survives the crumpling transition. To analyze the vibrational anharmonicity, temperature evolution of all zone center optic phonon modes are extracted, including experimentally forbidden IR and Raman active modes. Mode resolved phonon spectra exhibits red-shift in mode frequencies with temperature. The strong anharmonic phonon–phonon coupling is the predominant reason for the observed red-shift of phonon modes, the contribution of thermal expansion is marginal. Further, temperature sensitivity of all optic modes are analyzed by computing their first order temperature co-efficient ($\chi$), and it can be expressed as $B_{2g} > A_{1g} > B_{1g}^{1g} > B_{2g}^{1g} > B_{1g} > A_{2u}$ & $B_{2u} > B_{1u}$ for Raman and IR active modes, respectively. The quasi-harmonic $\chi$ values are much smaller than the SED and experimental values; which substantiate that quasi-harmonic methods are inadequate, and a full anharmonic analysis is essential to explain structure and dynamics of SLBP at finite temperatures.

Keywords: phosphorene, phonons, anharmonicity, thermal stability, temperature co-efficient, spectral energy density method, molecular dynamics simulation

(Some figures may appear in colour only in the online journal)

1. Introduction
The search for 2D materials with novel, structural, electronic and thermal properties has geared up in past few years [1]. Single layer of black phosphorous, known as black phosphorene (SLBP) is a special member in 2D family due to its intriguing structural and electronic properties [2–4]. The band gap ($\approx$1.5 eV) [5] and carrier mobility ($\approx$1000 cm$^2$ V$^{-1}$ s$^{-1}$) [2] of SLBP make it a promising candidate for nano [2, 4, 5] and opto-electronic device fabrications [3, 4]. SLBP also found its application in photo-transistors [2, 4–8], thermo-electric devices [6, 8, 9] and gas sensors [10].

Being a technologically promising material in many industries, it is essential to have knowledge on its vibrational and thermal properties. The vibrational dynamics of mono and few-layer phosphorene have been extensively studied using Raman scattering techniques [11–13]. Among the six Raman active modes only three have been detected in Raman spectroscopy due to the constraints imposed by Raman scattering geometry [14]. Similarly the temperature evolution of IR active modes are also not reported in literature. In Raman spectroscopy, factors like substrate effect, thickness, laser power, morphology etc, will alter the intrinsic phonon transport in SLBP [12, 15, 16].
Under such circumstances atomistic simulations will help to predict the intrinsic properties of materials. *Ab initio* simulation have been employed to study the lattice dynamics (LD) of SLBP [13, 14, 17, 18]. Strain evolution of phonon modes are studied in detail within the *ab initio* frame work [11, 17, 19]. Fei and Yang [11] analyzed the strain dependence of optic modes using density functional theory (DFT) calculations and compared with Raman spectra, they found a substantial peak shift under different strain conditions. A detailed study on strain dependent frequency shift of lattice vibrational modes shows that the shift in a particular modes can be used to find out the strain distribution in SLBP [17]. Raman spectra of single, few layer and bulk BP were studied using DFT calculation [18]. In the above study, authors reported the layer dependence of the in-plane and out of plane vibrational modes, and they argued that this layer dependent frequency shift will be helpful to identify the layer thickness in SLBP.

The aforementioned strain and layer dependent frequency shift of SLBP has been studied using harmonic and quasi-approximation (QHA), which is valid only at low temperatures [20]. As temperature increases, phonon population and their interactions become prominent. These phonon–phonon scattering events have far reaching consequences on the structure and dynamics of 2D materials [21–23]. Under harmonic and quasi-harmonic approximation, phonon modes are decoupled and hence cannot be used to model the phonon–phonon scattering events. Several authors used QHA to study the temperature dependent, structural, thermal and vibrational properties of SLBP [17, 24–26]. Aierken et al [17], studied the temperature evolution of specific heat, free energy and thermal expansion using QHA. The authors warned the usage of quasi-harmonic approach at high temperature due to the emergence of strong phonon–phonon interactions, which are not incorporated in QHA.

The strong anharmonic nature of 2D crystals are renowned [21, 27, 28] and it is ascribed to their light weight and single atom thick layered structure. Information on phonon anharmonicity is essential to explain the phonon spectroscopy and thermal transport phenomena. There are very few attempts to probe the strong anharmonic phonon–phonon interactions in SLBP [14, 29]. Cai et al [14] made an effort to quantify the anharmonicity in SLBP by computing the mode Grüneisen parameter ($\gamma$). They observed that the small momentum phonons are frozen with strain, and have smaller anharmonicity. Grüneisen parameter is computed as strain derivative to phonon frequencies obtained from QHA. In many circumstances, the system becomes unstable under large compressive strains, which compels one to compute the strain derivative and $\gamma$ using less accurate finite difference method around the $\Gamma$ point. Hence, Grüneisen parameter based approach is heuristic; it enables one to obtain the effects of strain coupling on mode frequency, but extra caution is needed to deduce other anharmonic effects [30].

Recently, Tristant et al [29] studied the anharmonicity of few layer black phosphorene using a combination of Raman spectroscopy and DFT calculations. Their anharmonic lattice dynamics calculation depicts that the quartic phonon decay is the dominant process at high temperatures. Despite all the methodological advancement, anharmonic LD calculations can include only cubic or quartic anharmonicity [21, 22]. Nevertheless, it has reported that higher order anharmonic terms have significant effect on phonon scattering events in graphene and cannot be ignored [31]. These observations enforces an analysis with anharmonicities of all orders in SLBP as well. Moreover, unlike graphene, optic modes of SLBP contribute significantly to thermal conductivity ($\sim$30%) [32], hence a detailed analysis of anharmonicity of all optic modes apart from the Raman active, are needed. Motivated from the above facts, the objective of the present study is to analyze the finite temperature structural stability and intrinsic vibrational anharmonicity of all zone center optic phonon modes of SLBP sheet with full anharmonicity of effective interaction between atoms. To accomplish the above task, harmonic, quasi-harmonic and full anharmonic calculations are performed in a systematic manner. The rest of the paper is organized as follows, theoretical and computational methods adopted is discussed in section 2. The major results obtained are presented and discussed in section 3. At end, conclusions (section 4) of the present study are unveiled.

2. Theoretical and computational methods

To compute the structural and vibrational properties at finite temperatures, a spectral energy density (SED) method is used in conjunction with MD simulation [28]. In SED method, anharmonicities of all orders are naturally incorporated, hence it would bring out the intrinsic phonon transport properties. A detailed theoretical derivation of SED can be found in our previous paper [28]. For the sake of readability, a brief description of SED method is given below. SED method works in two sequences, firstly a lattice dynamics (LD) calculation is done to obtain the polarization vector $\{v_\alpha (\kappa)_{f}\}$, $\alpha = x, y, z$; $\kappa = 1, \ldots, N_k$ of $j$th normal mode of vibration (where, $\vec{q} = \text{wave vector}, j = \text{mode index} & N_k = \text{number of basis atoms}$). Secondly, MD simulations are performed at desired temperature to obtain the velocities, $v_\alpha (\vec{r}(\kappa)_{f})_{i}$ of $i$th atom (where $\vec{r}$ is the cell-index) at time $t$. Further, these velocities are projected onto $j$th mode of vibration, and thus define a quantity $\psi (\vec{q}^j)_{t}$ as,

$$\psi (\vec{q}^j)_{t} = \sum_{\alpha,\kappa} \left( \sum_{i} v_\alpha (\vec{r}(\kappa)_{f})_{i} \exp \left(-i\vec{q} \cdot \vec{r}(\kappa)_{f}\right) \right) e^{\alpha}_\kappa (\vec{q}^j)_{t}.$$  

The Fourier transform and then power spectrum $\left| \tilde{\psi} (\vec{q}^j, \omega) \right|^2$ will yield the mode resolved phonon frequencies and linewidths of all phonon modes at any $\vec{q}$ point in the Brillouine zone.
In the present study, molecular dynamics (MD) simulations are performed using LAMMPS package [33]. The phosphorous–phosphorous interaction in SLBP is defined using Stillinger–Weber (SW) potential parametrized by Jiang et al [34]. The authors fit the SW parameters to phonon spectrum computed via ab initio simulation, which guarantees an accurate prediction of phonon dynamics. Also, they considered the cross pucker interaction, bond stretching and intra & inter group angle bending for their parametrization. The SW potential describes the non-linear properties of covalent crystals reasonably good [35], which makes the prediction of higher order phonon transport more accurate [36]. Periodic boundary conditions are employed in all three direction, and a vacuum separation of 20 Å is provided along c-axis to eliminate the un-physical interactions between the periodic images. Further, to get rid of the residual stresses, the system is relaxed in conjugate gradient algorithm. The lattice parameters of relaxed structures are $a = 4.596 \text{ Å} \quad \text{and} \quad b = 3.278 \text{ Å}$, which shows excellent agreement with earlier studies [12, 37]. Phonon frequencies and polarizations are computed under harmonic approximation ($T = 0 \text{ K}$) using a combination [28] of LAMMPS and PHONOPY [38]. To compute the finite temperature properties, a simulation cell of size $50 \times 50 \times 1$ (10,000 atoms) is adapted, and the system is equilibrated in in-isobaric–in-isothermal (NPT) ensemble for 0.5 ns. Once ensuring the thermal equilibrium, the NPT ensemble is unified and coupled to micro canonical (NVE) ensemble. Subsequently, the velocities of each atom is collected in a predefined interval of 5 fs, and the total simulations time is 3.2 ns.

3. Results and discussions

The unit-cell of SLBP is a rectangle containing four basis atoms and belongs to $\text{p}mn\alpha$ ($D_{2h}$) space group (figure 1). Similar to graphene and 2D h-BN, SLBP also possess a honeycomb lattice structure, where P atoms with covalent bonding forms a puckered like structure. SLBP unitcell contains 4 basis atom, hence there are 12 modes of vibration [3 acoustic ($A$) + 9 optic (O)]. Figure 2 shows the phonon dispersion (at $T = 0 \text{ K}$) of SLBP. The acoustic modes are labeled based on their polarization (L-longitudinal, T-transverse and Z-out of plane) and the optic modes are designated as per group theoretical notation at $\Gamma$ point [11]. The absence of imaginary modes in phonon dispersion ensures the structural stability of SLBP. The out of plane acoustic (ZA) mode shows a $q^2$ behavior near the long wavelength limit, which is a fingerprint of typical 2D system [39]. The slope and thus group velocities of LA and TA branch is relatively small along armchair ($\Gamma$–$Y$) with respect to zig-zag ($\Gamma$–$X$) direction, also the high frequency optic mode frequencies are more flat along the armchair direction in comparison with zig-zag and it is in accordance with previous observation [14].

According to group theoretical analysis, among nine optic modes, two are IR active ($B_{1u}$ and $B_{2u}$), six are Raman active ($A_{1g}$, $A_{2g}$, $B_{1g}$, $B_{2g}$, $B_{1u}$, $B_{2u}$) and one is inactive ($A_{u}$) [14]. Though there are six Raman active modes, only three ($A_{1g}$, $B_{2g}$, $A_{2g}$) of them have been reported experimentally [14]. The LD $A_{1g}$ mode frequency is 321.59 cm$^{-1}$, which is underestimated by 10.8% in comparison with Raman data (360.61 cm$^{-1}$) [5]. The $B_{2g}$ mode predicted by LD (439.55 cm$^{-1}$) shows an excellent agreement with Raman measurement (438.90 cm$^{-1}$) [5]. The difference is only 0.1% which is negligibly small. Whereas, the LD $A_{2g}$ mode frequency (446.90 cm$^{-1}$) is overestimated by 4.7% in comparison with Raman values (469.00 cm$^{-1}$) [5]. The agreement between the LD and experiment is satisfactory. Although, the present SW potential is the best among available in literature for predicting the dynamics of phonons and their non-linear interaction, it needs further refinement to make the prediction more accurate.

Finite temperature structural stability of free standing 2D crystals are a matter of concern always. As per Mermin–Wagner theorem [40], long wavelength thermal fluctuations would disrupt the long range order in 2D crystals. These thermal fluctuations are suppressed by the strong anharmonic coupling between the in-plane stretching and out of plane bending vibrations, which makes the sheet stable at finite temperature with height fluctuation on surface called ripples [28, 41]. Figure 1 shows the relaxed SLBP sheet at 300 K, thermally excited ripple deformations are clearly visible. Rippling is more along $a$-axis (zig-zag) and it forms a curved shape. Contrast to graphene and 2D h-BN, the ripple deformation is highly anisotropic in SLBP, which attributes to its distinct puckered geometry [37].

Thus before proceeding with further calculations, it is mandatory to analyze the thermodynamic stability of deformed sheet. In-order to analyze the thermal stability, phonon dispersion are computed at finite temperatures with rippled structure. Figure 3 shows the phonon dispersion curves at 100 & 300 K, they share a resemblance with LD phonon dispersion curves (figure 2). The quadratic nature of ZA mode is preserved at finite temperature as well. In SED phonon dispersion all modes are real and positive, which confirms that the SLBP sheet is thermodynamically stable and survives the crumpling transition at finite temperatures. Unlike LD phonon dispersion, there are temperature induced broadening of phonon branches in SED dispersion. Under harmonic

![Figure 1. The atomistic structure of SLBP sheet at 0 K and 300 K.](image-url)
Figure 2. (a) Phonon dispersion and (b) schematic of phonon polarization at \( T = 0 \) K. Modes are designated as per group theoretical notation at \( \Gamma \) point.

Figure 3. Phonon dispersion curve at \( T = 100 \) & \( 300 \) K; absence of imaginary modes confirms the dynamical stability of sheet at finite temperatures. Temperature induced shift and broadening of phonon branches are conspicuous.

approximation, phonon modes have infinite lifetime which leads to infinite thermal conductivity. But in reality, practical materials have finite thermal conductivity. At finite temperatures, phonon modes start to interact with each other and share their energy and hence they have finite life time and thermal conductivity, which is a manifestation of phonon anharmonicity. In figure 3, it can be seen that, both acoustic and optic branches are broadened. The temperature induced broadening is more for the optic branches than the low lying acoustic branches, which indicates that optic modes have lesser phonon life time than acoustic modes and they are more prone to temperature changes and would be strongly anharmonic in nature.

It should be noted that many optic mode branches are merged due to the broadening effect. Hence, in-order to analyze the vibrational anharmonicity of optic phonons, mode resolved phonon spectra are computed as a function of temperature at \( \Gamma \) point. In the present study, the calculations are restricted in the temperature range of 100–400 K. Above 500 K, there is an abrupt change in potential energy (figure 4), which signifies that system is unstable above this temperature. Experimentally, the decomposition temperature of SLBP is 598 K [12], which is corroborating with the above observation. Below 100 K the quantum effect will be dominant, that cannot be tapped in classical MD simulations. Figure 5 shows the mode resolved zone center phonon spectra at 100 and 300 K. The temperature induced peak shift and broadening are discernible. To extract the exact mode frequency shift, the peak positions are fitted to a Lorentzian function and is shown in figure 6.

There will be two distinct contributions to the anharmonic shift in mode frequency; one stems from the thermal expansion of lattice, and the other from the phonon–phonon scattering effects. The anharmonicity which arise from thermal expansion is of weak type and can be studied using quasi-harmonic methods. The strong anharmonic phonon–phonon scattering effects are described using change in phonon self energy (SE) [42]. Phonon SE is a complex function, which can be written as \( \Delta \left( \omega \left( \frac{\mathbf{q}}{\mathbf{j}} \right), T \right) + i \Gamma \left( \omega \left( \frac{\mathbf{q}}{\mathbf{j}} \right), T \right) \). The real part \( \Delta \left( \omega \left( \frac{\mathbf{q}}{\mathbf{j}} \right), T \right) \) describes the change in mode frequency
Figure 4. Potential energy variation with temperature. At 500 K, there is an abrupt change in potential energy, indicates that system is unstable above this temperature.

Figure 5. Temperature dependent optic mode phonon spectra at $\Gamma$ point. Peak shift and broadening are evident with temperature. The IR, Raman and inactive modes are labeled in blue, green and black color, respectively.

(i.e. re-normalization) due to the phonon–phonon scattering effect, and thus provide the temperature dependent mode frequency shift. The complex part $\Gamma(\omega q_j, T)$ gives the decay and broadening of phonon modes, which is inversely proportional to the phonon life time. In this study, two different types of calculations are performed to get a qualitative idea on role of different anharmonic contribution to the mode frequency shift. In the first one, the mode frequency shift is computed at temperature dependent lattice parameter, called quasi-harmonic LD (QH-LD). In the second one, SED method in conjunction with an isothermal–isobaric ensemble (NPT) molecular dynamics (MD) simulation (NPT-MD) is employed.

In QH-LD only thermal expansion effect is incorporated; while, in NPT-MD along with thermal expansion all phonon–phonon coupling effects are included. Among these phonon–phonon coupling events, simplest one is the three-phonon process in which, either one phonon decays in to two other phonons or two phonons annihilate to create a third one.

This can be formulated as

$$\bar{q}_1 = \bar{q}_2 + \bar{q}_3 + \bar{G}$$  \hspace{1cm} (1)

$$\bar{q}_1 + \bar{q}_2 = \bar{q}_3 + \bar{G}$$  \hspace{1cm} (2)

where $\bar{q}_1, \bar{q}_2$ & $\bar{q}_3$ are the phonon wavevectors and $\bar{G}$ is the reciprocal lattice vector. Zero and non-zero value of $\bar{G}$ indicates the normal (N) and Umklapp (U) processes. Phonon–phonon coupling events are modeled by incorporating third and higher order terms in the expansion of lattice potential energy around the equilibrium position. Attempts have been made to model the three-phonon process using finite difference methods [43, 44], as well as density functional perturbation theory (DFPT) [21, 22]. In general, it is difficult to model the quartic and higher order phonon process within ab initio framework. Since the un-truncated interatomic potentials are used in MD simulations, all higher order phonon–phonon scattering processes are naturally included, that enables to extract the true anharmonicity in materials.
Figure 6. Optic mode frequency shift with temperature, blue sphere and red squares are obtained from quasi-harmonic lattice (QH-LD) and NPT molecular dynamics (NPT-MD) simulations. The IR, Raman and inactive modes are labeled in blue, green and black color, respectively. Frequency shift is fitted with a linear equation $\omega = \omega_0 + \chi T$.

More detailed information on anharmonic phonon interactions and decay can be found in the following references [45, 46].

Figure 6 shows the temperature dependent mode frequency shift of all optic modes. It is evident that all QH-LD mode frequencies are red-shifted with increase in temperature. SLBP shows thermal expansion in these temperature range [17], once the lattice expands, the bonds and then the associated force constants become softer, leads to the red-shift in mode frequencies. The NPT-MD mode frequencies are also red-shifted with much steeper variations. The incorporation of strong phonon–phonon coupling leads to the enhanced red-shift of mode frequencies in NPT-MD simulations. From the above results, it can be concluded that, though thermal expansion contribute to the shift in mode frequencies, the pronounced shift stems from the phonon–phonon scattering effects. This results envisages the strong anharmonicity associated with optic phonon modes. At finite temperatures, the SED function and the power spectra are computed using the eigenvector obtained from LD calculations (section 2), with an assumption that the anharmonic effect are insignificant on phonon polarization. To check the validity of this assumption, the phonon peak positions of lowest ($B_{1u}$) and highest ($B_{2u}$) frequency modes are computed without eigenvector. The peak position obtained for $B_{1u} \& B_{2u}$ are 158.312 cm$^{-1}$ & 446.355 cm$^{-1}$, respectively. These values are 1.75 cm$^{-1}$ & 1.73 cm$^{-1}$ higher than that obtained via projection technique (with eigenvector), and the difference is too small to be considered significant.

Table 1. First order temperature co-efficients ($\chi$) in cm$^{-1}$ K$^{-1}$.

| Mode  | $\chi_{QH-LD}$ | $\chi_{NPT-MD}$ | Expt. |
|-------|----------------|-----------------|-------|
| $B_{1u}$ | $-0.0031$ | $-0.0473$ | — |
| $B_{1g}$ | $-0.0047$ | $-0.0377$ | — |
| $B_{1g}$ | $-0.0021$ | $-0.0610$ | — |
| $A_{1g}$ | $-0.0025$ | $-0.0290$ | $-0.0158$ [12] |
| $B_{2g}$ | $-0.0084$ | $-0.0401$ | — |
| $A_{1g}$ | $-0.0031$ | $-0.0547$ | — |
| $B_{2g}$ | $-0.0093$ | $-0.0668$ | $-0.0315$ [12] |
| $A_{2g}$ | $-0.0176$ | $-0.0663$ | $-0.0312$ [12] |
| $B_{2u}$ | $-0.0158$ | $-0.0692$ | — |

From the above discussion, it is found that all optic modes are red-shifted with temperature. To quantify the temperature dependence of each mode, their first order temperature co-efficient ($\chi$) is calculated. The linear relationship of phonon frequencies with temperature is valid at moderate and high temperature regimes [47]. Hence, to extract the values of first order temperature co-efficient ($\chi$) the frequency shift of each mode is fitted with a linear equation $\omega = \omega_0 + \chi T$ [12, 48, 49] where, $\omega$ is the peak frequency, $\omega_0$ is the extrapolated peak position to 0 K, $\chi$ is first order temperature co-efficient and $T$ is the temperature.

The $\chi$ values (table 1) are deduced from the slope of the $\omega$ vs $T$ plot. The quasi-harmonic (QH-LD) $\chi$ values are much smaller than that of NPT-MD and experimental $\chi$
values. Among the Raman active modes, quasi-harmonic $\chi$ value of $A_g^1$ mode is not much different from NPT-MD and experimental data in comparison with other modes. $A_g^1$ mode is an in-plane mode and its frequencies are sensitive to thermal expansion of in-plane lattice. At the same time, the out of plane vibrations, say $A_g^2$, mode does not change much with in-plane thermal expansion. This is evident from the large difference in experimental $\chi$ values of these modes (table 1). To verify this assumption, mode frequencies of one in-plane ($A_g^1$) & out of plane ($A_g^2$) modes are computed using a canonical (NVT) ensemble simulation and compared with NPT ensemble at 300 K. Since the volume of the simulation cell is fixed, thermal expansion effects are not included in the NVT ensemble simulation, and the shift in mode frequencies are purely due to phonon–phonon coupling effect.

From the table 2 it is clear that, the frequencies obtained from NPT and NVT simulations differ slightly for in-plane $A_g^2$ modes, whereas, the difference is too small to be significant for out of plane ($A_g^1$) vibration. Hence it can be inferred that, for in-plane modes, though the thermal expansion contributes to the mode frequency shift, the significant contribution comes from the phonon–phonon coupling effects. In the case of out of plane vibrations, the effect of thermal expansion is negligibly small and the shift is purely due to phonon–phonon coupling effects. Maradudin and Fein reported that, phonon self energy (SE) contains the anharmonic effects from higher order terms, hence it is not necessary to incorporate the effects of thermal expansion in phonon SE [42]. However, present results shows that, thermal expansion may be indirectly altering the anharmonic phonon–phonon coupling effects and then the mode frequency shift, particularly for in-plane modes. Overall, the weak dependence of frequency shift on thermal expansion substantiate that, quasi-harmonic methods are in-adequate to explain the frequency shift and a full anharmonic treatment is essential to bring out the intrinsic phonon dynamics in SLBP.

The $\chi$ value of NPT-MD $A_g^1$ mode ($-0.0290$ cm$^{-1}$ K$^{-1}$) shows good agreement with Raman data ($-0.0158$ cm$^{-1}$ K$^{-1}$). For other two Raman modes ($B_{3g}$ & $A_g^2$) the NPT-MD $\chi$ values are roughly twice that of experimental values. This again correlated with in-plane and out of plane nature of vibrations. $A_g^1$ mode is an out plane mode, while $B_{3g}$ & $A_g^2$ are in-plane modes. The in-plane mode frequencies are more susceptible to substrate effect. Due to the mismatch of thermal expansion co-efficients, the substrate could induce a compressive strain on film, which could alter the shift in mode frequencies, this phenomena had already been observed in graphene [50, 51]. The above arguments are strengthened with the findings of Su and Zhang [12], they found that the $\chi$ values of thin BP films are more sensitive to the substrate effect than thick BP film. Along with substrate effect, the temperature induced ripples have significant effect on thermal expansion of 2D materials [52], this ripple morphology get altered while transferring to substrate, which again affects the intrinsic vibrational properties [53]. The $\chi$ values of un-detected Raman active, IR and inactive modes are also tabulated in table 1. These modes also shows significant deviation from quasi-harmonic prediction, signifies their strong anharmonic nature. Based on the above analysis, the temperature sensitivity of Raman active modes can be expressed as $B_{3g} > A_g^2 > B_{1u} > B_{3g} > B_{1g} > A_g^1$. Fei and Yang [11] reported that the strain induced inter-atomic distance variation is more for $B_{3g}$ and $A_g^2$ modes than that of $A_g^1$, hence they shows significant shift in mode frequencies, which is in agreement with above observation. In the case of IR active mode, $B_{1u}$ mode shows more deviation from quasi-harmonic prediction and their temperature sensitivity can be written as $B_{2u} > B_{1u}$. This systematic study helps to understand temperature dependent optic phonon spectroscopy of all modes in SLBP, and it is complementary to the conventional Raman and IR techniques. Also, a comprehensive understanding of phonon anharmonicity will be helpful in interpreting the thermal properties of SLBP, which in turn helps in designing the SLBP based devices for thermal management and thermo-electric applications.

4. Conclusions

In conclusion, the structural stability and vibrational anharmonicity of optic phonon modes of single layer black phosphorene (SLBP) are studied beyond the conventional harmonic and quasi-harmonic lattice dynamics. The above task has been accomplished using a spectral energy density (SED) method. Finite temperature structural stability analysis shows that SLBP sheet is thermodynamically stable and survives the crumpling transition. Mode resolved optic phonon spectra, which includes experimentally forbidden IR and Raman active modes are extracted. Mode frequencies exhibit a red-shift with temperature, which is predominantly due to the strong anharmonic phonon–phonon coupling effects; the contribution of thermal expansion is marginal. Temperature sensitivity ($\chi$) of each mode is gauged by computing their first order temperature co-efficient. The strong deviation of quasi-harmonic $\chi$ values from the SED and the experimental data portrays the strong anharmonicity associated with optic modes in SLBP. The outcome of the present study has two fold effect. Firstly it brings out the strong anharmonic nature of phonon modes in SLBP. This physical insight will be helpful in interpreting the phonon spectroscopy of SLBP, which is conducive to fabricate SLBP based devices for thermo-electric applications. Secondly, the present study demonstrate the necessity of going beyond the conventional harmonic and quasi-harmonic analysis to explain the structural and vibrational dynamics of 2D crystals in which anharmonicity plays a crucial role at finite temperatures.
