Research Paper

First-principles investigation on thermal properties and infrared spectra of imperfect graphene

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HIGHLIGHTS

- Imperfect graphene properties were calculated based on first-principles theory.
- Defects in graphene structure results in lower specific heat and higher free energy.
- Specific heat rises quickly with temperature and flattens at high temperature.
- Peaks and splits were observed in Raman and IR spectra of imperfect graphene.

ARTICLE INFO

Article history:
Received 18 October 2016
Revised 14 December 2016
Accepted 20 December 2016
Available online 30 January 2017

Keywords:
Graphene
First-principles
Defects
Thermal properties
Optical spectra
Specific heat

ABSTRACT

In this study we used first-principles density functional theory to investigate the thermal and optical properties of graphene. Graphene phonon properties were first calculated by the density-functional perturbation theory and then used to acquire thermal properties such as the specific heat, free and total energy, and entropy, as well as the infrared and Raman spectra. Results show that the peaks of phonon density of states at about 40 and 45.5 THz in the perfect graphene (G) were shifted to 40.5 and 46 THz in the imperfect graphene (G-D), respectively. There are peaks at 16.5, 19, 25, and 43.5 THz in the G-D curve, while there is no obvious peak at same frequencies in that of the G. The specific heat and entropy are lower for the G-D than for the G at temperature >280 K, but the tendency is slightly reversed at temperature <200 K. The total energy, change in vibrational internal energy, and change in the vibrational Helmholtz free energy are all lower for the G-D than for the G. The infrared (IR) spectrum, no absorption peak exists for perfect graphene, but strong absorption is found at about 233, 830 and 1392 cm⁻¹ for the G-D. The character peak of sp² carbon atom in-plane vibration in the Raman spectrum is shifted from 1589 cm⁻¹ for the G to 1530 cm⁻¹ for the G-D. The defects in the G-D caused the peaks and splits in the IR and Raman spectra.

1. Introduction

Graphene, the two-dimensional carbon film has aroused tremendous research interests for exploring innovative electrical, mechanical, and thermal properties in the past few years [1,2]. Graphene could replace some materials in use for many existing applications. For example, the composite of graphene/Fe₂O₃ was used as an anode material for Li-ion batteries and it exhibited discharge and charge capacities of 1693 and 1227 mAh/g, respectively [1]. Graphene oxide/Fe₂O₃-nanotubes composites exhibited a high specific capacitance of 133.2 Fg⁻¹ and the electrode showed good long-term cycle stability [2]. Thermal conductivity of the graphite composite enhances the heat transfer rate about 3.35 times with Graphite at 5.0 vol.% in phase change materials [3]. Feng et al. [4] reported the measurement of thermal conductivity of a suspended single-layer graphene, and found the thermal conductivity at room temperature was 4840–5300 W/(m·K). Zhang et al. [5] calculated the thermal conductivity of graphene by Green-Kubo method. Their results showed 2903 ± 93 W/(m·K) for the pristine graphene, in which the out-of-plane phonon mode contribution was 1202 ± 32 W/(m·K). Wirth et al. [6] investigated how thermal conductance responded to edge defects in narrow graphene. They showed that Hydrogen absences produce reductions in conductance in planar graphene. Cao et al. [7] studied the thermal

http://dx.doi.org/10.1016/j.applthermaleng.2016.12.087
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transport behavior in an 18.2-nm-long graphene sheet and found a parallel relationship on ballistic resistances in parallel systems, and a complicated superimposed effect of arrangement mode on ballistic resistances in series systems governed by the phonon localization and corresponding change of phonon transmission angle.

The structure of graphene and its chemically derived forms were studied for realizing special properties [8]. The research of in-plane thermal conductivity of graphene showed that thermal conductivity increases with length. Surface oxidation and phonon-defect scattering at the surface oxidized groups suppress the density of state of the phonon mode due to C–C bonds [9]. Research showed that the graphene nano-ribbons (GNRs) exhibit a rapid drop in thermal conductivity with increasing degree of functionalization of methyl and phenyl groups at random positions. The thermal conductivity of nanoribbons with zigzag edges is more sensitive in the degree of functionalization than nanoribbons with armchair edges [10].

In addition to experimental works to explore new applications of graphene and new properties of the derivatives [11,12], theoretical studies have been carried out to simulate the structure and unique properties of the carbon nanotube [13,14] and graphene [15,16]. The simulation was done for the effect of optical and acoustic phonon-scattering in the presence of line-edge-roughness on the electronic properties of ultra-scaled armchair graphene nano-ribbons. It was shown that the edge roughness slightly reduces the onset of optical phonon emission, acoustic phonons reduce off-state conductance and optical phonons reduce on-state conductance [17]. The first-principles density functional calculations were performed for the hydrogen transfer reaction between graphene surface and a mixture of hydrogen carrier and electron donor to investigate the microscopic mechanism for the wet-chemical hydrogenation of graphene. The electronic structure and energetics of the hydrogen transfer from hydrogen carriers, such as CH$_3$OH or CH$_3$NH$_3$, are considered with an alkali atom as an electron donor, or with externally added electrons. Researchers deduced from the results that the hydrogen carrier system with CH$_3$NH$_3$ does not require the presence of an alkali atom [18]. The thermal transport properties of graphene and graphene nano-ribbons were simulated by non-equilibrium molecular dynamics simulation; results revealed abnormal thermal transport in graphene, and a low thermal conductivity at room temperature compared to graphene [19]. The atomistic Green’s function study was adopted to simulate the phonon transport through a heterogeneous interface between bulk TiC substrates and graphene nanoribbons [20].

The substitution of atom in graphene is important for production of soluble materials or adding the functional group onto the graphene wall to make novel composite materials [21,22]. However, it is very difficult for imaging techniques to visualize the substitution on the graphene wall and to reveal how the substitutions affect the properties of the graphene. The current work aims at investigating the sensitivity of infrared (IR) and Raman parameters and the phonon properties upon the absent C atom in graphene (see Fig. 1) using first-principles theoretical approach.

2. Theoretical method

The present calculations were carried out by VASP code [23,24], which is a complex package for performing ab-initio quantum-mechanical molecular dynamics (MD) simulations based on the first-principles density functional theory (DFT). For calculation of a system, the approach implemented in VASP is based on the (finite-temperature) local-density approximation with the free energy as variable quantity and an exact evaluation of the instantaneous electronic ground state at each MD time step. VASP uses efficient matrix diagonalization schemes and an efficient Pulay/Broyden charge density mixing. These techniques avoid all problems possibly occurring in the original Car-Parrinello method [25], which is based on the simultaneous integration of charged particles, both electronic and ionic, equations of motion. The interaction between them is described by ultra-soft Vanderbilt pseudopotentials (US-PP) [26] or by the projector-augmented wave (PAW) method. US-PP (and the PAW method) allows for a considerable reduction of the number of plane-waves per atom for transition metals and first row elements.

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**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A_T$</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>$C_V$</td>
<td>vibrational specific heat at constant volume</td>
</tr>
<tr>
<td>$d$</td>
<td>the number of degrees of freedom</td>
</tr>
<tr>
<td>$E_{elec}$</td>
<td>the electronic energy of formation</td>
</tr>
<tr>
<td>$E_0$</td>
<td>the total energy</td>
</tr>
<tr>
<td>$E_{vib(T)}$</td>
<td>the change in vibrational internal energy</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck constant</td>
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<tr>
<td>$j$</td>
<td>the phonon mode</td>
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<tr>
<td>$k_B$</td>
<td>the Boltzmann constant</td>
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<tr>
<td>$n$</td>
<td>the wave vector</td>
</tr>
<tr>
<td>$S_T$</td>
<td>the vibrational entropy</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
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<tr>
<td>$\chi$</td>
<td>the dimensional vector</td>
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**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\Delta\omega$</td>
<td>frequency interval</td>
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<tr>
<td>$\omega$</td>
<td>frequency</td>
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**Abbreviations**

<table>
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<tr>
<td>G-D</td>
<td>imperfect graphene</td>
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<tr>
<td>MD</td>
<td>molecular dynamics</td>
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<td>ZPE</td>
<td>the zero point energy</td>
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![Fig. 1. The structure of a unit cell of graphene with an absent C atom in the circled position for the G-D.](image)
The phonon density of states $g(o)$ provides the frequency distribution of normal modes and is obtained as a histogram plot from
\[ g(o) = \frac{1}{n \Delta o} \sum_{kj} \delta_{\Delta o}(o - \omega(k,j)) \] (1)
where $n$ is the wave vector; $\omega$ is frequency; $\Delta o$ is frequency interval of the histogram; $d$ is dimension of the dynamical matrix; $k$ is the discrete wave vector; $j$ is the phonon mode. The phonon density of states can be normalized as
\[ \int g(o) \, d\omega = 1 \] (2)
The partial phonon density of states of provides the contribution of one specific atom $\mu$ vibrating along a particular Cartesian direction
\[ g_{i,\mu}(o) = \frac{1}{n \Delta o} \sum_{kj} |e_i(k,j;\mu)|^2 \delta_{\Delta o}(o - \omega(k,j)) \] (3)
where the $i$th Cartesian component of the polarization vector for particle $\mu$ is $e_i(k,j;\mu)$ and phonon frequency is $\omega(k,j)$.
Since the dimension of the dynamical matrix is the number of phonon branches and the number of degrees of freedom in the unit cell, the normalization condition holds:
\[ \int g_{i,\mu}(o) \, d\omega = \frac{1}{d} \] (4)
The off-diagonal partial phonon density of state can be defined as
\[ g_{i,\mu}(o) = \frac{1}{n \Delta o} \sum_{kj} \delta_{\Delta o}(o - \omega(k,j)) \] (5)
The contribution of lattice vibrations to thermodynamic functions is derived from the integrated phonon density of states.
The heat capacity of graphene, $C_v$, is represented in terms of contributions of all atoms and possible directions by
\[ C_v = \sum_{i,\mu} C_{i,\mu} \] (6)
\[ C_{i,\mu} = d\kappa T \int g_{i,\mu}(o) \left( \frac{\hbar o}{2\kappa T} \right)^2 \frac{\exp \left( \frac{\hbar o}{\kappa T} \right)}{\exp \left( \frac{\hbar o}{\kappa T} \right) - 1} \, d\omega \] (7)
In which, $C_{i,\mu}$ is the contribution of any atom in any possible direction to the heat capacity. $T$ is temperature in Kelvin, $\kappa$ is the Boltzmann constant, and $\hbar$ is the Planck constant. At the low and high temperature limits, we have
\[ \lim_{T \to 0} C_{i,\mu} = 0, \lim_{T \to \infty} C_{i,\mu} = \kappa g. \] (8)
The Helmholtz free energy of a unit cell, $A_T$, is in harmonic approximation
\[ A_T = \sum_{i,\mu} A_{i,\mu} \] (9)
\[ A_{i,\mu} = d\kappa T \int_0^\infty g_{i,\mu}(o) \ln \left( 2 \sin \frac{\hbar o}{\kappa T} \right) \, d\omega \] (10)
The entropy of a unit cell, $S_T$, is described by
\[ S_T = \sum_{i,\mu} S_{i,\mu} \] (11)
\[ S_{i,\mu} = d\kappa \int_0^\infty g_{i,\mu}(o) \left( \frac{\hbar o}{2\kappa T} \cos \left( \frac{\hbar o}{2\kappa T} \right) - 1 \right) - \ln \left( 1 - \exp \left( -\frac{\hbar o}{\kappa T} \right) \right) \, d\omega \] (12)
Internal energy is the total kinetic energy of a thermodynamic system, which is the energy due to motion of particles, including rotational, translational, and vibrational motion. The potential energy is associated with the vibrational energy of atoms within given molecules or crystals. It includes energy in all of chemical bonds in a system, and the energy of the free electrons or conduction electrons in metals. In this work, the total energy ($E_T$) at temperature $T$ is the electronic energy of formation plus the vibrational internal energy, i.e., $E_T = E_{\text{elec}} + ZPE + E_{\text{vib}(T)}$, where $ZPE$ is the zero point energy. $E_{\text{vib}(T)} = E_T - E_0$ is the change in vibrational internal energy from 0 K. The following relationship holds between the Helmholtz free energy, total energy, and entropy:
\[ A_T = E_T - TS_T \] (13)
In the present simulations, the phonon spectra were calculated on an optimized structure by DFT. All the DFT calculations have been performed in the framework of generalized gradient approximation (GGA) technique considering the exchange and correlation functional as proposed by Perdew-Burkett-Emzerhof (PBE) [27]. There is no magnetic moment in the present model, and the default plane wave cutoff energy is 500 eV. The electronic iterations convergence is $1.00 \times 10^{-5}$ eV using the blocked Davidson algorithm and reciprocal space projection operators. The requested $k$-spacing is 0.25 per Angstrom, which leads to a $4 \times 4 \times 2$ ($a \times b \times c$) mesh as shown in Fig. 1. The $k$-mesh is forced to center on the gamma point. For a perfect graphene, a unit cell contains 18 C atoms (13 whole atoms in the central region, the 8 atoms at the four side surfaces accounts for 4 whole atoms, and the 4 atoms on the vertex attributes to one whole atom); for the G-D considered in this work the central atom is absent. The linear-tetrahedron method is used with Blochcl corrections to the energy.

3. Results and discussion
3.1. Phonon density of states

Phonon is a collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter. It represents an exciting state in the quantum mechanical quantization of the modes of vibrations of elastic structures of interacting particles. Phonons play a major role in many of the physical properties of condensed matter, like thermal conductivity and electrical conductivity. The phonon properties of graphene were calculated by the density-functional perturbation theory (DFPT). The results of phonon density of states for both the G-D and G in this work were shown in Fig. 2. As shown in the figure, there are more peaks in the curve of phonon density of states (DOS) for the imperfect graphene G-D than for the perfect graphene G. For the G, the peak at about 45.5 THz is the carbon lattice of the sp² in-plane stretching vibration of the carbon atoms, which are related to the Raman spectrum [28]. For the G-D, the peak shifts to a high frequency at 46 THz because of the absence of atoms [29]. The peak at 40 THz for the G is shifted to 40.5 THz for the G-D. There are also sharp peaks at 16.5, 19, 25, and 43.5 THz in the G-D curve, while there is no obvious peak at the same frequency locations in the G curve. The peaks in the G-D are generally sharper and stronger. This may be caused by the different tension of the chemical bond at defects in the G-D. The atoms around the defects have higher energy because of the lack of a chemical bond. Therefore, the vibration of the G-D results in more peaks in the phonon density of state.

3.2. Thermal properties

Heat capacity is a measurable physical quantity equal to the ratio of the heat added to or removed from an object to the
Fig. 2. Comparison of phonon density of states between the G-D and G.

resulting temperature change [30]. The commonly-called specific heat, is the heat capacity per unit mass of a material, i.e., the amount of heat needed to raise the temperature of 1 kg of mass by 1 null or Kelvin. The molar (volumetric) heat capacity is the heat capacity per unit amount of a pure substance. The volumetric heat capacity is often used in engineering contexts. Fig. 3 shows the capacity per unit amount of a pure substance. The volumetric heat, is the heat capacity per unit mass of a material, i.e., the resulting temperature change [30]. The commonly-called specific heat, is the heat capacity per unit mass of a material, i.e., the amount of heat needed to raise the temperature of 1 kg of mass by 1 null or Kelvin. The molar (volumetric) heat capacity is the heat capacity per unit amount of a pure substance. The volumetric heat capacity is often used in engineering contexts. Fig. 3 shows the capacity per unit amount of a pure substance. The volumetric heat, is the heat capacity per unit mass of a material, i.e., the.

Fig. 3 shows the specific heat of graphene. It is seen that the \( C_v \) curves for both the G and G-D rise with temperature; both the curves change faster at temperature lower than 1000 K, and tend to flatten at temperature higher than 1500 K. At same temperature, \( C_v \) value of the G-D is lower than that of the G at temperature greater than about 200 K, but slightly higher at temperature below that value. This might be caused by the higher atom energy besides the defects of the G-D at low temperature. However, the G system could absorb more energy than that of the G-D at high temperature because of more atoms in the G system.

The Helmholtz free energy is a thermodynamic potential that measures the "useful" work obtainable from a closed thermodynamic system at constant temperature. The negative of the difference in the Helmholtz energy is equal to the maximum amount of work that a system can perform in a thermodynamic process of constant volume, which is certainly zero. Thus, the drop in the Helmholtz energy is equal to the maximum amount of useful work. Fig. 4 presents the Helmholtz free energy variation with temperature. As shown in the figure, both the G and G-D have the same trend in \( A_T \) in the simulated temperature range. Both the \( A_T \) curves start flat when the temperature is lower than 100 K, and then turn down with rising temperature. The \( A_T \) value of the G-D is higher than that of the G at a given temperature when the temperature is higher than about 1300 K, and lower at temperature below 1250 K. That means the G is more stable than the G-D at temperature smaller than 1250 K. At high temperature the atom vibration is very violent, which needs more space. In the same space, every atom of the G-D has more space than that of the G. As known, \( A_T \) is the function of \( E_T \) and \( S_T \). So we will need the values of \( E_T \) and \( S_T \) to analyze \( A_T \).

Fig. 5 shows the variation of total energy \( E_T \) vs. temperature. It is observed that the \( E_T \) curve for the G-D is under that for the G. They are almost flat when temperature is lower than 100 K, but arise quickly with temperature, particularly when temperature is higher than 300 K. The difference between the two curves augments as temperature rises. The total energy of a system includes all matters, the structure and the motion of the matters. Therefore, the G-D has lower \( E_T \) because of absence of atoms in the system.

Entropy is a measure of the number of microscopic configurations that correspond to a thermodynamic system in a state specified by certain macroscopic variables. It is the amount of additional information needed to specify the exact physical state of a system, given its thermodynamic specification. It can be understood as a measure of molecular disorder within a macroscopic system. For a given set of macroscopic variables, the entropy measures the degree to which the probability of the system is spread out over different possible microstates. In this work, the calculated vibrational entropy vs. temperature for both the G-D and G is plotted in Fig. 6. Both the \( S_T \) curves increase with temperature in the simulated temperature range, which conform to its definition of the entropy. The disorder of a system increases with temperature and the higher disorder is the system, the greater is the entropy. The \( S_T \) curve for the G-D is generally lower than that of the G. The gap between the two curves increases with temperature. \( S_T \) is related directly to the quantity and structure of the matters. At temperature below 280 K, \( S_T \) of the G-D is slightly higher than that of the G. That might be caused by the broken integrity of the structure.

\( E_T - E_0 \) is the change in vibrational internal energy from 0 K, where \( E_0 \) is the electronic energy of formation \( E_{elec} \) plus the zero point energy (ZPE), i.e., \( E_0 = E_{elec} + ZPE \), which is also called quantum vacuum zero-point energy, is the lowest possible energy that a quantum mechanical physical system may have. It is the
energy at ground state. Fig. 7 shows the curve of $E_T - E_0$ for both the G and G-D. Both the curves have the same trend and increase with temperature. The reason may be that the vibration of the particles increases with temperature. The curve for the G-D is lower than that of the G in the simulated temperature range. When the temperature is lower than 250 K, $E_T - E_0$ for both the G and G-D is very low, close to zero. It means that $E_T$ is nearly equal to $E_{	ext{elec}} + ZPE$ at low temperature. The value of $E_T - E_0$ is related to the thermal motion of the particles in the system. At low temperature, the system has low value of $E_T - E_0$ because of weak thermal motion.

The change in the vibrational Helmholtz free energy is a useful function in thermodynamics. The change in the vibrational Helmholtz free energy from 0 K can be marked as $\Delta(T - E_0)$. Fig. 8 shows $\Delta(T - E_0)$ variation with temperature. Both the curves increase with temperature. The curve of the G-D is under that of the G. $\Delta(T - E_0)$ is related to structure and quantity and it reflects the stability of system. The slopes of both the curves increase gradually with temperature.

3.3. Optical properties

IR spectroscopy is useful in chemical, thermal, and optical analyses and related to IR light interacting with a molecule. IR light imposed on a molecule will not create electronic transitions. It only interacts with a molecule and makes the molecule change with vibrational and rotational modes of the chemical bonds. In other words, a molecule can absorb the energy of IR photons, resulting in a faster rotation or a more pronounced vibration. Resonant frequencies are determined by the shape of the molecular potential energy surface, the mass of the atoms, and the associated vibrational coupling. The resonant frequencies are also related to the strength of the bond and the mass of the atoms at either end of it. Therefore, the frequencies of the vibrations are associated with a particular normal mode of motion and a particular bond type. A molecule can vibrate in many ways, which are called the vibrational modes or vibrational degrees of freedom. There are $(3N-5)$ vibrational states for linear molecules and $(3N-6)$ vibrational states for non-linear molecules where $N$ is the number of atoms.

For perfect graphene, there exists only one kind of active absorption in its IR spectroscopy because of symmetry of the G system. Therefore, the G has no resonant infrared frequency theoretically. In general, graphene used in any experimental study may not be a perfect one, i.e., defects are common in graphene and the G-D vibration modes split because of the defects. The calculated IR spectrum of the G-D is plotted in Fig. 9. It is seen that very strong absorption (resonant frequency) for the G-D occurs at about 233, 830, and 1392 cm$^{-1}$. Except for these strong absorption frequencies, there are slight absorptions at 287, 1133, 1235 and 1515 cm$^{-1}$. 

![Fig. 5. Comparison of total energy between the G-D and G.](image5)

![Fig. 6. Comparison of entropy between the G-D and G.](image6)

![Fig. 7. $E_T - E_0$ of graphene vs. temperature.](image7)

![Fig. 8. $\Delta(T - E_0)$ of graphene vs. temperature.](image8)
density distributions for both the G and G-D were used to calculate the thermal properties, including the specific heat, free and total energy, and entropy, as well as the optical properties such as the IR and Raman spectra. The following concluding remarks can be drafted:

- The peaks of phonon density of states in the G-D are generally sharper and stronger than those in the G. The peaks at about 40 and 45.5 THz for the G are shifted to 40.5 and 46 THz for the G-D, respectively. There exist peaks at 16.5, 19, 25, and 43.5 THz for the G-D, but no obvious peak exists at same frequency locations for the G.
- The specific heat curves for both the G and G-D vary quickly at temperature below 1000 K, and become flat at temperature higher than 1500 K. At same temperature, C_v of the G-D is lower than that of the G at temperature greater than about 200 K, but slightly higher at temperature below that value.
- The Helmholtz free energy A_T of the G-D is higher than that of the G at temperature higher than 1300 K, but it is lower at temperature below 1250 K. That means the G is more stable than the G-D at temperature <1250 K.
- The total energy E_T curve of the G-D is lower than that of the G. The difference between the two curves augments as temperature rises. The difference between the two curves augments as temperature rises. The total energy of a system includes all matters, the structure, and the motion of the matters. Therefore, the G-D has lower E_T because of absence of atoms in the system.
- The entropy S_T value for the G-D is lower than that of the G at temperature >280 K, while it is slightly higher at lower temperatures. The S_T curve for both the G-D and G increases with temperature.
- Both E_T – E_0 and –(A_T – E_0) have similar trends like E_T, i.e., they increase with temperature and have a lower value for the G-D than for the G.
- Inspection of the Raman and IR spectroscopies, it is found that the defects in graphene caused the absorption peaks and splits for the G-D. There is no detectable IR peak for perfect graphene, but exist a few strong IR absorption bands in the G-D at about 233, 830, and 1392 cm⁻¹.
- In the Raman spectrum, the resonant wavenumber 1589 cm⁻¹ of the G is shifted to a strong peak at 1530 cm⁻¹ in the G-D. There also exist a few other resonant wavenumbers for the G-D including a peak at 1372 cm⁻¹, which is a typical character of defect.

4. Conclusions

First-principles density functional theory was adopted to investigate the thermal and optical properties of imperfect graphene in real world in comparison with perfect graphene. The phonon density of states and the phonon dispersion were first calculated based on the density-functional perturbation theory. Then the photon

The Raman active is a form of inelastic light scattering when a photon interacts with a molecule in either the ground rovibronic state or an excited rovibronic state. Raman spectroscopy shows very important information for chemical, thermal, and optical properties analyses [31]. Fig. 10 presents the calculated Raman spectroscopy for graphene under laser excitation at frequency of 614.330 THz at 300 K. It is seen that the biggest peak at 1530 cm⁻¹ exists in the imperfect graphene G-D, and this value is shifted as compared to the peak at 1589 cm⁻¹ for the perfect graphene. This G peak is the sp² carbon atom in-plane vibration in Raman spectroscopy. The peak at 1372 cm⁻¹ for the G-D is a typical character of defect, which is the breathing vibration of the six rings at the edge of defect. The peaks in the calculated G-D system at lower wavenumber can be explained by that the defect caused the peaks and the splits.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 51306108).

References


