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Stokes and anti-Stokes Raman scattering in mono- and bilayer graphene

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Stokes and anti-Stokes Raman spectroscopy associated with the intervalley double resonance process in carbon materials is a unique technique to reveal the relationship between their characteristic electronic band structures and phonon dispersion. In graphene, the dominant resonant behavior for its 2D mode is an intervalley triple resonance Raman process. In this paper, we report the Stokes and anti-Stokes Raman scattering of the 2D mode in pristine graphene. The excitation energy (E_{ex})-dependent frequency discrepancy between anti-Stokes and Stokes components of the 2D mode ($\Delta\omega(2D)$) is observed, which is in good agreement with the theoretical results. This is attributed to the nonlinear dispersion of the in-plane transverse optical (iTO) phonon branch near the K point, confirmed by the nonlinear E_{ex} -dependent frequency of the 2D mode ($\omega(2D)$) in the range of 1.58–3.81 eV. The wavevector-dependent phonon group velocity of the iTO phonon branch is directly derived from $\Delta\omega(2D)$. The Stokes and anti-Stokes Raman scattering of the D mode in defected graphene and the 2D mode in bilayer graphene associated with intervalley double resonance Raman processes is also reported.

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1 Introduction

In first-order Raman scattering, a phonon at the center of the Brillouin zone (BZ), Γ point, may be detected. The frequency ω of the corresponding Raman mode does not depend on the excitation energy (E_{ex}). And the same phonon is involved in the Stokes and anti-Stokes Raman processes, leading to the same frequency for the Stokes (ω_{S}) and anti-Stokes (ω_{AS}) components of the Raman mode. The Raman spectrum of graphene materials can be used to probe their plentiful physical properties,^{1–3} especially for monolayer graphene (1LG). The Raman spectrum of 1LG consists of a set of distinct Raman modes, such as the D, G and 2D modes. The G and D modes appear around 1580 and 1350 cm^{-1} , respectively. The D mode comes from iTO phonons around the K point, being activated in Raman scattering by defects, and has been widely used to identify disorder or defects in 1LG.^{4,5} The 2D mode is the overtone of the D mode and is present in pristine graphene. The 2D mode is also present in multilayer graphene (MLGs) and its line shape is sensitive to the stacking order^{6–9} and the number of layers of MLGs.^{1,10}

The D and 2D modes in graphene materials are closely related to the intervalley double resonance (DR) Raman scattering,^{1–3,11–13} which plays a pivotal role in Raman spectra of other condensed matter systems, such as graphite,^{14–17} MoS_2 ,¹⁸ and MoTe_2 .¹⁹ Because of the peculiar linear band structures in 1LG, the corresponding Raman scattering of the 2D mode is triple resonance (TR).^{1,3,12} In general, the frequency of the Raman modes related to the DR or TR Raman process is dependent on E_{ex} , unveiling electronic bands and phonon dispersion of the related system.^{11,20} For example, ω_{S} of the D and 2D modes, $\omega_{\text{S}}(\text{D})$ and $\omega_{\text{S}}(2\text{D})$, are found to be linearly dependent on E_{ex} in graphene materials with a slope α_{S} of $\sim 50 \text{ cm}^{-1} \text{ eV}^{-1}$ and $\sim 100 \text{ cm}^{-1} \text{ eV}^{-1}$, respectively.²¹ It is also true for the case of ω_{AS} of the D and 2D modes, *i.e.*, $\omega_{\text{AS}}(\text{D})$ and $\omega_{\text{AS}}(2\text{D})$, once they are measured. The anti-Stokes Raman scattering of the D, 2D and other dispersive Raman modes in graphene materials has been investigated in detail, such as in highly oriented pyrolytic graphite,²² graphite whisker,²³ multiwalled carbon nanotubes,²⁴ and two-dimensional graphite,²⁵ in which E_{ex} -dependent frequency discrepancies ($\Delta\omega$) between anti-Stokes (ω_{AS}) and Stokes (ω_{S}) components of the dispersive Raman modes ($\Delta\omega = |\omega_{\text{AS}}| - |\omega_{\text{S}}|$) are reported. $\Delta\omega(2\text{D}) (= |\omega_{\text{AS}}(2\text{D})| - |\omega_{\text{S}}(2\text{D})|)$ is found to be 4 times larger than $\Delta\omega(\text{D}) (= |\omega_{\text{AS}}(\text{D})| - |\omega_{\text{S}}(\text{D})|)$.^{23,24} However, the anti-Stokes Raman scattering of the dispersive Raman modes in 1LG has not been investigated yet, and the relationship between $\Delta\omega$ and the unique electronic band structure or phonon dispersion has not been experimentally revealed.

In this work, we investigated anti-Stokes Raman scattering of pristine and ion-implanted monolayer graphene (1LG) by

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1.58, 1.96, 2.33 and 2.54 eV laser excitation. $\Delta\omega$ of the corresponding D and 2D modes is reported, which is significantly dependent on E_{ex} . The experimental results are in excellent agreement with the theoretical ones. The group velocity of the iTO phonon is revealed to be notably dependent on the phonon wavevector q around the K point, which can be precisely obtained *via* E_{ex} -dependent $\Delta\omega$. This is confirmed by the non-linear dependence of $\omega_{\text{S}}(2\text{D})$ on E_{ex} in the range of 1.58–3.81 eV. The anti-Stokes and Stokes Raman spectra of bilayer graphene (2LG) are also investigated and similar results to those of the 1LG are obtained.

2 Experiment and method

1LG and 2LG flakes were prepared by mechanical exfoliation from the highly oriented pyrolytic graphite onto a Si/SiO₂ substrate. The number of layers of graphene flakes was identified by a spectral profile of the 2D mode.^{10,11} The peak position of the D and 2D bands in graphene is dependent on its doping level.^{2,26} According to the peak area ratio of the G mode to the 2D mode, the Fermi level of the studied 1LG is estimated to be about 0.06 eV,^{3,27,28} corresponding to an electron concentration of $3.76 \times 10^{11} \text{ cm}^{-2}$. This indicates that the studied graphene is intrinsic and the corresponding doping level is very low. Raman measurements were performed under the back-scattering geometry in a micro-Raman system (Horiba Jobin Yvon HR800), equipped with a liquid nitrogen-cooled charge-coupled detector (CCD), a 100 $\times$ objective lens (numerical aperture of 0.90), and several gratings. The laser excitation energies are 1.58 eV and 1.96 eV from a He–Ne laser; 2.33 eV from a Kr⁺

laser; and 2.54 eV from an Ar⁺ laser. Some graphene flakes were implanted with Ar⁺ ions using an LC-4 type system. The kinetic energy of Ar⁺ ions is 100 keV with a subjected ion dosage of $2 \times 10^{12} \text{ cm}^{-2}$. Stokes and anti-Stokes Raman spectra of pristine 1LG and 2LG with $E_{\text{ex}} = 1.96, 2.33$ and 2.54 eV are recorded at high temperature *via* a heating stage, while the other spectra are recorded at room temperature, and all frequencies of anti-Stokes Raman peaks are converted into absolute values in the figures.

The intensity of the double-resonance Raman processes is calculated using a fourth order time-dependent perturbation theory where the energies and matrix elements are calculated within a tight-binding approach with parameters fitted to *ab initio* calculations, based on the density functional theory, corrected by many-body effects. This method has been successfully applied for the calculation of the Stokes DR Raman spectra of 1LG leading to a very good agreement with experimental results shown in ref. 12, where more details and explicit equations of the model are given. Since the absolute calculated Raman shifts are prone to slight (2%) over/under-estimations due to limitation of phonon frequency calculations, the calculated spectra were shifted within 2% to allow a better comparison with the respective experimental spectra in this work.

2.1 Results and discussion

2.1.1 Anti-Stokes and Stokes Raman spectra of 1LG. Fig. 1 shows the Stokes and anti-Stokes Raman spectra of ion-implanted (Fig. 1(a)) and pristine (Fig. 1(b)) 1LG flakes excited by 4 lasers with photon energies from 1.58 eV to 2.54 eV.

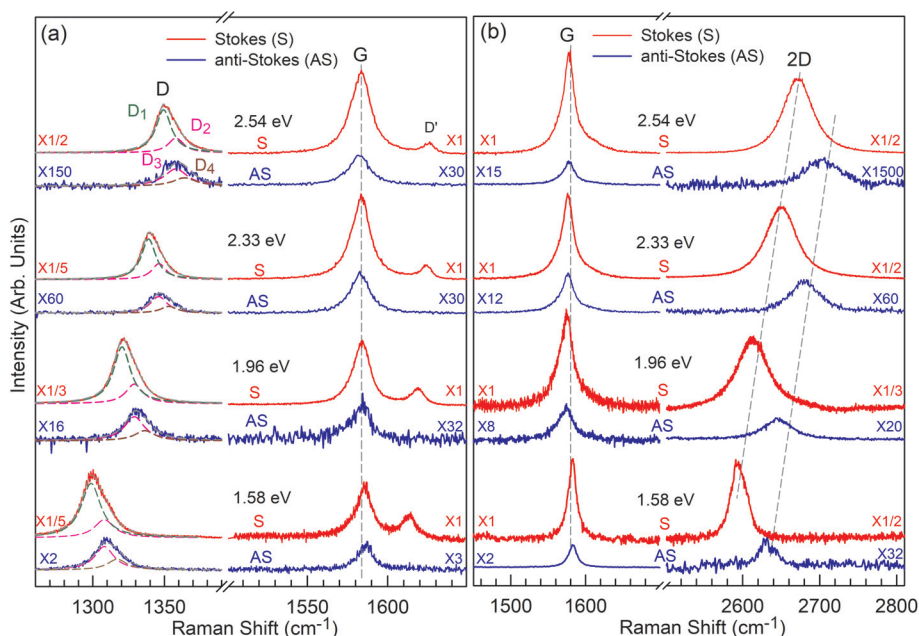


Fig. 1 Stokes (red) and anti-Stokes (blue) Raman spectra of the D and G modes in ion-implanted 1LG (a) and the G and 2D modes in intrinsic 1LG (b), where $E_{\text{ex}} = 1.58, 1.96, 2.33$ and 2.54 eV. The D mode is fitted by the two Lorentzian peaks with the same FWHM, D₁ and D₂ at the Stokes side, and D₃ and D₄ at the anti-Stokes side. The spectra are scaled and offset for clarity along with the scaling factor for each spectrum.

$|\omega_{AS}(G)| = |\omega_S(G)|$ and $\omega(G)$ are independent of E_{ex} because the G mode corresponds to the E_{2g} phonon at Γ . Because different E_{ex} can excite different wavevectors of dispersive iTO phonons around K in the DR Raman process, both $\omega_S(D)$ and $\omega_S(2D)$ are dependent on E_{ex} . The Stokes Raman component of the D mode in 1LG exhibits an asymmetry profile and can be fitted by two subpeaks, D_1 and D_2 , with the same full-width at half-maximum (FWHM), similar to the previous reports,^{29,30} while the anti-Stokes Raman component of the D mode can also be fitted by two subpeaks with the same FWHM, D_3 and D_4 , as shown in Fig. 1(a). The two subpeaks in the Stokes and anti-Stokes Raman components of the D mode result from the inelastic scattering event by emitting a phonon or one elastic scattering event by crystal defects in its double resonance (DR) Raman process.³ For all the employed excitation energies, $\omega(D_2)$ and $\omega(D_3)$ are almost equal to each other, similar to the cases in graphite whisker and two-dimensional graphite.^{23–25}

In contrast to the G mode of $|\omega_S(G)| = |\omega_{AS}(G)|$, $|\omega_S(D)| < |\omega_{AS}(D)|$ and $|\omega_S(2D)| < |\omega_{AS}(2D)|$. This can be well understood by their DR Raman processes, as demonstrated in Fig. 2(a) and (b), respectively. The Stokes and anti-Stokes DR Raman processes can select different iTO phonons around K with different wavevectors for the D and 2D modes. The iTO phonon branch exhibits strong dispersion close to the K point due to the Kohn anomaly,^{12,31} as presented in Fig. 2(c). This leads to the observation of significant frequency discrepancies between the Stokes and anti-Stokes components of the two modes. $\Delta\omega(2D)$ is as large as $\sim 30\text{ cm}^{-1}$. The 2D mode of 1LG exhibits a single Lorentzian peak and its $\omega_S(2D)$ and $\omega_{AS}(2D)$ can be obtained by Lorentzian fitting. It is found that $\Delta\omega(2D)$ is dependent on E_{ex} , going from 36.2 cm^{-1} to 31.4 cm^{-1} , when E_{ex} varies from 1.58 to 2.54 eV. $\Delta\omega(D)$ is also dependent on E_{ex} . In comparison with other carbon

materials, such as graphite and carbon nanotubes,^{23–25} 1LG displays simpler band structures and phonon dispersions. Therefore, it offers us opportunities to better understand the Stokes and anti-Stokes DR Raman processes from both experimental and theoretical points of view. The theoretical results of the Stokes and anti-Stokes spectra of 1LG are depicted in Fig. 2(d) and (e). Similar to the experimental results, the calculated Stokes and anti-Stokes components of the D mode can be fitted by two Lorentzian subpeaks. Fig. 3(a) presents Stokes Raman spectra of the G and 2D modes in the E_{ex} range from 1.58 eV to 3.82 eV, and Fig. 3(b) summarizes the calculated $\omega_{AS}(2D)$ and $\omega_S(2D)$ along with the experimental data of E_{ex} -dependent $\omega_S(2D)$. Generally, Fig. 3 shows a good agreement between experimental and theoretical results. An interesting observation in both experimental and theoretical results is the dependence of $\Delta\omega(2D)$ on E_{ex} . If the dependence of $\omega_S(2D)$ and $\omega_{AS}(2D)$ on E_{ex} is considered to be linear, then the theoretically determined slopes (α_S and α_{AS}) would be 95.8 and $94.3\text{ cm}^{-1}\text{ eV}^{-1}$, respectively. However, if we carefully check the experimental data, $\omega_S(2D)$ is slightly nonlinear for E_{ex} in the range of 1.58–3.82 eV. In the low (1.59–2.33 eV) and high (2.33–3.81 eV) E_{ex} ranges, $\omega_S(2D)$ is almost linear with slopes of $107.7\text{ cm}^{-1}\text{ eV}^{-1}$ (α_S^L) and $95.1\text{ cm}^{-1}\text{ eV}^{-1}$ (α_S^H), respectively. Since $\Delta\omega(2D) = \hbar\omega_S(2D) \cdot \alpha_S$,^{23,24} as α_S^L is higher than α_S^H it results in a larger $\Delta\omega(2D)$ observed at an E_{ex} of 1.58 eV.

2.1.2 Phonon group velocity of the iTO phonon branch.

Based on the Stokes and anti-Stokes DR Raman processes in 1LG, the observed E_{ex} -dependent $\omega_S(2D)$ and $\Delta\omega(2D)$ result from its linear electronic bands and large phonon dispersion of the iTO branch in the vicinity of K and K' points. Therefore, the Stokes and anti-Stokes Raman spectra of the 2D mode provide a convenient method to detect the electronic band structure and phonon dispersion.²⁰

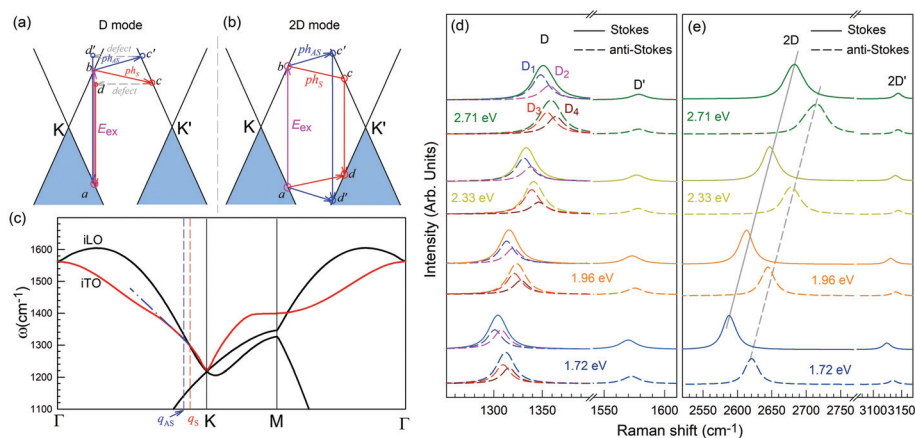


Fig. 2 The inner intervalley double (a) and triple (b) resonance Stokes and anti-Stokes Raman processes for the D and 2D modes, respectively. Blue arrows for the Stokes Raman process and red arrows for the anti-Stokes Raman process. (c) The phonon dispersion of graphene. The blue and red dash lines indicate the selected wavevectors by the Stokes and anti-Stokes Raman processes of the 2D mode excited by $E_{ex} = 1.96\text{ eV}$, respectively. Calculated Stokes (solid lines) and anti-Stokes (dashed lines) Raman spectra of the D (d) and 2D (e) modes excited by $E_{ex} = 1.72, 1.96, 2.33$ and 2.71 eV . The D modes are fitted by two Lorentzian peaks, D_1 (green) and D_2 (pink) dash lines at the Stokes side, and D_3 (red) and D_4 (dark red) dash lines at the anti-Stokes side.

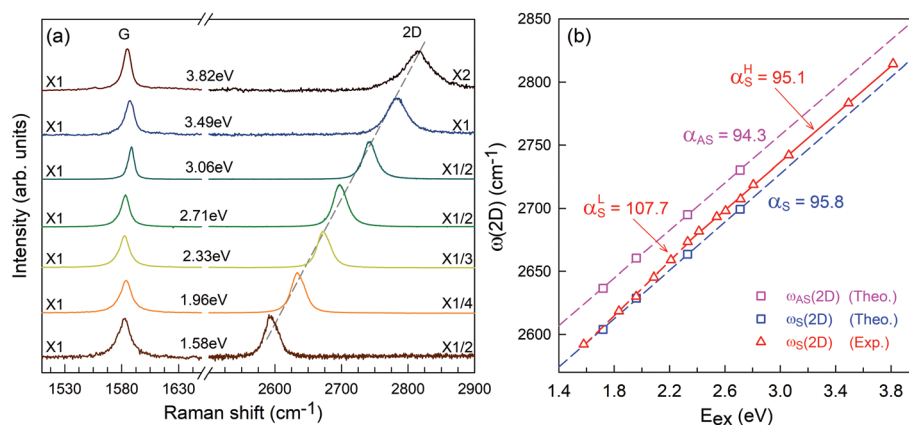


Fig. 3 (a) Stokes Raman spectra of 1LG with various E_{ex} in the G and 2D mode regions. (b) Linear fits to the theoretical (Theo.) $\omega_{\text{S}}(2\text{D})$ (blue square) and $\omega_{\text{AS}}(2\text{D})$ (pink square) as a function of E_{ex} . The experimental (Exp.) data of $\omega_{\text{S}}(2\text{D})$ in an E_{ex} range from 1.59–3.81 eV. Linear fits to the experimental $\omega_{\text{S}}(2\text{D})$ in the lower E_{ex} range (1.59–2.33 eV) and higher E_{ex} range (2.33–3.81 eV). The fitted linear slope to each E_{ex} range is given.

The phonon group velocity of the iTO branch associated with a phonon excited by E_{ex} can be obtained from E_{ex} -dependent $\omega_{\text{S}}(2\text{D})$. As demonstrated in Fig. 2(b), for the electronic states a , b , c and d , whose energies are in proportion to Fermi velocity, v_{F} , we have $E_a = -v_{\text{F}}k_a$, $E_b = v_{\text{F}}k_b$, $E_c = -v_{\text{F}}k_c + E_0$ and $E_d = v_{\text{F}}k_d - E_0$, where $k_a = k_b$ and $k_c = k_d$ are the wavevectors with K as the origin of coordinates and E_0 is the intercept, ~ 9.4 eV. As for the phonon dispersion, the iTO phonon branch near the reciprocal vectors q_{ph} probed by the Stokes TR Raman process (q_{S}) is described as $\omega_{\text{S}}(2\text{D})/2 = -v_{\text{ph}}q_{\text{S}} + \omega_0$, where ω , q_{S} , v_{ph} and ω_0 are the corresponding energy, wavevector, group velocity of the selected phonon, and the intercept, respectively. Based on the energy conservation conditions for the Stokes TR Raman process ($E_{\text{ex}} = E_b - E_a$ and $E_{\text{ex}} - \omega_{\text{S}}(2\text{D}) = E_c - E_d$) along with the expressions of four electronic states, one can obtain $k_{a(b)} = \frac{E_{\text{ex}}}{2v_{\text{F}}}$ and $k_{c(d)} = \frac{2E_0 - E_{\text{ex}} + \omega_{\text{S}}(2\text{D})}{2v_{\text{F}}}$, where all the vectors can be approximately regarded as a scalar quantity due to isotropic electronic bands and phonon dispersion near the K point. Then, based on the momentum conservation conditions of the Stokes TR Raman process ($k_b + q_{\text{S}} = k_c$), we have $q_{\text{S}} = \frac{E_0 - E_{\text{ex}} + \omega_{\text{S}}(2\text{D})/2}{v_{\text{F}}}$. Consequently, the E_{ex} -dependent $\omega_{\text{S}}(2\text{D})$ can be expressed as follows:

$$\omega_{\text{S}}(2\text{D})/2 = \frac{v_{\text{ph}}}{v_{\text{F}} + v_{\text{ph}}}E_{\text{ex}} + \frac{v_{\text{F}}}{v_{\text{F}} + v_{\text{ph}}}\omega_0 - \frac{v_{\text{ph}}}{v_{\text{F}} + v_{\text{ph}}}E_0. \quad (1)$$

And thus, the frequency of phonons selected by the Stokes TR Raman process is:

$$\omega_{\text{S}}(2\text{D})/2 = \frac{v_{\text{ph}}}{v_{\text{F}} + v_{\text{ph}}}E_{\text{ex}} + \omega'_0, \quad (2)$$

where $\omega'_0 = \frac{v_{\text{F}}}{v_{\text{F}} + v_{\text{ph}}}\omega_0 - \frac{v_{\text{ph}}}{v_{\text{F}} + v_{\text{ph}}}E_0$. According to the experimental slope (α_{S}) of E_{ex} -dependent $\omega_{\text{S}}(2\text{D})$, we have $v_{\text{ph}} = \frac{\alpha_{\text{S}}/2}{1 - \alpha_{\text{S}}/2}v_{\text{F}}$. Based on the linear fits to the calculated

$\omega_{\text{S}}(2\text{D})$ in Fig. 3(b), we can extract $\alpha_{\text{S}} = 95.8 \text{ cm}^{-1} \text{ eV}^{-1} \sim 0.0118 \ll 1$, and thus v_{ph} can be simplified as:

$$v_{\text{ph}} = v_{\text{F}} \cdot \alpha_{\text{S}}/2. \quad (3)$$

According to calculated $\omega_{\text{S}}(2\text{D})$ as a function of E_{ex} , we can obtain $v_{\text{ph}} = 5.94 \times 10^{-3}v_{\text{F}}$ in graphene, which is similar to the previous result ($v_{\text{ph}} = 6 \times 10^{-3}v_{\text{F}}$).² Here, if we take Fermi velocity of graphene $v_{\text{F}} = 5.52 \text{ eV } \text{\AA}^{-1}$ ($\sim 1.33 \times 10^6 \text{ m s}^{-1}$) from theoretical and experimental results,^{32–34} the group velocity of the iTO phonon is obtained as $v_{\text{ph}} = 264.5 \text{ cm}^{-1} \text{ \AA}$. Based on the experimental results of $\alpha_{\text{S}}^{\text{L}}$ and $\alpha_{\text{S}}^{\text{H}}$ shown in Fig. 3(b), the average experimental v_{ph} of $\sim 299.2 \text{ cm}^{-1} \text{ \AA}$ ($6.68 \times 10^{-3}v_{\text{F}}$) and $\sim 262.7 \text{ cm}^{-1} \text{ \AA}$ ($5.90 \times 10^{-3}v_{\text{F}}$) can be obtained from $\omega_{\text{S}}(2\text{D})$ probed by E_{ex} in the 1.58–2.33 eV and 2.33–3.82 eV ranges, respectively. The relationship between the above three phonon group velocities with Fermi velocity is summarized in Table 1 along with the corresponding E_{ex} ranges. The smaller E_{ex} is, the closer it is to the K or K' point for the involved phonon wavevectors q_{S} . The q_{S} ranges of the iTO phonon determined by the corresponding E_{ex} ranges are also listed in Table 1. Therefore, the deduced v_{ph} is actually an average value in the q_{S} range. The different v_{ph} values for $\alpha_{\text{S}}^{\text{L}}$ and $\alpha_{\text{S}}^{\text{H}}$ indicate the different phonon dispersions of the iTO phonons in the two probed q_{S} ranges.

The above analysis for v_{ph} can also be deduced for the anti-Stokes TR Raman process and thus v_{ph} can be obtained from

Table 1 The fitted linear slope α_{S} (in $\text{cm}^{-1} \text{ eV}^{-1}$) of the experimental (Exp.) and theoretical (Theo.) E_{ex} -dependent $\omega_{\text{S}}(2\text{D})$ in 1LG, and the selected phonon wavevectors q_{S} (in $\text{\AA}^{-1}$) by E_{ex} (in eV) via the TR Raman process in the different E_{ex} ranges, and the phonon group velocity v_{ph} of the iTO phonon branch calculated from the corresponding α_{S}

E_{ex}	α_{S}	q_{S}	$v_{\text{ph}}(\times 10^{-3}v_{\text{F}})$
1.58–2.33 (Exp.)	107.7($\alpha_{\text{S}}^{\text{L}}$)	1.44–1.31	6.68
2.33–3.81 (Exp.)	95.1($\alpha_{\text{S}}^{\text{H}}$)	1.31–1.22	5.90
1.72–2.71 (Theo.)	95.8(α_{S})	1.39–1.21	5.94

$\Delta\omega(2D)$. Analogously, based on the energy conservation conditions for the anti-Stokes TR Raman process ($E_{\text{ex}} = E_b - E_a$, $E_{\text{ex}} + \omega_{\text{AS}}(2D) = E_{c'} - E_{d'}$), one can obtain $k_{a(b)} = \frac{E_{\text{ex}}}{2v_F}$ and $k_{c'(d')} = \frac{2E_0 - E_{\text{ex}} - \omega_{\text{AS}}(2D)}{2v_F}$. Similar to $\omega_S(2D)/2$, the energy of phonons selected by the anti-Stokes TR Raman process is $\omega_{\text{AS}}(2D)/2 = -v_{ph}q_{\text{AS}} + \omega_0$. Based on the momentum conservation conditions of the anti-Stokes TR Raman process ($k_b + q_{\text{AS}} = k_{c'}$), we have $q_{\text{AS}} = \frac{E_0 - E_{\text{ex}} - \omega_{\text{AS}}(2D)/2}{v_F}$. Combining the expressions for q_S and q_{AS} , the group velocity around the selected phonon can be obtained as follows:

$$v_{ph} = \frac{\frac{1}{2}\omega_{\text{AS}}(2D) - \omega_S(2D)}{q_S - q_{\text{AS}}} \quad (4)$$

$$\simeq \Delta\omega(2D) \cdot v_F / 2\omega_S(2D).$$

Applying the experimental $\Delta\omega(2D)$ and $\omega_S(2D)$ to eqn (4), v_{ph} values of the involved phonons in the iTO phonon branch are obtained for different E_{ex} , which are summarized in Table 2. Because the difference between q_{AS} and q_S is quite

Table 2 $\omega_S(2D)$ (in cm^{-1}) and $\Delta\omega(2D)$ (in cm^{-1}) of the 2D mode excited by four E_{ex} (in eV), the corresponding wavevectors q_{ph} (i.e., q_S and q_{AS} in $\text{\AA}^{-1}$), and the deduced v_{ph} by eqn (4) based on the corresponding $\omega_S(2D)$ and $\Delta\omega(2D)$

E_{ex}	$\omega_S(2D)$	$\Delta\omega(2D)$	q_S	q_{AS}	$v_{ph}(\times 10^{-3}v_F)$
1.58	2594.9	36.2	1.44	1.39	6.98
1.96	2612.8	32.8	1.38	1.32	6.28
2.33	2649.9	30.6	1.31	1.25	5.77
2.54	2672.0	31.4	1.27	1.21	5.88

small for a specific E_{ex} , the measured v_{ph} in Table 2 is more accurate in a smaller q_{ph} range. It is obvious that v_{ph} significantly increases with increasing q_{AS} or q_S , suggesting the nonlinear phonon dispersion of iTO phonons in the measured q_{ph} range, which is in agreement with the theoretical phonon dispersion.^{12,31} Eqn (4) is based on a linear approximation for involved electronic bands in the DR Raman process. This linear approximation is consistent with previous work,¹² which shows that the nonlinearity of the involved electronic bands in the DR Raman process can be neglected for $E_{\text{ex}} \lesssim 2.4$ eV. Therefore, the E_{ex} -dependent v_{ph} deduced from $\Delta\omega(2D)$ for $E_{\text{ex}} = 1.58, 1.96, 2.33$ and 2.54 eV results from the nonlinearity of the iTO branch close to the K point. Furthermore, combining eqn (3) and (4), one can obtain $\Delta\omega(2D) \simeq \alpha_S\omega_S(2D)$, which is consistent with previous experimental studies on other carbon materials.^{23,24}

v_{ph} in Tables 1 and 2 are in agreement with each other. v_{ph} obtained by α_S^H is almost equal to that obtained by eqn (4) with $E_{\text{ex}} = 2.33$ and 2.54 eV, due to linear phonon dispersion in the range, while v_{ph} obtained by α_S^L is approximate to average of v_{ph} obtained by E_{ex} -dependent $\Delta\omega$ with $E_{\text{ex}} = 1.59$ and 1.96 eV. v_{ph} of the iTO phonon branch obtained by eqn (3) is relevant to α_S in an E_{ex} range, which actually accounts for the average of v_{ph} involving phonons excited by different E_{ex} . And E_{ex} -dependent v_{ph} obtained by eqn (4) confirms nonlinear phonon dispersion of the iTO branch near the K points, as evidenced by the nonlinear behavior of the experimental $\omega_S(2D)$ in a wide E_{ex} range of 1.58–3.82 eV.

2.1.3 Anti-Stokes Raman spectra of the 2D mode in 2LG.

We also investigated E_{ex} -dependent Stokes and anti-Stokes Raman spectra of 2LG in the G and 2D band ranges, as presented in Fig. 4. Similar to that of 1LG, $|\omega_S(2D)| < |\omega_{\text{AS}}(2D)|$ for

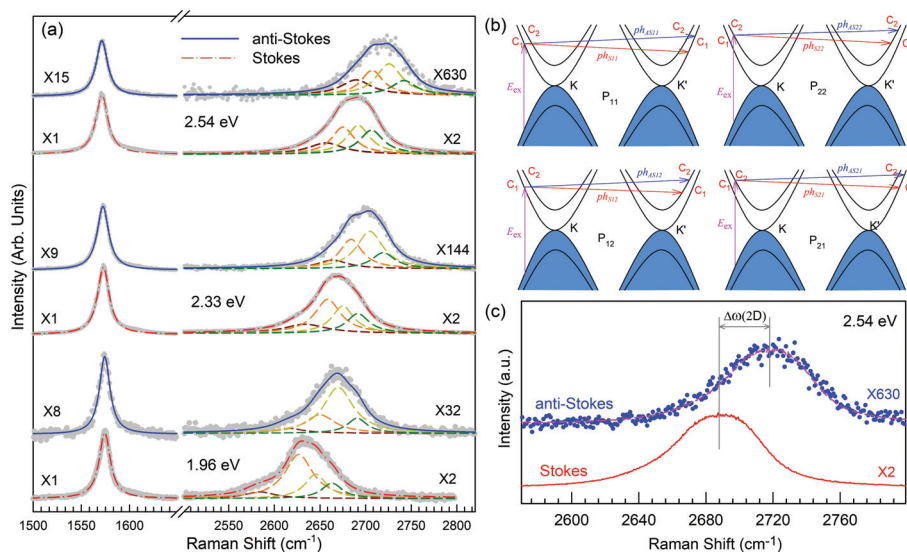


Fig. 4 (a) Stokes and anti-Stokes Raman spectra of the G and 2D modes in 2LG, excited by $E_{\text{ex}} = 1.96, 2.33$ and 2.54 eV. The 2D modes are fitted by four Lorentzian peaks (dash lines). (b) The four allowed DR processes in 2LG, denoted as P_{11}, P_{22}, P_{12} , and P_{21} , respectively. (c) The anti-Stokes and Stokes components of the 2D mode excited by $E_{\text{ex}} = 2.54$ eV. The anti-Stokes component can be well fitted by the corresponding Stokes component (pink dash line). The gray dash line is a guide to the eye to indicate $\Delta\omega(2D)$.

all E_{ex} . The 2D peak of 2LG can be well fitted by four Lorentzian peaks, as shown in Fig. 4(a). The four Lorentzian peaks indicate four inequivalent DR Raman processes, as shown in Fig. 4(b). Due to the doubled electron bands (C_1 and C_2) and iTO phonon branches compared with 1LG, the electrons can be excited from a valence band to a C_1 or C_2 band near K or K' points. The two iTO branches for 2LG have two different symmetries, which allow the electron scattering processes of $C_1 \rightarrow C_1$, $C_1 \rightarrow C_2$, $C_2 \rightarrow C_1$, and $C_2 \rightarrow C_2$, between electronic bands near K and K' points. This selects iTO phonons with wavevectors of q_{11} , q_{12} , q_{21} and q_{22} , respectively. So, both the Stokes and anti-Stokes 2D bands can be fitted by four subpeaks, as shown in Fig. 4(a). And the four subpeaks are assigned P_{11} , P_{12} , P_{21} and P_{22} , respectively, in the order of lower to higher frequency. However, $\Delta\omega$ of each subpeak of the 2D mode in 2LG cannot be properly revealed because of the large fitting error.

As shown in Fig. 4(a), the anti-Stokes and Stokes components of the 2D mode in 2LG have a similar spectral profile. Thus, we can use the whole profile of the Stokes component to fit that of the anti-Stokes component by changing its peak position and intensity, as demonstrated in Fig. 4(c). The frequency difference between the two profiles is $\Delta\omega(2D)$ of 2LG, and $\Delta\omega(2D)$ of 31.98, 29.11 and 29.88 cm^{-1} can be revealed for $E_{\text{ex}} = 1.96$, 2.33 and 2.54 eV, respectively. Under the same E_{ex} , $\Delta\omega(2D)$ is almost the same in 1LG and 2LG.

3 Conclusions

In conclusion, we have investigated the Stokes and anti-Stokes Raman spectra of the D and 2D modes in ion-implanted and pristine 1LG, respectively. The E_{ex} -dependent ω_S and $\Delta\omega$ of the D and 2D modes are well comprehended by the corresponding resonance Raman processes. The average ν_{ph} of the iTO phonon branch can be obtained by $\omega_S(2D)$ in the q_{ph} range probed by E_{ex} . E_{ex} -Dependent ν_{ph} are also revealed from E_{ex} -dependent $\Delta\omega(2D)$, which unveils nonlinear phonon dispersion of the iTO branch near the K and K' points. The Stokes and anti-Stokes Raman spectra of the 2D mode in 2LG are also investigated. This work suggests that Stokes and anti-Stokes Raman spectroscopy of graphene materials is a useful technique to probe their phonon dispersion information.

Conflicts of interest

There are no conflicts to declare.

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