Beyond double-resonant Raman scattering: UV Raman spectroscopy on graphene, graphite and carbon nanotubes

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We present an analysis of deep-UV Raman measurements of graphite, graphene and carbon nanotubes. For excitation energies above the strong optical absorption peak at the M point in the Brillouin zone (≈ 4.7 eV), we partially suppress double-resonant scattering processes and observe the two-phonon density of states of carbon nanomaterials. The measured peaks are assigned to contributions from LO, TO, and LA phonon branches, supported by calculations of the phonon dispersion. Moreover, we gain access to the infrared-active $E_{1u}$ mode in graphite. By lowering the excitation energy and thus allowing double-resonant scattering processes, we demonstrate the rise of the 2D mode in graphite with ultra-short phonon wave vectors.

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Graphite, graphene and carbon nanotubes have experienced increasing interest in fundamental research in the last decade. In this context, Raman spectroscopy has been established as a powerful experimental technique, since it provides access to both the electronic and vibrational properties of carbon materials.1,2 Due to its high sensitivity, it is possible to probe properties like the crystallographic orientation of graphene,3,4 the number of graphene layers,5,6 doping,7,8 and strain,9 as well as the diameter and chiral indices $(n,m)$ of carbon nanotubes.9

In general, the Raman spectra of graphite, graphite or carbon nanotubes in the two-phonon region are dominated by double-resonant Raman modes10–12. Especially in single-layer graphene, the prominent 2D mode outperforms the intensity of the first-order G mode by a factor of up to five.13 However, these strong double-resonant Raman modes are very unique only for graphitic materials. In common semiconductors, away from optical resonances, the second-order spectrum typically shows the two-phonon density of states14. A possible route to observe the two-phonon density of states also in graphite, graphene, and carbon nanotubes is the suppression of double-resonant Raman modes. Here, Raman spectroscopy with photon energies in the ultraviolet (UV) spectral range seems most promising, as the strong optical absorption around the M point in the Brillouin zone is then suppressed. Thus, all so-called ‘inner’ double-resonant scattering processes are selectively inhibited.

In this work, we investigate the Raman process in graphene, graphite, and carbon nanotubes under UV excitation. For excitation energies well above the M-point transition energy of approximately 4.7 eV, we can selectively suppress the dominant Raman processes that are commonly identified with ‘inner’ double-resonant Raman scattering. In these cases the two-phonon density of states (pDOS) is observed. Therefore, we gain access to phonon frequencies at high-symmetry points in the Brillouin zone, in particular the infrared-active $E_{1u}$ mode in graphite, which are otherwise not accessible in either first-order or double-resonant Raman scattering in the visible optical range. By lowering the excitation energy towards the M-point transition energy, we can initiate inner double-resonance processes and therefore demonstrate the onset of the 2D mode in graphite. Our interpretations are supported by calculations of the pDOS for graphene, graphite, and carbon nanotubes. Furthermore, we calculate Raman spectra for graphite in the UV range and observe good agreement with our experimental data.

We used a Horiba T64000 spectrometer equipped with an Argon ion laser, providing second-harmonic generation of all fundamental laser lines. All spectra are calibrated via the Raman-active vibrational mode of molecular nitrogen ($^{14}$N$_2$) from the atmosphere. We measured exfoliated graphite, CVD-grown graphene on SiO$_2$/Si, and a HiPCO-produced buckypaper carbon nanotube sample with a diameter range of 7 Å to 13 Å. In order to avoid laser-induced oxidation and degradation of our samples, we integrated the Raman signals over a large area on our samples.

Density functional theory calculations of the phonon spectra of graphite and graphene were performed on the

![Phonon dispersion and the phonon density of states (pDOS) of graphite. Inset shows the splitting of the LO/TO and LA phonon branches at Γ and M, respectively.](image-url)
level of the local density approximation as implemented in the Quantum ESPRESSO suite\textsuperscript{15}. The electrons in the system were modeled by projector augmented waves with cutoff energies of 80 Ry for the electronic wavefunctions. Reciprocal-space integration for the ground state was performed by a discrete sampling of $21 \times 21 \times 1$ $k$-points in the Brillouin zones of graphene and $21 \times 21 \times 6$ $k$-points for graphite. We fully optimized the atomic positions and cell parameters of the considered systems until the interatomic forces were smaller than 0.001 eV/Å and the pressure on the unit cell was below 0.001 GPa. Interactions of the slabs with residual periodic images due to the 3D periodic boundary conditions were minimized by maintaining vacuum layers of at least 25 Å. Phonon dispersion relations were calculated through density functional perturbation theory using the same $k$-point samplings as before. The phonon density of states was then obtained by Fourier interpolation of the calculated spectra onto a denser grid of $500 \times 500 \times 1$ points ($500 \times 500 \times 10$ for graphite) and applying a Gaussian broadening of 1 cm$^{-1}$.

Figure 1 shows the calculated phonon dispersion of graphite with its density of states (pDOS). The insets illustrate regions with a high pDOS originating from the LO (longitudinal optical), TO (transverse optical), and LA (acoustic) phonon branches at the high symmetry points $\Gamma$ and $M$, respectively. The Raman-active $\Gamma$-point vibration at $\sim 1586$ cm$^{-1}$ ($E_{2g}$ irreducible representation) is associated with the $G$ band in graphene. In the case of graphite, the single-layer $E_{2g}$ mode gives rise to two modes with the irreducible representations $E_{2g}$ and $E_{1u}$, of which the latter is infrared active. Its frequency is $\omega_{E_{1u}} \sim 1591$ cm$^{-1}$ and therefore slightly higher than the Raman-active mode $\omega_{E_{2g}}$ at $\sim 1586$ cm$^{-1}$.

Figure 2 (a) shows a Raman spectrum of graphite at an excitation energy of $E_L = 5.08$ eV. In contrast to previous works on UV Raman spectroscopy on graphene and graphite\textsuperscript{16,17}, we observe a distinct Raman signal in the two-phonon region from our samples. In fact, we observe five peaks that we assign, in ascending order, to the two-phonon density of states at the $M$ point (LA/LO-derived and TO-derived phonon branches), the overtones of the $E_{2g}$ and $E_{1u}$ modes at the $\Gamma$ point and of the maximum of the LO-branch overbending near the $\Gamma$ point. Assignments are done via comparison of the Raman spectrum with the calculated pDOS, as shown in Fig. 1. The intensity distribution in the pDOS does not fully reflect the intensity distribution in the measured Raman spectrum since coupling matrix elements are not considered. For instance, the electron-phonon coupling of the LO phonon at the $\Gamma$ point is large compared to LO-derived phonons with wavevectors $q \neq 0$\textsuperscript{12}. Thus, the calculated high intensity of the LO-overbending pDOS is not observed experimentally. Instead, in the experiment, the $\Gamma$-point contribution is dominant in Fig. 2 (a). We find the maximum of the LO overbending at 1626 cm$^{-1}$. The frequency of the $E_{1u}$ and $E_{2g}$ $\Gamma$-point vibrations deduced from our experiment are 1592 cm$^{-1}$ and 1578 cm$^{-1}$, respectively, in good agreement with previous theoretical and experimental results\textsuperscript{18,19}.

From the measured spectrum in Fig. 2 (a), we further find the $M$-point frequency of the TO-derived phonon branch to be 1408 cm$^{-1}$, in good agreement with calculations. Therefore, we can experimentally determine the bandwidth of the two TO phonon branches between the $\Gamma$ and the $M$ point in graphite to exhibit at least 170 cm$^{-1}$. The peak at 2688 cm$^{-1}$ cannot be distinguished between the LO- and LA-derived branches, since they are very close in frequency at the $M$ point. However, we can determine the upper bound of the LA-phonon branch in graphite to be 1344 cm$^{-1}$.

In Figure 2 (b)-(d) we show a comparison of Raman spectra from graphene and carbon nanotubes with their calculated two-phonon pDOS. The excitation energy is again $E_L = 5.08$ eV. The pDOS for carbon nanotubes was calculated using the POLSym code\textsuperscript{20}. It contains 40 different carbon nanotubes that we have found by analyzing Raman resonance profiles of the radial-breathing modes in the visible optical range. In contrast to graphite, graphene exhibits only one peak at 3162 cm$^{-1}$, attributed to the second-order spectrum of...
the $E_{2g}$ Γ-point vibration. The second order of the LO overbending frequency is found at 3246 cm$^{-1}$. Compared to graphene and graphite, the UV Raman spectrum of carbon nanotubes only consists of one broad peak at $\approx 3150$ cm$^{-1}$. This observation can be directly understood from the fact that phonon frequencies in carbon nanotubes sensitively depend on the nanotube diameter and chiral angle$^{21}$. Since the investigated tubes exhibit a broad diameter range from 7 Å to 13 Å, this directly results in a broad range of phonon frequencies. For instance, we calculate a range of $\Delta \omega = 40$ cm$^{-1}$ for the high-energy modes (HEM) in our CNT ensemble$^{20}$. This translates into a range of $2\Delta \omega = 80$ cm$^{-1}$ in the two-phonon density of states shown in Fig. 2, explaining the broad lineshape observed experimentally. In contrast to graphene or graphite, we cannot observe distinct peaks that are related to the LO overbending or the pDOS at the M point. Again, also these phonon frequencies show a dependence on tube diameter and chiral angle$^{21}$. The expected range of LO-phonon maxima in our CNT sample is $\Delta \omega_{\text{overbending}} = 10$ cm$^{-1}$ and thus all different contributions will add up to a broad shoulder on the high-frequency side of the main peak. The shoulder towards lower wavenumbers is attributed to LO-, LA-, and TO-derived phonon bands from the M point.

We will now turn our discussion to the double-resonant Raman scattering process in the ultraviolet range. Figure 3 (a) shows a contour plot of equi-energy lines from the electronic band structure of graphene with $E_c - E_v = \text{constant}$ ($E_c$: conduction band; $E_v$: valence band). We highlight the contour where $E_c - E_v = 5.08$ eV, i.e., the equi-energy line where the absorption for an excitation wavelength of 244 nm occurs. In contrast to excitation in the visible range, UV-excitation contours form circles around the Γ point rather than closed triangles around the K point. Furthermore, using laser excitation energies above the M-point transition energy, we can selectively suppress optical transitions along the $K - M$ high-symmetry direction in the double-resonance process [compare Figure 3 (b)]. These transitions are so-called ‘inner’ processes, whereas excitations along the $K - \Gamma$ direction with phonons from $K - M$ are ‘outer’ processes. However, due to low intensity, the latter contribute only marginally to the Raman spectrum in the double-resonance process$^{12,22}$. Therefore, the UV spectra shown in Fig. 2 are dominated by the (non-resonant) two-phonon pDOS signal. Tuning the excitation energy from the deep UV to 4.7 eV, allows optical transitions from the $K - M$ direction and thus activates dominant inner processes.

In the following, we present and discuss calculated Raman spectra of graphite for excitation energies between 25 eV - 4.7 eV in the spectral range from 2600 cm$^{-1}$ to 3300 cm$^{-1}$ [see Fig. 4 (b)]. Double-resonant Raman spectra were calculated using the equation$^{10}$

$$
I \propto \sum_{\alpha=1}^{6} \left| \sum_{a,b,c} (E_{L} - E_{ai} - i\gamma)(E_{L} - E_{bi} - \hbar \omega_{\alpha} - i\gamma) \frac{M}{(E_{L} - E_{ci} - 2\hbar \omega_{\alpha} - i\gamma)^{2}} \right|^{2},
$$

where we assumed the matrix elements $M$ to be constant. $E_{ci}$ denote the energy differences between the intermediate electronic states $a, b, c$ and the initial state $i$. We considered the six highest phonon branches (LO, TO, LA), which are indexed with $\alpha$. The integration is performed along the $\Gamma - K - M$ high-symmetry line. The broadening
factor $\gamma$ was set to 120 meV for all excitation energies. The electronic bands are GW corrected, in order to fit the experimentally observed $M$-point energy. The calculated spectrum in Fig. 4 (b) for an excitation energy of $E_L = 25$ eV resembles the pDOS of graphite since only off-resonant contributions dominate the Raman spectrum. A decrease in the excitation energy to values of 5 eV or less activates inner double-resonant processes with phonons exhibiting ultra-short wave vectors [Fig. 4 (a)]. They mediate double-resonant scattering processes between two electronic states close to the $M$ point. Due to the flat slope of the electronic bands around the $M$ point, the double-resonance process can be fulfilled by a broad range of phonon wave vectors. This directly results in broad peaks in the Raman spectra around 3100 cm$^{-1}$, as can be seen in Fig. 4 (b). A further decrease of the excitation energy results in a smaller peak width and a downshift of the double-resonant Raman peak, corresponding to the slope of the electronic bands and TO/LO phonon branches. As can be seen, the relative intensity of the LO-overbending Raman peak increases with lower excitation energies, since the resonant phonon wave vector approaches the maximum of the LO phonon branch. The maximum exhibits a wave vector of 0.46 Å and can be resonantly accessed by excitation energies marginally lower than 4.7 eV (Fig. 4).

In Figure 4 (b), we also highlight the spectral range that is associated with ‘outer’ double-resonant processes and exhibits several low-intensity Raman peaks. These peaks are due to ‘outer’ scattering processes with LA, LO and TO phonons and exhibit resonant phonon wave vectors with $q \approx 2.3/\AA$ [Fig. 4 (a), marked by the star]. Thus, we can observe phonons with large wave vectors close to the $M$ point using excitations in the deep-UV. For $E_L = 25$ eV, the lineshape of the low-intensity peaks directly corresponds to the pDOS, whereas they transform into Lorentzian lineshapes for lower excitation energies, since they correspond to outer double-resonant processes. In general, the contributions from the pDOS-related Raman bands drastically decrease at lower excitation energy, as the enhancement of the double-resonant processes outperforms the pDOS-related peaks by orders of magnitude.

The experimental Raman spectra of graphite for four different excitation energies are presented in Fig. 5. As predicted by the calculations (Fig. 4), by lowering the excitation energy, we clearly observe the evolution of a broad and dispersive peak around 3050 cm$^{-1}$. This peak is the rise of the $2D$ mode in graphite. As explained above, this peak is due to a double-resonance process at the $M$ point with two TO phonons exhibiting ultra-short wave vectors. As predicted theoretically, we further observe an intensity increase of the LO-overbending Raman peak for lower excitation energies. In Fig. 5 (b), we explicitly decompose the calculated spectra into contributions from the TO and the LO phonon branch in the double-resonance process for two different excitation energies. It shows the radical change in both the experimental and calculated Raman spectra mainly caused by the TO phonon branches (blue, dashed lines), when inner processes are activated. This fact emphasizes the importance of inner contributions in double-resonant Raman processes in graphite and graphene.

In conclusion, we performed an analysis of deep-UV Raman spectra for graphite, graphene and carbon nanotubes. At an excitation energy of 5.08 eV, we observe the phonon density of states in the second-order spectra of all samples. Decreasing the excitation energy towards the transition energy of the $M$ point, we can activate inner double-resonant processes that are mediated by ultra-short phonon wave vectors. We observe the evolution of a broad and dispersive peak for excitation energies below 4.9 eV, which is the rise of the $2D$ mode in graphite. Our calculated Raman spectra show good agreement with the experimental data and support our interpretation of the Raman process in the UV spectral range.
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