

## 14

### Summary of Raman Spectroscopy on $sp^2$ Nanocarbons

This chapter provides a brief summary of the behavior of the various  $sp^2$  nanocarbon Raman features, focusing on those properties which can be used for sample characterization. The physics behind each feature in the Raman spectrum has been discussed in detail in this book, and the main results are summarized in this chapter, ending with a short perspective for the future of Raman spectroscopy in  $sp^2$  nanocarbons.

#### 14.1

##### Mode Assignments, Electron, and Phonon Dispersions

The Raman spectra from  $sp^2$  nanocarbons are very rich, composed of first-order and higher-order Raman modes, as well as disorder-induced features. The Raman features can all be related to phonons in graphene, at the  $\Gamma$  point, within the interior of the Brillouin zone and near the Brillouin zone boundary. The modes associated with interior points are, activated either as higher-order (combination modes and overtones) or as defects-induced processes. The Brillouin zone center modes can be dispersive and, therefore, they can be used for measuring the electron and phonon dispersion of  $sp^2$  nanocarbons, using the double resonance (DR) model (see Figure 12.11 and Figure 13.5). The advantages, when comparing phonon dispersion relations obtained by Raman spectroscopy using the DR model with those obtained by neutron or electron inelastic scattering, is the simplicity and the high precision of the Raman measurements regarding phonon properties. The drawback is that the DR Raman scattering mechanism selects only the  $|\mathbf{k}|$  and  $|\mathbf{q}|$  wave vector modulus for electrons and phonons, respectively. Therefore, the Raman features are composed of averages of phonons around the high symmetry  $\Gamma$  or  $K$  points. Furthermore, the response depends both on the electron and phonon dispersions, and theory is needed to decouple these two dispersions. Table 14.1 provides a summary for the assignment of many of these features in the Raman spectra. Most notations have been introduced in the book, and the footnotes explain notations which are especially created for the table. The results give average values that usually exhibit small deviations depending on the  $sp^2$  structure (single vs. multi-layer

graphene, graphene nanoribbons, nanotubes with different diameters and chiral angles, etc.), and on the ambient conditions (temperature, pressure, environment, etc.). Summaries of the characteristics for the most intense Raman features are given in the following sections: the G-band in Section 14.2, the RBM in Section 14.3, the G'-band in Section 14.4 and the D-band in Section 14.5.

## 14.2

### The G-band

The science behind the G-band is discussed in Chapters 7 and 8. Below we list a summary of the general properties of the G-band:

- G1 The G-band is the Raman signature for  $sp^2$  carbons, and is observed as a peak (or a multi-peak feature) at around  $1585\text{ cm}^{-1}$  for all  $sp^2$  carbons (see Figure 1.5).
- G2 Hydrostatic pressure on graphene: shifts  $\omega_G$  (see Section 7.1.1).
- G3 Uniaxial stretching of graphene: splits the G peak into  $G^-$  and  $G^+$ , which are, respectively, related to atomic motion along and perpendicular to the stretching direction. Increasing the stretching, red-shifts both  $\omega_G^+$  and  $\omega_G^-$  (see Figure 7.1).
- G4 Doping graphene: blue-shifts  $\omega_G$  (see Section 8.3.1 for 1-LG, and Section 8.3.2 for 2-LG) for weak doping (changes in the Fermi level near the  $K$  point). Higher doping levels can cause blue(red)-shift for  $p(n)$  doping.
- G5 Temperature: generally, increasing  $T$ , red-shifts  $\omega_G$ . Different effects take place, such as changes in the electron-phonon renormalization, phonon-phonon coupling and  $\omega_G$  shifts due to thermal expansion-induced volume changes (see Section 8.2.1).
- G6 Polarization: when choosing light polarized in the graphene plane (propagation perpendicular to the sheet), then rotating the polarization is irrelevant for unstrained or homogeneously strained graphene. If graphene is non-homogeneously strained, then the relative intensity between the  $G^+$  and  $G^-$  peaks  $I_{G^+}/I_{G^-}$  will give the strain direction (see [198, 230, 231]).
- G7 Linewidth: usually in the range of  $10\text{--}15\text{ cm}^{-1}$ , although it changes with strain, temperature and doping (see Section 8.3.1).
- G8 Bending the graphene sheet: splits the G-band into  $\omega_G^+$  and  $\omega_G^-$ , which have their atomic vibrations preferentially along and perpendicular to the folding axis, respectively (see Section 7.2).
- G9 Rolling up the graphene sheet into a seamless tube (SWNT): (1) bending splits the G-band into  $\omega_G^+$  and  $\omega_G^-$  (see Figure 4.12), which are preferentially along (LO) and perpendicular (TO) to the tube (folding) axis, respectively, for semiconducting SWNTs (see Section 7.2.1). For metallic tubes, electron-phonon coupling softens the LO modes, so that  $\omega_G^+$  and  $\omega_G^-$  are actually associated with TO and LO modes, respectively. In the case of achiral tubes,  $\omega_G^+/\omega_G^-$  is strictly proportional to  $I_{LO}/I_{TO}$ . (2) Quantum confinement gener-

**Table 14.1** Assignments and frequency behavior for the Raman modes from  $sp^2$  carbon materials.

Name <sup>a</sup>	$\omega$ [ $\text{cm}^{-1}$ ] <sup>b</sup>	Res. <sup>c</sup>	$\partial\omega/\partial E$ <sup>d</sup>	Notes <sup>e</sup>
iTA	288	DRd1	129	intraV ( $q \sim 2k$ near $\Gamma$ )
LA	453	DRd1	216	intraV ( $q \sim 2k$ near $\Gamma$ )
RBM <sup>f</sup>	$227/d_t$	SR	0	SWNT vibration of radius
IFM <sup>-</sup> (oTO-LA)	750	DR2	-220	intraV+intraV ( $q \sim 2k$ near $\Gamma$ )
oTO	860	DRd1	0	intraV ( $q \sim 0$ near $\Gamma$ ), IR active
IFM <sup>+</sup> (oTO+LA)	960	DR2	180	intraV+intraV ( $q \sim 2k$ near $\Gamma$ )
D (iTO)	1350	DRd1	53	interV ( $q \sim 2k$ near K)
G (iTO,LO) <sup>g</sup>	1585	SR	0	$q = 0$ , i. e., at $\Gamma$
D' (LO)	1620	DRd1	10	intraV ( $q \sim 2k$ near $\Gamma$ )
M <sup>-</sup> (2oTO)	1732	DR2	-26	intraV+intraV ( $q \sim 2k$ near $\Gamma$ )
M <sup>+</sup> (2oTO)	1755	DR2	0	intraV+intraV ( $q \sim 0$ near $\Gamma$ )
iTOLA (iTO+LA)	1950	DR2	230	intraV+intraV ( $q \sim 2k$ near $\Gamma$ )
G* (LA+iTO)	2450	DR2	-10	interV+interV ( $q \sim 2k$ near K) <sup>h</sup>
G' (2iTO) <sup>i</sup>	2700	DR2	100	interV+interV ( $q \sim 2k$ near K)
G + D	2935	DRd2	50	intraV+interV <sup>j</sup>
D' + D	2970	DRd2	60	intraV+interV <sup>j</sup>
2G	3170	SR	0	overtone of G mode
G + D'	3205	DRd2	10	intraV+intraV
G''(2LO) <sup>i</sup>	3240	DR2	20	intraV+intraV ( $q \sim 2k$ near $\Gamma$ )

- a** Usually the respective graphene phonon branch labels the Raman peaks. When other names are given in the literature, the respective phonon branch appears between parenthesis.
- b** The frequencies quoted in the table are observed at  $E_{\text{laser}} = 2.41$  eV.
- c** The notation for resonances is: SR: single resonance, Raman allowed; DR2: double resonance, 2-phonon Raman allowed; DRd1: double resonance Raman activated by disorder, 1-phonon; DRd2: double resonance Raman activated by disorder, 2-phonons.
- d** The change of phonon frequency in  $\text{cm}^{-1}$  obtained by changing the laser excitation energy by 1 eV defines the phonon dispersion.
- e** Terms intraV: intravalley scattering; interV: intervalley scattering.
- f** The radial breathing mode (RBM) only occurs for carbon nanotubes and is unique for carbon nanotubes.
- g** The iTO and LO phonons are degenerate at  $\Gamma$  for graphene. For nanoribbons and SWNTs, the G-band splits into several peaks due to symmetry, and differs for metallic and semiconducting nanotubes. The G-band frequency depends strongly on doping and strain.
- h** There is another assignment for G\* of 2iTO ( $q \sim 0$  near K) with  $\partial\omega/\partial E \sim 0$ .
- i** Notation G' and G'' are frequently named 2D and 2D', respectively. Strictly speaking, the overtone assignment is not fully correct, since one of the elastic scattering event which appears in the one-phonon emission spectra in the D(D') mode does not exist in the two-phonon emission Raman spectra in the G'(G'') mode (see Section 12.2.1). Here we adopt the notation where the letter D only appears for defect-induced features.
- j** This combination mode consists of intra V + inter V scattering and thus the elastic scattering process also exists for some combination modes.

ates up to six Raman-allowed G-band peaks, three of each exhibiting LO- or TO-like vibrations, two totally symmetric  $A_1$  modes, two  $E_1$  modes and two  $E_2$  symmetry modes (see Section 7.2.1). Due to the depolarization effect and special resonance conditions, the  $A_1$  modes usually dominate the G-band spectra.

- G10 Decreasing the SWNT diameter: increases the effect of bending and shifts mostly  $\omega_G^-$ . The  $\omega_G^-$  shift can be used to measure the SWNT diameter (see Section 7.2.2 and Eq. (7.15)).
- G11 Changing the chiral angle: changes the intensity ratio between LO-like and TO-like modes [274].
- G12 Hydrostatic pressure on SWNT bundles: shifts  $\omega_G$  (see [236, 243]).
- G13 Strain on isolated SWNTs: hydrostatic and uniaxial deformation, torsion, bending, etc., change  $G^+$  and  $G^-$ , depending on  $(n, m)$  (see Section 7.4).
- G14 Doping SWNTs: changes  $\omega_G$ , mainly for metallic SWNTs. There is a rich doping dependence on  $(n, m)$ , but a strong effect is felt mostly on the broad and down-shifted  $G^-$  peak in metallic SWNTs, with doping usually causing an upshift and sharpening of the  $G^-$  feature (see Section 8.4).
- G15 Temperature change: similar effect in SWNTs and graphene. Increasing  $T$  softens and broadens the G-band peaks in SWNTs (see Section 8.2.1 and [242]).
- G16 Polarization analysis in SWNTs: can be used to assign the G-band mode symmetries (see Sections 7.3.1 and 7.3.2).

### 14.3

#### The Radial Breathing Mode (RBM)

The science behind the RBMs is discussed in Chapters 9 and [282], 10 and 11. Below we list the general properties of the RBMs:

- RBM1 RBM: the Raman signature for the presence of nanotubes, and the RBM is observed as a peak (or a multi-peak feature) in the 50–760  $\text{cm}^{-1}$  range<sup>1)</sup> (see Figure 1.5).
- RBM2 The  $\omega_{\text{RBM}}$  dependence on diameter ( $d_t$ ):

$$\omega_{\text{RBM}} = \frac{227}{d_t} \sqrt{1 + C_e * d_t^2}, \quad (14.1)$$

where  $C_e$  ( $\text{nm}^{-2}$ ) probes the effect of the environment on  $\omega_{\text{RBM}}$ . Table 9.1 gives the  $C_e$  values fitting the RBM results for several samples in the literature (see Section 9.1).

- RBM3 The  $\omega_{\text{RBM}}$  dependence on chiral angle  $\theta$ : predicted to depend on SWNT diameter and  $E_{\text{laser}}$ , but the dependence of  $\omega_{\text{RBM}}$  on  $\theta$  is rather weak,

1) The highest RBM frequency (760  $\text{cm}^{-1}$ ) is that for the (2,2) nanotube [420].

even for SWNTs with  $d_t < 1$  nm, where the dependence of  $\omega_{\text{RBM}}$  reaches a few wave numbers (see Section 9.1.5).

- RBM4  $E_{\text{laser}}$  dependence: for a given SWNT, the RBM peak intensity  $I(E_{\text{laser}})$  is a function of  $E_{\text{laser}}$  and can be evaluated by Eq. (9.9). The RBM is intense when the incident light ( $E_{\text{laser}}$ ) or the scattered light ( $E_{\text{laser}} \pm \hbar\omega_{\text{RBM}}$ ) is in resonance with the SWNT optical transition energies  $E_{ii}$ .
- RBM5 The optical transition energies  $E_{ii}$ : The  $E_{ii}$  can be obtained using an empirical formula (see Eq. (9.10)), in which the various fitting parameters are discussed in Section 9.3.2. The theoretical description depends on an accurate analysis of the nanotube structure, exciton effects and dielectric screening, as discussed in detail in Chapter 10.
- RBM6 Intensity dependence on  $(n, m)$ : the electron–photon and electron–phonon matrix elements, as well as the resonance broadening factor  $\gamma_r$ , strongly depend on  $(n, m)$ . This dependence has been obtained experimentally (see Section 11.2) and described theoretically (see Chapter 11).
- RBM7 Polarization: the RBM is a totally symmetric mode. The polarization dependence is dominated by the antenna effect, where a strong Raman signal is observed when both the incident and scattered light are chosen along the tube axis (see Section 9.2.3).
- RBM8 Tube–tube interaction: the same inner  $(n, m)$  tube within a DWNT can exhibit different  $\omega_{\text{RBM}}$  values if surrounded by different outer  $(n', m')$  tubes (see Section 9.1.3).
- RBM9 Linewidth: usually in the range of  $3 \text{ cm}^{-1}$ , although it can reach much larger values (by one order of magnitude) due to environmental effects (see Section 9.1.4), or smaller (also by as much as one order of magnitude) when measured for the inner tube of a DWNT and at low temperature (see [292–294]).
- RBM10 Due to the relatively low RBM frequency, changes in  $\omega_{\text{RBM}}$  with temperature, doping, strain and other such effects are less pronounced in the RBM than in the G-band. However, the RBM becomes important when looking for the effects on one single  $(n, m)$  specie among many SWNTs, since the RBM feature is unique for each  $(n, m)$  ( $\omega_{\text{RBM}}$  depends strongly on tube diameter), while the G-band appears within the same frequency range for most SWNTs (very weak  $d_t$  dependence).
- RBM11 Changing  $E_{ii}$ : as discussed above, changes in temperature, pressure or the dielectric constant of the environment does not change  $\omega_{\text{RBM}}$  significantly. However, these factors do change  $E_{ii}$ , and changing the resonance condition changes the RBM intensity. Therefore, the RBM can be used to probe resonance effects sensitively (see Chapter 9), and for understanding the importance of excitonic effects for a theoretical description of the observed Raman spectra (see Chapter 10). Increasing the temperature decreases  $E_{ii}$ , and the temperature-dependent change in  $E_{ii}$  also depends on  $(n, m)$ . Increasing the pressure changes  $E_{ii}$ , and the pressure-dependent changes in  $E_{ii}$  also depend on  $(n, m)$ . Here a change in  $E_{ii}$  can be positive or negative, depending on  $i$  and on the  $\text{mod}(2n + m, 3)$  type.

Increasing the dielectric constant of a SWNT wrapping agent decreases  $E_{ii}$  (see Section 10.5.2).

- RBM12 Stokes vs. anti-Stokes RBM intensities: the S/aS intensity ratio for the RBM features is strongly sensitive to the energy displacement of  $E_{\text{laser}}$  with respect to  $E_{ii}$  (see Section 9.2.2).

#### 14.4

##### **G'-band**

The science of the G'-band is discussed in Chapter 12. Below we list the general properties of the G'-band:

- G'1 G'-band: also an  $sp^2$  Raman signature, observed for all  $sp^2$  carbons as a peak (or a multi-peak feature) in the range 2500–2800  $\text{cm}^{-1}$  (see Figure 1.5).
- G'2 The G' frequency:  $\omega_{G'}$  appears at  $\sim 2700 \text{ cm}^{-1}$  for  $E_{\text{laser}} = 2.41 \text{ eV}$ , but its frequency changes by changing  $E_{\text{laser}}$  (see Section 12.2.2). Its dispersion is  $(\partial\omega_{G'}/\partial E_{\text{laser}}) \simeq 90 \text{ cm}^{-1}/\text{eV}$  for monolayer graphene, and this dispersion changes slightly by changing the  $sp^2$  nanocarbon structure (see Section 12.2.2). The sensitivity of  $\omega_{G'}$  to the detailed  $sp^2$  structure makes this band a powerful tool for quantifying the number of graphene layers and the stacking order in few layer graphenes and graphite, and for characterizing SWNTs by the diameter and chiral angle dependence of  $\omega_{G'}$  and of the G'-band intensity.
- G'3 The number of graphene layers: 1-LG exhibits a single Lorentzian peak in the G'-band, and the intensity of the G'-band is larger (2–4 times) than that of the G-band in 1-LG. In contrast, 2-LG with AB Bernal stacking exhibits four Lorentzian peaks in the G'-band, and the intensity of the G'-band with respect to the G-band is strongly reduced (same magnitude or smaller). For 3-LG with AB Bernal stacking, 15 scattering processes are possible for the G'-band, but the 15 peaks occur close in frequency and cannot all be distinguished from each other. Usually the G'-band from 3-LG is fitted with six peaks (see Section 12.2.3). Highly oriented pyrolytic graphite (HOPG) exhibits two peaks. Turbostratic graphite exhibits only a single G' peak, and care should be taken when assigning the number of layers based on the G' feature. The single G' peak in turbostratic graphite is slightly blue-shifted ( $\sim 8 \text{ cm}^{-1}$ ) from the G' peak in 1-LG (see Section 12.2.4).
- G'4 Stacking order: while HOPG (considered a three-dimensional structure) exhibits a two-peak G' feature, turbostratic graphite (no AB Bernal stacking order, and considered a two-dimensional structure) exhibits a single Lorentzian line. Therefore, the single vs. double peak G' structure can be used to assign the amount of stacking order present in actual graphite samples (see Section 12.2.4).
- G'5 Probing electron and phonon dispersion: Eq. (12.8) gives the electron and phonon wave vectors selected by the double resonance process. By changing

- $E_{\text{laser}}$ , it is possible to probe different electrons and phonons in the interior of the Brillouin zone. The  $G'$ -band probes the iTO phonons near the K point, where the strongest electron–phonon coupling occurs (see Section 12.2).
- G'6 Doping: the  $G'$  feature can be used to assign  $p$  and  $n$  type doping in graphene and SWNTs. A blue-shift (red-shift) is observed for  $p$  ( $n$ ) doping. The magnitude of the shift depends also on the specific type of doping atom, while the relative intensity between doped-shifted and undoped-pristine  $G'$ -band peaks can be used to obtain the dopant concentration (see Section 13.6).
- G'7 SWNTs and  $(n, m)$  dependence: carbon nanotubes show a very special  $G'$ -band feature, where the number of peaks and their frequencies depend on  $(n, m)$  due to both curvature-induced strain and the quantum confinement of their electronic and vibrational structures. The resonance condition is restricted to  $E_{\text{laser}} \approx E_{ii}$  and  $E_{\text{laser}} \approx E_{ii} + E_{G'}$ , and this fact gives rise to a  $\omega_{G'}$  dependence on the SWNT diameter and chiral angle (see Section 12.4.2).

## 14.5

### D-band

The science behind the D-band is discussed in Chapter 13. Below we list the properties of the D-band:

- D1 D-band: The dominant  $sp^2$  Raman signature of disorder. The D-band is observed as a peak in the range 1250–1400  $\text{cm}^{-1}$  (see Figure 1.5).
- D2 The D-band frequency:  $\omega_D$  appears at  $\sim 1350 \text{ cm}^{-1}$  for  $E_{\text{laser}} = 2.41 \text{ eV}$ , but its frequency changes by changing  $E_{\text{laser}}$  (see Section 13.2). Its dispersion is  $(\partial\omega_{G'}/\partial E_{\text{laser}}) \simeq 50 \text{ cm}^{-1}/\text{eV}$  for monolayer graphene, and it changes slightly by changing the  $sp^2$  nanocarbon structure (see Chapter 13). For SWNTs, the frequency  $\omega_D$  depends on the nanotube diameter, according to Eq. (13.13).
- D3 The D-band intensity: can be used to quantify disorder. The effect of nanocrystallite size and  $\text{Ar}^+$  bombardment dose has been used to characterize the disorder in both SWNTs and graphene and a quantitative phenomenological model has been developed for explaining the D-band intensity evolution with the amount of disorder (see Section 13.3).
- D4 The D-band linewidth: Being disorder related, the D-band linewidth can change from  $7 \text{ cm}^{-1}$  (observed for isolated SWNTs [242]) to a hundred wavenumbers (for very defective carbon materials see Figure 13.6).
- D5 Type of graphene edge: The D-band scattering is forbidden at edges with zigzag structure. This property can be used to analyze the edge structure and to distinguish zigzag from armchair edges (see Section 13.4).
- D6 The  $I_D/I_G$  ratio: Because absolute intensity measurement is a difficult task in Raman spectroscopy, the normalized intensity  $I_D/I_G$  ratio is largely used to measure the amount of disorder. This ratio depends not only on the amount of disorder, but also on the excitation laser energy, since  $I_G \propto E_{\text{laser}}^4$ , while  $I_D$  is  $E_{\text{laser}}$ -independent for graphite/graphene nanocrystallites (when measured

in the 1.9–2.7 eV range) (see Sections 13.3.3 and 13.3.4). The  $E_{\text{laser}}$  dependence for  $I_D/I_G$  in ion bombarded graphene has not been established.

- D7 Coherence length for Raman scattering: Since the D-band is activated by defects, it can only be observed near the defect within a coherence length  $\ell$ . In [194] the D-band was used to obtain  $\ell = 2$  nm for ion bombarded graphene measured with  $E_{\text{laser}} = 2.41$  eV (see Section 13.3.2).

## 14.6

### Perspectives

Over nearly one century Raman spectroscopy has been used to study the science of  $sp^2$  materials, revealing more and more fundamental aspects of their electronic and vibrational properties. This non-stop development is due to improvements in experimental techniques, theoretical calculations, and to advances in the nanosciences generally. For the future perspectives, from the experimental side, near-field optics can now unravel Raman spectra with spatial resolution below the diffraction limit [191], a former limitation for Raman spectroscopy. Time-dependent Raman and coherent-phonon spectroscopy provide new frontiers for vibrational spectroscopy [43]. From the theoretical side, the simplicity of  $sp^2$  carbon materials (only one atom species on a hexagonal structure) is making possible the development of fancy tight binding and first-principles calculations, reaching unprecedented levels of accuracy for the description of electronic and vibrational levels. New theoretical insights, such as electron–electron correlation, excitonic effects and electron–phonon interactions were successfully applied to  $sp^2$  nanocarbons, but now can perhaps also be applied to other systems. In the field of carbon, the transition from molecular to crystalline behavior, and the transition from low levels to high levels of disorder might be addressable with detailed experimental inputs. Measuring the Raman signal from one single sheet of atoms, or one single rolled up tube, together with the ability of applying controlled perturbations to these nanomaterials (strain, doping, etc.), will keep generating unprecedented levels of detail in describing the physics of  $sp^2$  carbons. Such knowledge has raised more and more fundamental questions. The experience gained from the studies discussed in this book indicates that Raman spectroscopy provides a powerful tool for finding and addressing the new physics that is needed.