

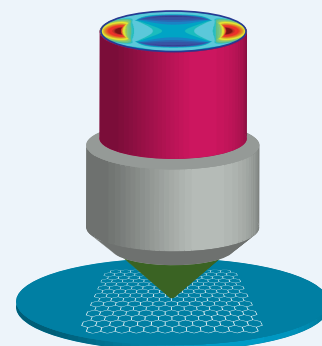
Observing the Angular Distribution of Raman Scattered Fields

Luiz Gustavo Cançado^{*,†} and Lukas Novotny[§]

[†]Departamento de Física, Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, MG 30123-970, Brazil

[§]Photonics Laboratory, ETH Zürich, 8093 Zürich, Switzerland

ABSTRACT: In conventional optical spectroscopy, lenses are used to focus light on the sample and to collect light scattered from the sample. Focusing increases the signal intensity, but it amounts to angular (k-space) averaging and leads to information loss. In this issue of *ACS Nano*, Budde and collaborators record radiation patterns of Raman scattering from a single layer of graphene, revealing the angular distribution of the scattered field. The authors show that the radiation patterns render the spatial symmetry of vibrational modes. Furthermore, their results demonstrate that depolarization effects occurring in the focal region must be taken into account for proper interpretation of Raman intensities. We outline here the working principle of this new approach and discuss future applications for studies of graphene and other low-dimensional systems.



Polarized Raman spectroscopy is broadly employed to study the symmetries of solids¹ and molecules.² The objective is to determine the components of the polarizability derivative tensor R_i of a specific vibrational mode i of the material system. A standard polarized Raman experiment is illustrated in Figure 1. The incident laser field, polarized along the direction \hat{e}_L , excites the material system, and the scattered field, represented by the field emitted by an incoherent sum of oscillating point dipoles,³ is passed through a polarizer with orientation \hat{e}_S . The scattered intensity in the angular direction $\Omega = (\theta, \phi)$ becomes $dI(\Omega) \propto |(\hat{e}_S \cdot R_i \hat{e}_L)|^2 d\Omega$. In standard Raman spectroscopy, the signal collected by an objective is directed to a spectrometer to render a Raman scattering spectrum. Since the objective bins the total light emitted into a wide angular range Ω_0 , the Raman scattering signal becomes $I \propto \int_{\Omega_0} |(\hat{e}_S \cdot R_i \hat{e}_L)|^2 d\Omega$, and the information about the angular distribution gets lost (see Figure 1).

In this issue of *ACS Nano*, Budde and collaborators record angle-resolved Raman scattering from a monolayer of graphene deposited on a glass substrate.⁴ More specifically, they image the intensity distribution of specific vibrational modes in the back-focal plane of the objective. The back-focal plane contains the angular distribution of the light scattered at the focus of the objective, and represents the spatial Fourier transform of the intensity in the focal plane.⁷ The authors record the intensity distribution in the back focal plane for both the first-order allowed bond-stretching G band ($\sim 1580 \text{ cm}^{-1}$) and the two-phonon totally symmetric two-dimensional (2D) band ($\sim 2700 \text{ cm}^{-1}$). This measurement is done by placing a charge-coupled device (CCD) camera in the detection beam path, as shown in Figure 1 (see also Figure 6a of ref 4). Because the G band originates from a double-degenerate vibrational mode,⁵ its

radiation pattern is described by the incoherent superposition of the fields generated by two perpendicular point dipoles. On the other hand, the radiation pattern of the 2D band can be understood as the incoherent superposition of three point dipoles rotated by 120° with respect to each other, resembling the three-fold symmetry of the electronic populations involved in the double-resonance scattering mechanism.⁶

In this issue of *ACS Nano*, Budde and collaborators record angle-resolved Raman scattering from a monolayer of graphene deposited on a glass substrate.

The experimental results obtained by Budde *et al.*⁴ not only provide access to the symmetries of vibrational modes but also demonstrate that polarization scrambling, occurring in the focal region of high NA objective lenses, should be taken into consideration for proper analysis of Raman intensities. Although this aspect is not relevant for experiments using low numerical aperture (NA) (<1) lenses, it becomes quite important for high NA setups that aim to obtain high spatial resolution. The situation is simple but difficult to analyze quantitatively: if a linearly polarized laser beam is focused by a high NA lens, then the fields in the focal region also feature polarization components in the direction of the beam and fields that are orthogonal to both the incident polarization and the optical axis.⁷ The same happens to the scattered field, and therefore, an accurate evaluation of the scattered intensity has

Published: February 10, 2016

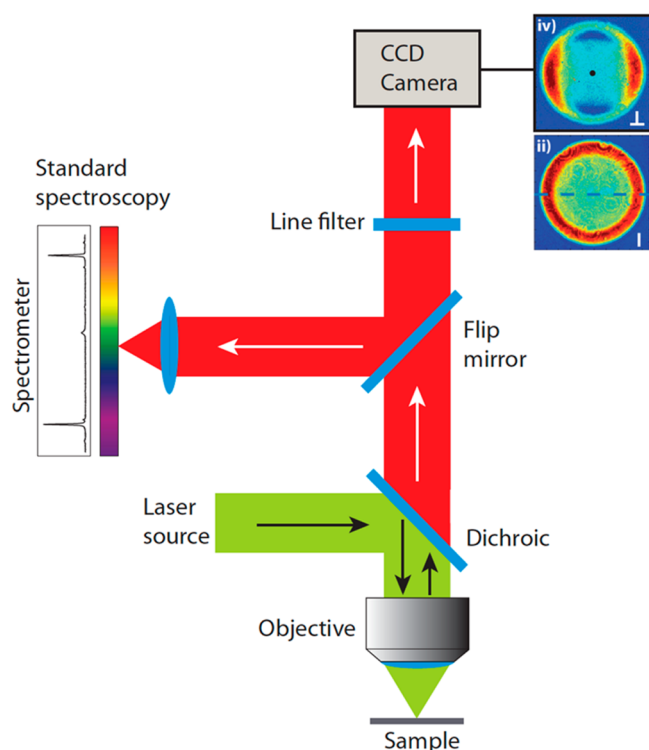


Figure 1. Illustration of momentum-resolved Raman spectroscopy. An objective focuses incident laser radiation on the sample and collects the scattered light. In standard Raman spectroscopy, the scattered radiation is focused on the entrance slit of a spectrometer, which leads to a loss of angular (momentum) information. In the approach by Budde *et al.*, the scattered light is sent through a narrow bandpass filter to select a particular Raman line spectrally and it is then projected on a CCD camera.⁴ The system is configured such that the back-aperture of the objective is imaged on the CCD. The two panels on the right show Raman radiation patterns of the G band intensity obtained with and without polarizers. Adapted from ref 4. Copyright 2016 American Chemical Society.

to take into account depolarization factors for both incident and scattered fields. The depolarization factors depend on the NA of the illumination/collection lenses and affect the intensities of Raman bands. Budde *et al.*⁴ show that this effect depends on the symmetry of the Raman mode. By recording Raman scattering spectra with different NAs, they demonstrate that the ratio of 2D-band intensity to G-band intensity (I_{2D}/I_G) decreases by $\sim 30\%$ when the NA is increased from 0.5 to 1.3. Polarized *versus* unpolarized detection also affects the I_{2D}/I_G ratio. Since this ratio is broadly used to estimate the doping level of graphene (charged carrier density),^{8,9} the work by Budde *et al.*⁴ provides important information about the different parameters that must be taken into consideration for the interpretation of experimental data.

OUTLOOK AND FUTURE CHALLENGES

The investigation of Raman radiation patterns should be extended to other types of low-dimensional systems such as carbon nanotubes and transition metal dichalcogenides. This analysis is especially important in the case of resonance Raman scattering involving noncenter phonon modes (such as the 2D band in graphene), since the angular distribution of the radiation field reveals important symmetry aspects of the excitations involved (electrons and phonons). In the graphene

case, the previously established protocols based on intensity ratios (e.g., I_{2D}/I_G for doping evaluation, or I_D/I_G and I_D/I_D' for defect analysis)^{8,9} can be revisited and recalibrated, taking into account the geometry of the illumination/collection optics.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cancado@fisica.ufmg.br.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Loudon, R. The Raman Effect in Crystals. *Adv. Phys.* **1964**, *13*, 423–482.
- (2) Long, D. A. *The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules*; John Wiley & Sons Ltd: Chichester, U.K., 2002.
- (3) Cançado, L. G.; Beams, R.; Jorio, A.; Novotny, L. Theory of Spatial Coherence in Near-Field Raman Scattering. *Phys. Rev. X* **2014**, *4*, 031054.
- (4) (1) Budde, H.; Coca-López, N.; Shi, X.; Ciesielski, R.; Lombardo, A.; Yoon, D.; Ferrari, A. C.; Hartschuh, A. Raman Radiation Patterns of Graphene. *ACS Nano* **2016**, DOI: 10.1021/acsnano.5b06631.
- (5) Tuinstra, F.; Koenig, J. L. Raman Spectrum of Graphite. *J. Chem. Phys.* **1970**, *53*, 1126–1130.
- (6) Yoon, D.; Moon, H.; Son, Y.-W.; Samsonidze, G.; Park, B. H.; Kim, J. B.; Lee, Y.; Cheong, H. Strong Polarization Dependence of Double-Resonant Raman Intensities in Graphene. *Nano Lett.* **2008**, *8*, 4270–4274.
- (7) Novotny, L.; Hecht, B. *Principles of Nano-Optics*; Cambridge University Press: Cambridge, U.K., 2012.
- (8) Ferrari, A. C.; Basko, D. M. Raman Spectroscopy as a Versatile Tool for Studying the Properties of Graphene. *Nat. Nanotechnol.* **2013**, *8*, 235–246.
- (9) Beams, R.; Cançado, L. G.; Novotny, L. Raman Characterization of Defects and Dopants in Graphene. *J. Phys.: Condens. Matter* **2015**, *27*, 083002.