Observing the Angular Distribution of Raman Scattered Fields

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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 solids† and molecules. The objective is to determine the components of the polarizability derivative tensor $\mathbf{R}$ 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,$^7$ is passed through a polarizer with orientation $\hat{e}_p$. The scattered intensity in the angular direction $\Omega=(\theta, \phi)$ becomes $\text{d}I(\Omega) \propto |\langle \hat{e}_S \cdot \hat{R} \hat{e}_L \rangle|^2 \text{d}\Omega$. 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 $\Omega_0$, the Raman scattering signal becomes $I \propto \int_{\Omega_0} |\langle \hat{e}_S \cdot \hat{R} \hat{e}_L \rangle|^2 \text{d}\Omega_0$, 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.‡ 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. The authors record the intensity distribution in the back focal plane for both the first-order allowed bond-stretching $\Gamma$ 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 $\Gamma$ 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.$^6$

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
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.\textsuperscript{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),\textsuperscript{6,9} the work by Budde et al.\textsuperscript{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 $I_D^\prime/I_G$ for defect analysis)\textsuperscript{8,9} can be revisited and recalibrated, taking into account the geometry of the illumination/collection optics.

REFERENCES