

Characterizing Graphene with Raman Spectroscopy

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Introduction

The interest in graphene has been growing rapidly over the past several years. This is primarily driven by its potential as a material with which to manufacture nanoelectric devices – although this is far from its only application. Raman spectroscopy is used extensively to characterize graphene, as the material is composed almost entirely of symmetric sp^2 bonded carbon which is represented in great detail in the Raman spectrum.

The Raman Spectrum of Graphene

A great deal of detail on the fine structure of graphene can be extracted from the Raman spectrum if you know where to look. At first glance the Raman spectrum of graphene or graphite can appear fairly simple – usually consisting

of only two main bands and a few more very small bands. However, these bands actually tell us quite a bit about the material. Figure 1 shows a typical Raman spectrum of graphite. The Raman spectrum of graphene is very similar as we would expect since graphite is composed of multilayer graphene. (The differences will be explained a little later in this note.) The two main bands in the graphite spectrum are known as the G-band at $\sim 1582\text{ cm}^{-1}$ and the 2D band at $\sim 2685\text{ cm}^{-1}$. A third band known as the D-band at $\sim 1350\text{ cm}^{-1}$ is also worth some discussion, although it is usually very weak in graphite. Now we will take a closer look at each of these bands.

The G-band

The G-band is the primary mode in graphene and graphite. It represents the planar configuration sp^2 bonded carbon that constitutes graphene. The band is resonant, which means that it is much more intense than we would expect it to be otherwise. The band position is pretty much independent of excitation laser frequency though, making it different from the other graphene bands that will be discussed. The position of the band and to a certain extent the shape can provide you with more information. One common application for the G-band is to aid in determination of graphene layer thickness. Figure 2 demonstrates the effect that layer thickness has on the position of the G-band. As the layer thickness increases, the band position shifts to lower energy representing a slight softening of the bonds as the layer thickness increases. The positions of the bands shown here are in very close agreement with calculated positions for these band locations. It is also worth noting that the position of the G-band is quite sensitive to doping and even very minor strain. This needs to be considered when attempting to use the band position of this band to determine graphene layer thickness.

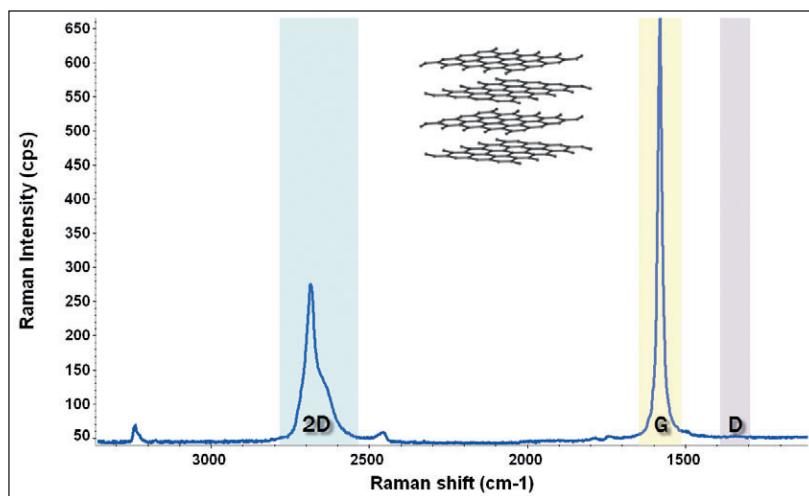


Figure 1: Raman spectrum of highly ordered pyrolytic graphite (HOPG). 633 nm excitation laser

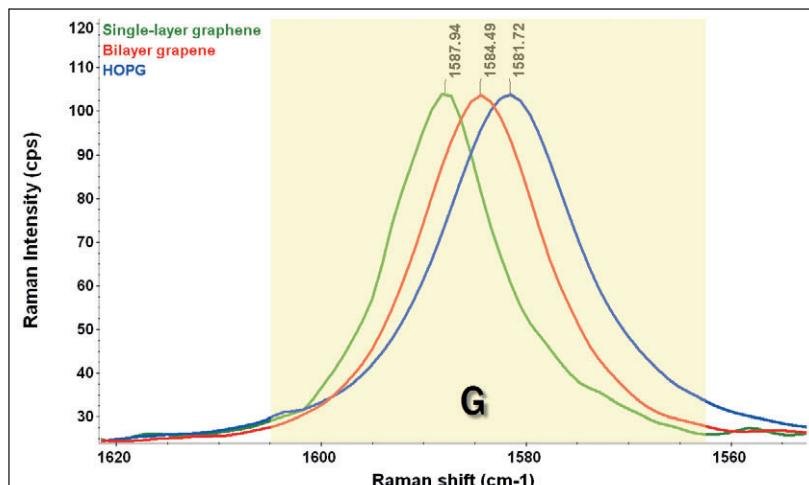


Figure 2: Shifting of G-band as graphene layer thickness increases. 633 nm excitation laser.

The D-band

The D-band is known as the disorder band or the defect band. It represents a ring breathing mode from sp^2 carbon rings, although to be active the ring must be adjacent to a graphene edge or a defect. The band is the result of a one phonon lattice vibrational process. The band is typically very weak in graphite and is typically weak in graphene as well. If the D-band is significant, it indicates that there are a lot of defects in the material. The intensity of the D-band is directly proportional to the level of defects in the sample.

The last thing to note about the D-band is that it is a resonant band that exhibits what is known as dispersive behavior. This means that there are a number of very weak modes underlying this band and the choice of excitation laser used will enhance different modes. The consequence of this is that both the position and the shape of the band can vary significantly with different excitation laser frequencies, making it is important to use the same excitation laser frequency for all measurements when characterizing the D-band.

The 2D-band

The 2D-band is the final band discussed here. Note that the 2D band is sometimes referred to as the G'-band when discussing similar materials such as carbon nanotubes. However it is more commonly referred to as the 2D-band when referring to spectra of graphene. The 2D-band is the second order of the D-band, sometimes referred to as an overtone of the D-band. It is the result of a two phonon lattice vibrational process, but unlike the D-band, it does not need to be activated by proximity to a defect. As a result the 2D-band is always a strong band in graphene even when no D-band is present, and it does not represent defects. This band is also used when trying to determine graphene layer thickness; however the differences between single and bilayer graphene in this band are more complex than a simple band shift, as was observed with the G-band.

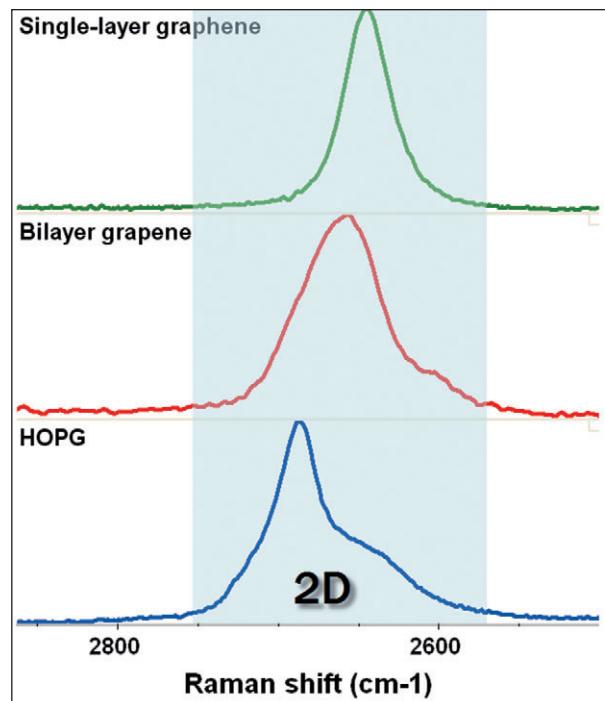


Figure 3: Changes within 2D-band structure as graphene layer thickness increases. 633 nm excitation laser

Figure 3 demonstrates the effect of increasing layer thickness on the 2D-band. Note that while there is a general shifting to higher wavenumbers as the layer thickness increases, the more noticeable changes have to do with the band shape. The changes in band shape have to do with changes to the active components of the vibration. With single layer graphene, there is only one component to the 2D-band, but with bilayer graphene, there are four components to the 2D-band. This is why the shape of the band is so different. Just like the D-band, the 2D-band is resonant. It exhibits



strong dispersive behavior so the position and shape of the band can be significantly different with various excitation laser frequencies. Again, it is important to use the same excitation laser frequency for all measurements when doing characterization with the 2D-band. Finally, it is also worth noting that the 2D-band is very sensitive to graphene folding, which needs to be considered when trying to use this band to determine layer thickness in graphene samples.

Instrumental Considerations

There are a few things which should be considered when selecting a Raman instrument for graphene characterization. First, since graphene samples are usually very small, it is important to select a Raman instrument with microscopy capabilities.

The next issue to consider is which excitation laser to select. While graphene measurements can be made successfully with any of the readily available Raman lasers, it is also important to consider what substrate that the graphene will be deposited on. It is common for graphene to be deposited on either Si or SiO₂ substrates. Both of these materials can exhibit fluorescence with NIR lasers such as 780 nm or 785 nm, so for this reason visible lasers are usually recommended. Typically a 633 nm or 532 nm laser.

Next, since relatively small wavenumber shifts can have significant impact on the interpretation of the Raman spectra, it is important to have a robust wavelength calibration across the entire spectrum. With some other applications it may be sufficient to use a single point wavelength calibration, but this really only insures that one wavelength is in calibration and leaves room for an uncomfortable margin of error. A multipoint wavelength calibration that is regularly refreshed, such as the standard calibration routine used with the Thermo Scientific DXR Raman instruments, will provide considerably more confidence in the results. It is also necessary to have an instrument with high wavenumber precision to insure that small wavenumber shifts observed when altering the sample are in fact representative of changes in the sample rather than representative of measurement variability from the instrument. A common myth states that it is necessary to utilize high resolution in order to achieve high wavenumber precision. Not only is this incorrect, high resolution will actually add considerable noise to the spectrum, which will add to the wavenumber variability. It has been previously demonstrated¹ that a Thermo Scientific DXR Raman microscope configured with a 5 cm⁻¹ resolution grating will provide wavenumber precision of at least 0.066 cm⁻¹. This level of wavenumber precision will give you a high level of confidence even when evaluating band shifts from low levels of strain or doping.

Finally, it is important to have very precise control of your laser power at the sample and to be able to adjust that laser power in small increments. This is important to control temperature related effects and to provide flexibility to maximize Raman signal while still avoiding sample damage from the laser. Thermo Scientific DXR Raman systems are equipped with a unique device called a laser power regulator which maintains laser power with unprecedented accuracy and provides exceptional ability to fine tune laser power and optimize it for each experiment.²

Conclusions

Raman spectroscopy is a great tool for the characterization of graphene. Few techniques will provide as much information about the structure of graphene samples as Raman spectroscopy and any lab doing graphene characterization without Raman would be at a significant disadvantage. The Thermo Scientific DXR Raman microscope is an ideal Raman instrument for graphene characterization providing the high level of stability, control, and sensitivity needed to produce confident results.

References

1. Guide to Evaluating Spectral Resolution on a Dispersive Raman Spectrometer, Thermo Scientific technical note, 2009.
2. The Importance of Tight Laser Power Control When Working with Carbon Nanomaterials, Thermo Scientific application note, 2010.

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