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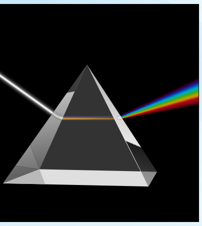
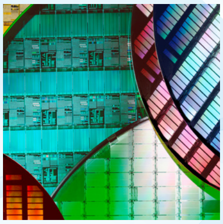
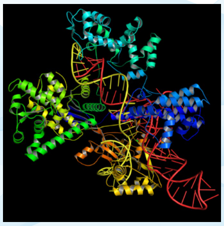


Spectral Resolution

RA-TN14





Important factors to consider when acquiring a Raman spectrum

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Spectral resolution is one of the most important factors to think about when acquiring a Raman spectrum. Defined as the wavenumber, wavelength, or frequency difference of two still distinguishable lines in a spectrum[1], spectral resolution requirements vary depending on the information one would like to obtain. High spectral resolution is not always necessary for routine identification and analysis. However, if information about material properties, such as polymorphism, stress/strain, crystallinity, hydrogen bonding, and/or protein folding are to be obtained, high spectral resolution is necessary. The reason for this is because changes in these material properties can very subtly alter the shape and/or position of the Raman peaks, which may not be detectable with lower spectral resolution.

The most important factor affecting spectral resolution is the spectrometer focal length. As shown in Figure 1, a longer focal length spectrometer provides a greater dispersion and hence, higher spectral resolution.
The tradeoff comes in as lower spectral coverage on the CCD chip, but this can be overcome by implementing a movable grating to scan across all wavelength ranges and still maintain high spectral resolution. The typical focal lengths of Raman spectrometers can vary from about 200 mm to 800 mm and even higher. It is important to note, however, that a higher spectral resolution instrument (longer focal length) can also be used as a lower spectral resolution instrument, depending on the choice of grating. In this sense, a higher spectral resolution instrument can be used for both routine analyses requiring low spectral resolution, and for more advanced applications where higher spectral resolution is necessary.

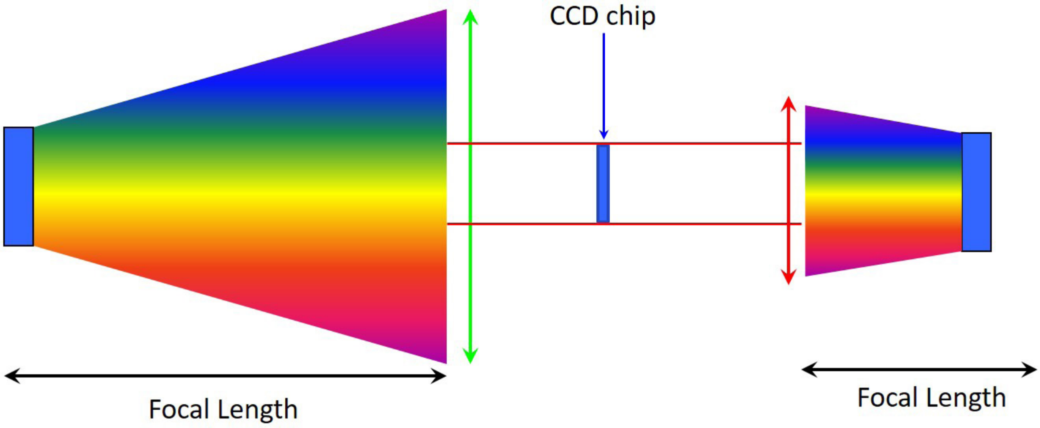
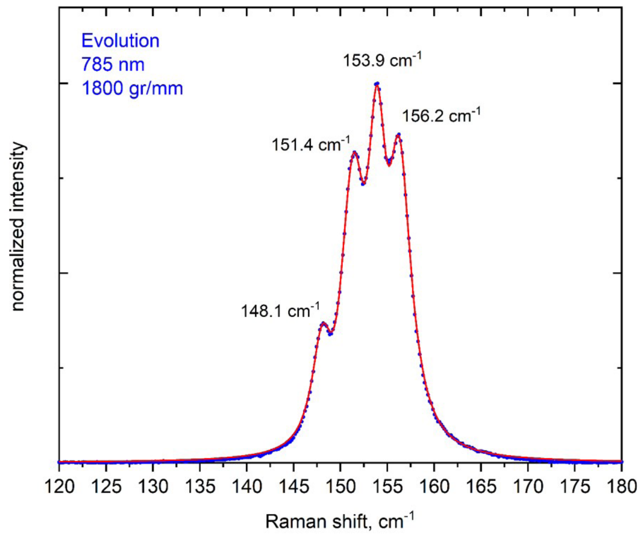


Figure 1: An illustration of dispersion, and hence spectral resolution and spectral coverage, between a short and a long focal length spectrometer.



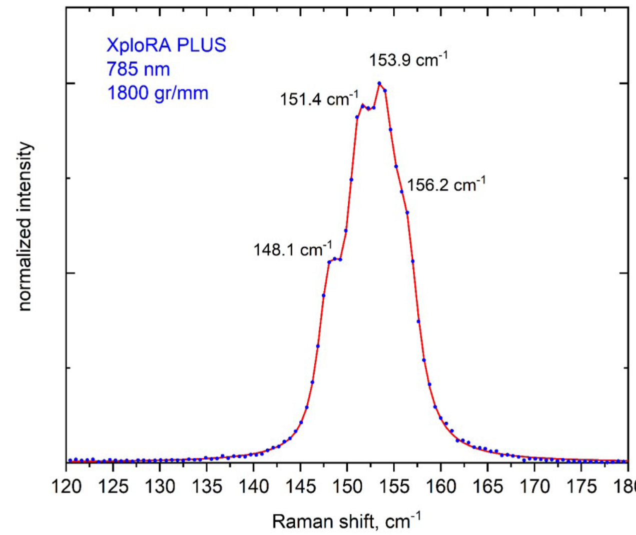


FIgure 2: A select section of the Raman spectrum of sulfur acquired with the HORIBA LabRAM HR Evolution with focal length 800 mm (Left) and the HORIBA XploRA PLUS with focal length 200 mm (Right).

As an example of the importance of focal length, shown in Figure 2 is a comparison of a select section of the Raman spectrum of sulfur (S). On the left, data were acquired with the HORIBA LabRAM HR Evolution (focal length 800 mm) and on the right, data were acquired with the HORIBA XploRA PLUS (focal length 200 mm).

Both data sets were acquired with all other measurement parameters identical, so that the only difference is the focal length. As one can see, the difference in spectral resolution is obvious and the longer focal length helps to resolve peaks that are not easily separated when measuring with a shorter focal length. The HORIBA LabRAM HR Evolution provides the longest focal length and hence the best spectral resolution in its class.

The second most important factor affecting spectral resolution is the diffraction grating. As shown in Figure 3, for a fixed focal length, a higher groove density grating produces a wider dispersion angle, resulting in a higher spectral resolution.

The tradeoff again comes in as lower spectral coverage, but once again, this can be overcome by implementing a movable grating to scan across all wavelength ranges. Typical gratings used in Raman spectrometers vary from about 300 gr/mm (low resolution) up to 1800 gr/mm (high resolution); more specialized gratings, such as 2400 gr/mm and 3600 gr/mm can also be used, but they have certain physical and practical limitations (to be discussed, following).

As an example of the importance of the groove density of the grating, Figure 4 shows a comparison of a select section of the Raman spectrum of sulfur acquired with the HORIBA XploRA PLUS.

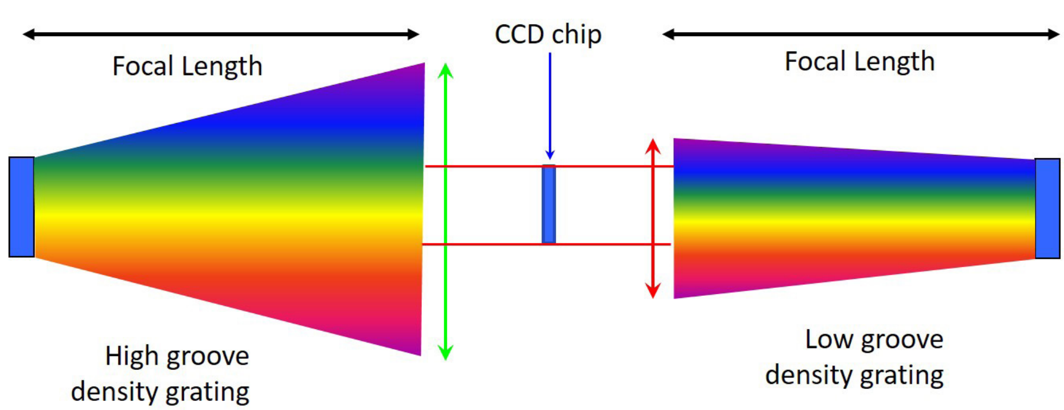


Figure 3: An illustration of dispersion, and hence spectral resolution and spectral coverage, between a high groove density grating and a low groove density grating (spectrometer focal length fixed).

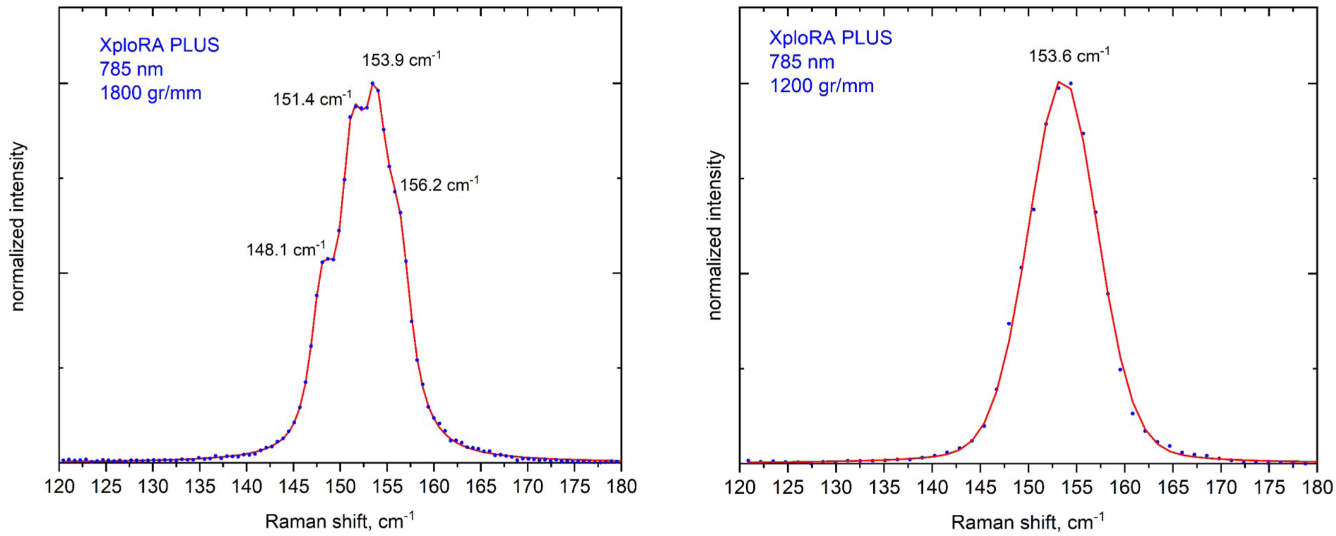


Figure 4: A select section of the Raman spectrum of sulfur acquired with the HORIBA XploRA PLUS and an 1800 gr/mm grating (Left) and a select section of the Raman spectrum of sulfur acquired with the HORIBA XploRA PLUS and an 1200 gr/mm grating (Right).

The data on the left were acquired with an 1800 gr/mm grating and the data on the right were acquired with a 1200 gr/mm grating. All other measurement parameters were identical, so that the only difference is the grating. As one can see, the difference in spectral resolution is once again obvious and important. When using the smaller groove density grating (1200 gr/mm), only one peak at 153.6 cm^{-1} is present. However, when switching to the higher groove density grating (1800 gr/mm), one can see that there are actually four peaks present, which are now properly resolved due to the higher spectral resolution. The HORIBA XploRA PLUS includes four automatically switchable and movable gratings (600 gr/mm, 1200 gr/mm, 1800 gr/mm, and 2400 gr/mm), which allow the user to easily choose the grating to optimize the spectral resolution required for their specific application needs.

Focal length and the groove density of the grating can be used together to provide the best spectral resolution, but there are some limitations. In the best-case scenario, a long focal length spectrometer combined with a medium groove density grating (e.g. 1800 gr/mm) provides the best spectral resolution without any limitations. In some cases, a higher groove density grating (greater than 2400 gr/mm) may be able to compensate for a shorter focal length to provide enhanced spectral resolution, but this is not generally recommended for several reasons. The first main reason is that not all gratings will work for all laser wavelengths, so compensating with a higher groove density grating will not work for all applications. The second main reason is that a higher groove density grating provides a lower overall efficiency and hence a lower intensity signal, resulting in a reduced signal to noise ratio. This may then lead to a longer acquisition time. The third main reason has to do with the fact that a higher groove density grating has low spectral coverage, as was shown in Figure 3. This means that one must move the grating multiple times in order to cover a wide spectral range. This increases the acquisition time significantly and could cause stitching issues, as each part of the spectrum must be stitched together to get the complete spectrum. There are also other issues, but these three are the most important.

Other important factors that can affect spectral resolution include detector size (smaller pixel size corresponds to a higher spectral resolution), laser wavelength (increasing laser wavelength from UV to visible to IR will provide better spectral resolution) and slit size (a smaller slit size provides better spectral resolution). These three factors, along with focal length and grating, can be used in many various combinations to determine the highest spectral resolution that can be obtained with a particular Raman instrument. Of course, as mentioned above, there are some limitations to all these factors that limit the highest possible spectral resolution attainable in theory.

References:

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