Spectral Resolution : a key parameter for Raman analysis

A lot of information is contained in a Raman spectrum and in many cases spectral resolution is a key parameter in extracting the relevant information. The better the spectral resolution, the easier it is to identify close chemical compounds, to distinguish between similar molecular structures and to measure stress/temperature effects on materials accurately.

1. Spectral resolution

The spectral resolution (R) of a spectrograph is defined as its ability to resolve features in the spectrum. It is defined by $R = \lambda/\Delta\lambda$, where $\Delta\lambda$ is the smallest difference in wavelengths that can be distinguished, at a wavelength of λ. In the Raman spectrum, the information of interest may be provided by **small peak shifts**, **separation of close bands, slight variation of band width**. The potential loss of information that can result from low spectral resolution performance is rather significant as schematically illustrated in Figure 1.
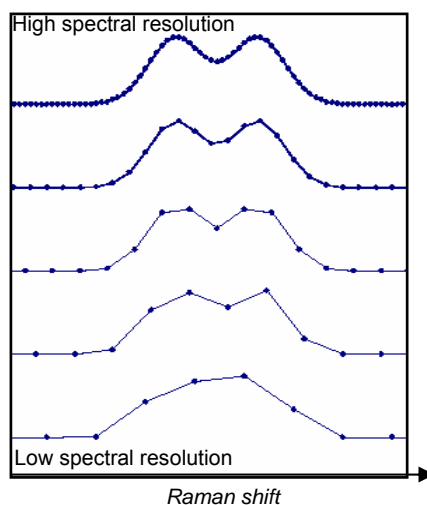

Figure 1 : Effect of the resolution on the definition of Raman features.

The parameters of a modern dispersive Raman spectrometer that can effect the spectral resolution will be reviewed and some examples will illustrate the discussion.   In this note, we focus the discussion on a single monochromator instrument.   Among the dispersive Raman spectrometers, the single monochromator is the most common configuration as it provides high throughput and a compact volume for lab instrumentation. A schematic of a single monochromator based on a *Czerny Turner* design is shown in Figure 2. The entrance slit width, the groove density of the diffraction grating (N), the focal length (F) and the geometry of the detector all together define the final spectral resolution achievable within the Raman spectrum.
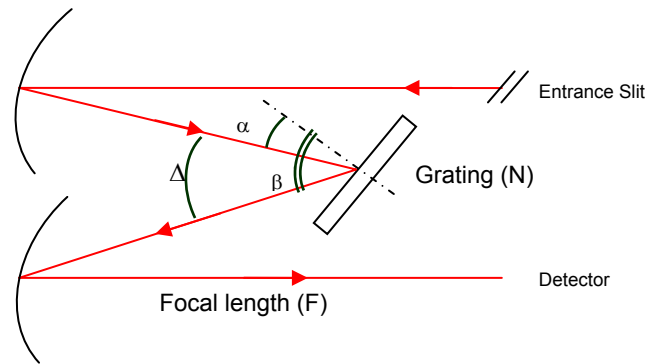
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Figure 2 : Schematic of a Czerny-Turner set-up showing the optical components determining the spectral resolution.

2. Groove density and focal length : two key features defining the DISPERSION

The dispersion (D) of the spectrometer is a property which is commonly used to describe its ability to disperse the light. It is an intermediate step to fully understand the resolution. For any order of diffraction (k), the dispersion (D) is linked to the cosine of the diffracted angle (β) as expressed in the following equation: **D=dλ/dx= cosβ/kNF**

2a. Effect of the Diffraction Grating on the Dispersion

A diffraction grating is made of fine parallel and equally spaced grooves on the surface material. This optical component disperses the light such that a higher groove density (N in grooves/mm) provides a larger dispersion. The improvement of the dispersion is linear with the increase of the groove density (ex : a 1800gr/mm grating provides a dispersion 3 times better than a 600gr/mm). However, we will see that the groove density cannot be indefinitely increased as explained in §2d.

As illustrated in figure 3a, a 600gr/mm grating provides an image of a spectral range 2 times wider than a 1200gr/mm grating on the chip of the CCD but with a resolution twice a lower. To collect with a 1200gr/mm grating a spectral range as wide as the one of a 600gr/mm grating, it is necessary to record 2 shots with different α angle of the grating.
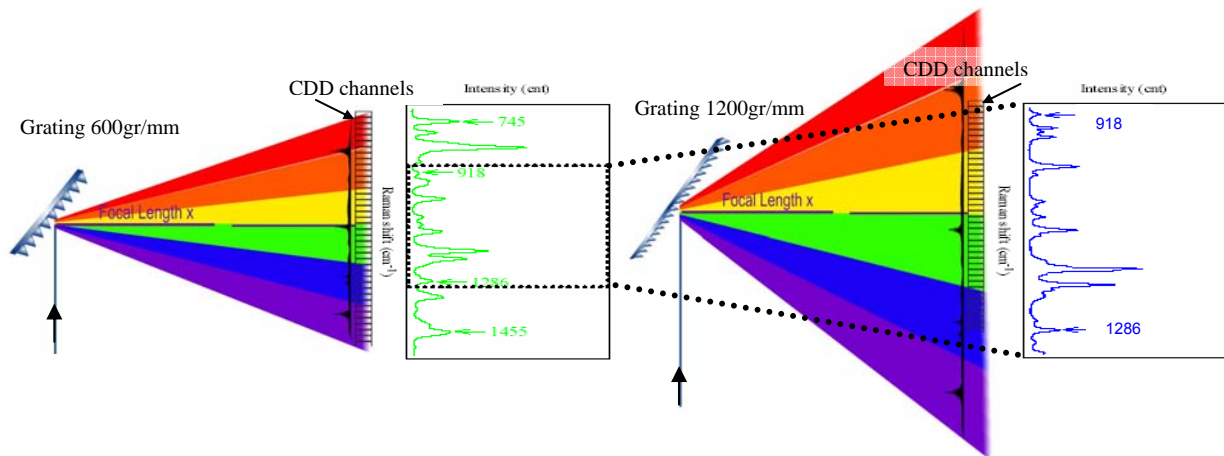

Figure 3a : Schematic to illustrate the dispersive effect of 2 gratings with different groove densities. In each case, the spectral range collected on the CCD chip is displayed.

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Figure 3b shows how a higher groove density grating offers a higher dispersion and thus a higher spectral resolution. A higher dispersion sharpens the bands closer to their natural width. It reveals the presence and the shape of two or several close peaks. In figure 3b, a 600gr/mm grating provides a coarse spectrum of ibuprofen whereas a 1800gr/mm grating gives a refined spectrum displaying many details. These details are necessary, for example, to identify the structure of a crystal (polymorphy).
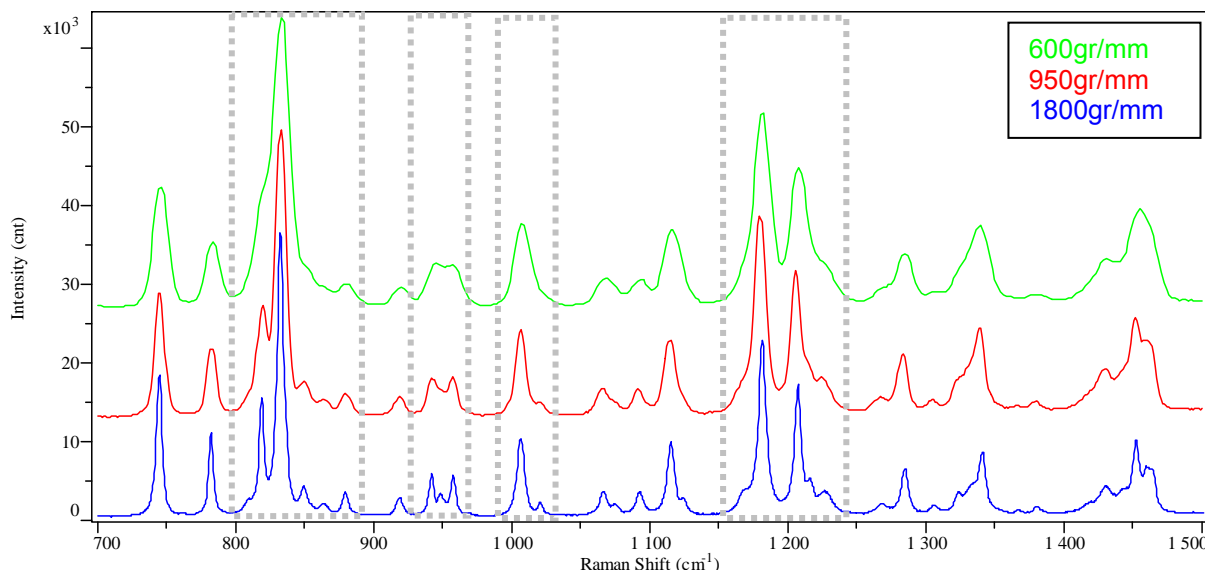

Figure 3b : Raman spectra of Ibuprofene showing the improvement in spectral resolution with increasing grating groove density (N= 600,950,1800 grooves/mm). Data measured on the LabRAM ARAMIS which offers a selection of up to 4 interchangeable gratings.

To conclude, the choice of the grating is a parameter that the user must optimize by considering spectral resolution requirements and speed of measurement.

2b. Effect of the focal length on the dispersion

The focal length "F" also effects the dispersion such that the longer the focal length, the higher the dispersion. This is schematically illustrated in figure 4b and a comparison of two spectra recorded in the same conditions with LabRAM $(F_1=300mm)$ and LabRAM HR $(F_2=800mm)$ is shown in figure 4a.

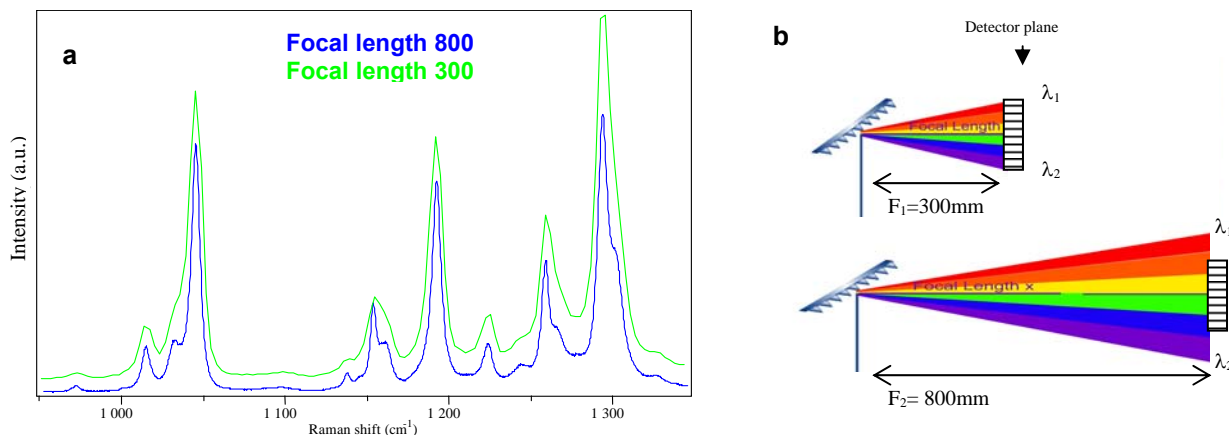*Figure 4 : Effect of the focal length 300/800mm- (a) comparison of an excerpt of the Raman spectrum of aspirin recorded with a LabRAM $(F_1=300mm)$ and LabRAM HR $(F_2=800mm)$ in strictly the same configuration. (b) Illustration of the changes in dispersion due to different focal length.*

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The focal length is fixed and not interchangeable in a spectrometer (unlike the grating). All components being the same, the focal length eventually makes the difference to improve the dispersion and resolution. Having a long focal length is an asset to observe fine details in the spectrum. If high dispersion is not needed it is always possible to lower the dispersion by using a low groove density grating whereas the contrary is not true as explained in the following section.

2c. Balancing the focal length and the groove density for an optimal spectral resolution

To a certain extent, the groove density and the focal length can compensate each other. However there is a limitation in using a high groove density (N) grating to compensate a short focal length. Indeed there is a maximum wavelength (λ_{max}) that can be reached with a grating and this value can be calculated from the *fundamental grating law*:

$$\lambda = (\sin\alpha + \sin\beta)/(10^{-6}kN) \quad (\lambda \text{ in nm, N in gr/mm})$$

In +1 order, k=1 and the maximal wavelength (λ_{max}) is collected for $\alpha = \pi/2 - \Delta$ and $\beta = \pi/2$ where deviation angle Δ is measured from incidence to diffracted beam. In these conditions, $\sin\beta = 1$ and $\sin\alpha < 1$ so $\lambda_{max} < \mathbf{2.10^6/N}$.

For example the theoritical maximum wavelength (λ_{max}) reached with a 1800gr/mm is 1111 nm and with a 3600gr/mm grating this maximum wavelength falls to 555 nm meaning that no Raman spectrum could be recorded with a green laser (lasing at 532nm).

However, in these theoretical considerations we do not examine the limitations due to the non-optimal coverage of the grating when it is at the λ_{max} geometry. In the following schematic we compare a long focal length (F=800mm) and a short focal length (F=300mm) spectrometer. For a similar dispersion at a given wavelength, the long focal length is equipped with a 1200gr/mm grating working at a low α angle (Figure 5a) whereas the short focal length requires a 3600gr/mm grating working at a larger α angle (Figure 5b). In the latter case the grating collects only partially the light coming from the entrance slit resulting in significant signal losses.
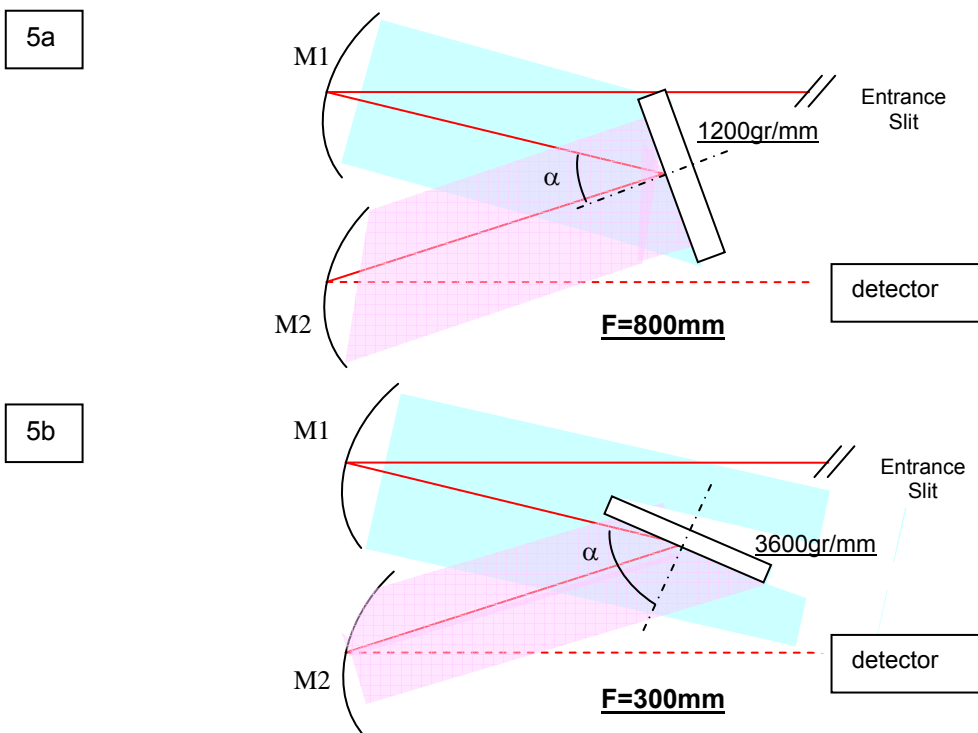

Figure 5: Comparison of the configuration of a long focal length (F=800mm) and a short focal length (F=300mm) equipped respectively with a 1200gr/mm grating and a 3600gr/mm grating to provide the same dispersion at a given wavelength λ. The blue beam corresponds to the incoming light and the pink beam represents the dispersed λ light which reaches the detector.

With the LabRAM HR configuration, we can combine the long focal length (F=800mm) with a medium groove density to provide a high spectral resolution in the whole Raman range from UltraViolet (200nm) to Near InfraRed (1064nm) without inducing any signal losses. The design of the LabRAM HR also keeps the configuration of the spectrometer close to its optimal throughput.

2.d. How to express the Dispersion

The optical setup (grating + focal length) results in a linear spread of λ at the focal plane of the spectrometer where the detector is positioned. Hence, the Dispersion, D, is expressed as a number of nm per mm. One can also define a Bandpass in nm per pixel, knowing the dimension of a pixel of the detector.
Ex : D= 1nm/mm if 1 pixel is 26µm then BP=0,026nm/pixel
For the Raman spectroscopist, the Dispersion can also be translated in Raman shift (cm^{-1}) per pixel. The Raman shift ($\Delta\nu$) is expressed as $\Delta\nu_{peak}=1/\lambda_{excitation}-1/\lambda_{peak}$. A result of using this unit is that the dispersion is improved when increasing the excitation wavelength. (see Figure 6). If the dispersion is expressed in cm^{-1}/pixel then the wavelength at which it has been calculated must be specified.

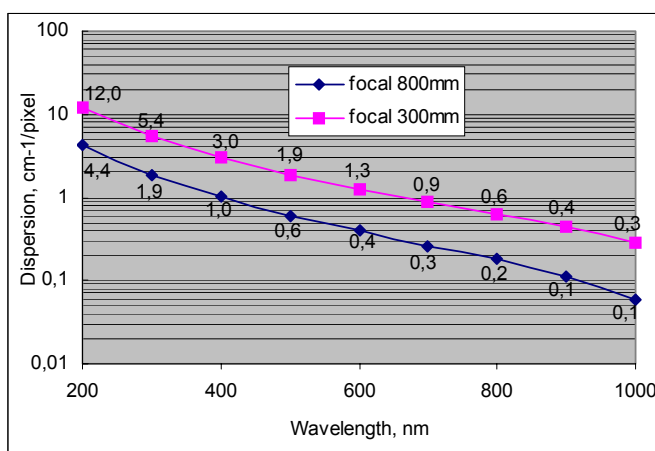Figure 6 : Dispersion in cm^{-1}/pixel as a function of the wavelength and the focal length. Values are given considering a LabRAM HR (F=800mm) and a LabRAM (F=300), grating 1800gr/mm, pixel size 26µm.

3. The entrance slit : the link between dispersion and resolution

The physical width of the entrance slit is imaged on the detector located at the focal plane of the spectrograph. The width of the imaged slit, Ws, gives the resolution, R, of the image on the detector. To convert this information in wavenumber :

$$R\ (cm^{-1}) = D(cm^{-1}/mm) \times Ws\ (mm)$$

The effect of the slit width on the resolution is illustrated in figure 7. Note that Ws cannot be infinitely decreased as the signal collection must also be optimised considering other coupling parameters.
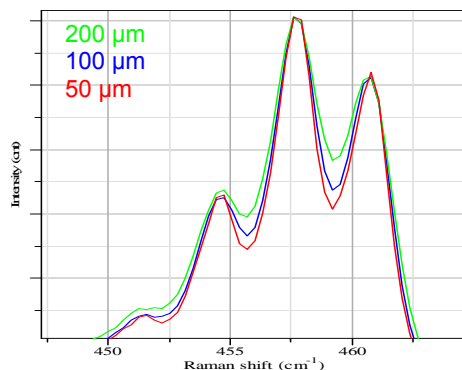

Figure 7 : Effect of the slit width Ws on the spectral resolution of the CCl_4 modes.

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4. Application examples

4a. Stress in a Silicon cap-layer structure

Devices in the electronic industry are using stressed Silicon exhibiting enhanced properties (in comparison to relaxed Si). To produce this strained silicon, a thin crystalline layer of Si is grown on a Si_xGe_{1-x} substrate. It is possible to use Raman spectroscopy with a green laser source (532nm) to probe at the same time the stress in the Si_xGe_{1-x} and Si layers. The parameter to monitor the stress is the position of the Si-Si vibrational mode in Si_xGe_{1-x} and Si located at 511cm^{-1} and 518cm^{-1} respectively. Such a measurement requires high spectral resolution as the peaks exhibit very subtle shifts.

A characteristic spectrum of such a sample is displayed in figure 8a. As we can see a 1800gr/mm grating (higher dispersion) surpasses a 600gr/mm grating (lower dispersion) to distinguish the 2 Si-Si vibrational modes. The definition of the Si-Si cap-layer mode at 518cm^{-1} is especially improved.

The maps in figure 8b clearly demonstrate that the resolution offered by a 1800gr/mm grating is necessary to properly monitor the very small frequency shift of this cap-layer Si-Si mode in order to properly characterise the strain structure.
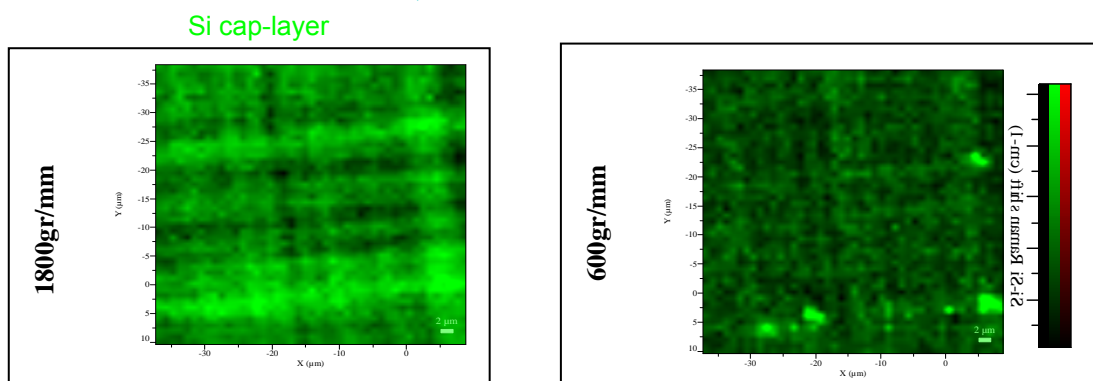
8a.

8b.

Si cap-layer
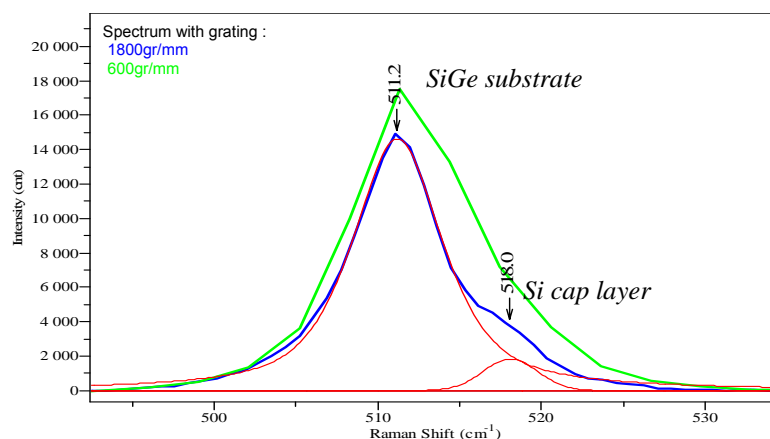
Figure 8: 8a: Spectra recorded with grating 600gr/mm and 1800gr/mm showing the 2 peaks of interest and their better resolution with 1800gr/mm. In red are plotted the fitting curve used to provide the peak shift images
8b: Peak shift images over a 40x40µm area of a Si cap-layer on SiGe wafer containing a crosshatch pattern. The same area is mapped on a LabRAM HR with a 1800gr/mm grating and with a 600gr/mm grating. The position of the Si-Si peak in the cap-layer is displayed, highlighing the increased definition of the image obtained with a higher resolution (1800gr/mm).

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4b. Highlight of a weak band to characterise natural diamonds

A flexible Raman spectrometer allows the measurement of both the Raman diffusion and the Photoluminescence of diamond samples. The photoluminescence spectrum provides critical information about quality of the diamonds (see Application Note ref: Carbon 04). In the example displayed in figure 9, the spectral resolution given by a LabRAM HR equipped with a 2400gr/mm grating brings sufficient resolution to observe a weak but important band at 575.7nm (dotted square).
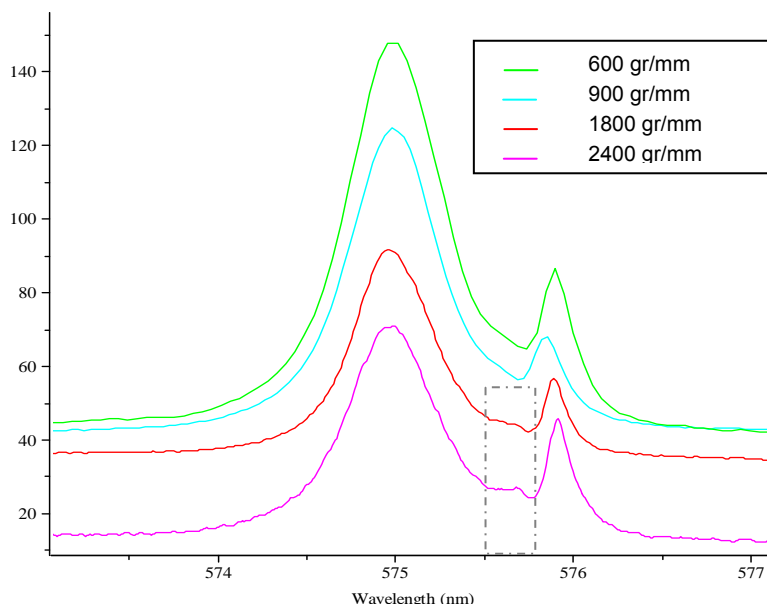

Figure 9: Spectra recorded with a 514.5nm laser excitation at a temperature of -190°C. 4 spectra are recorded on the same point using gratings from lower (600gr.mm) to higher (2400gr/mm) spectral resolution on a LabRAM HR (800mm focal length).

Conclusion

In many application fields, the spectral resolution can make a difference by enhancing subtle variations, thereby improving the contrast in a single spectrum or in an image. With a low resolution system, the spectroscopist misses, in many cases, very valuable information required to get the full picture about its samples' properties.

The influence of the main parameters (focal length, dispersion grating, slit width) is significant and determines the ability of a given instrument to extract the relevant information.

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