

Abstract

We investigated the requirements for spectral performance of a Raman instrument in routine laboratory and industrial use. An innovative spectrograph design delivers 4 cm⁻¹ resolution and 50–3500 cm⁻¹ spectral range in a single exposure with a fixed grating. Since 98% of Raman spectra are fully resolved at 4 cm⁻¹, the new design translates into a high-performance, routine use, analytical tool. The design avoids pitfalls in Czerny-Turner and echelle designs and permits interchangeable gratings (and excitation laser wavelengths).

Introduction

Development of a routine use Raman spectrometer afforded the opportunity to design a new spectrograph tailored specifically for Raman spectroscopy. Design requirements included spectroscopic performance, ease of use, and manufacturability.

Analysis of spectra culled from our commercial Raman spectral library suggest that many compounds have Raman spectra with peak widths of 4 cm⁻¹, but narrower peaks are rare. At the very least, the spectrograph for a routine use instrument should provide 4 cm⁻¹ resolution over a spectral range that covers both “fingerprint” and C-H stretching mode bands. This is a Raman shift range of roughly 50 to 3500 cm⁻¹. However, a robust instrument should provide this level of spectral performance in a single exposure, without moving the diffraction grating. An additional requirement for a routine-use instrument is the ease of exchanging gratings for use with multiple laser wavelengths.

Historically, Raman spectrometers were built around CCD detector arrays with roughly 1024 pixels along the wavelength axis, corresponding to a resolution of no better than 1/512 of the spectral range. A 1k-pixel detector is also good match for the optical performance that can be achieved with a practical Czerny-Turner spectrograph.

Ironically, “routine use” translates into a requirement for better resolution performance. Covering 3500 cm⁻¹ at 4 cm⁻¹ resolution is a resolution of a part in 875 of the spectral range. The spectrograph will need an array detector with at least 1750 pixels. But simply installing a high resolution detector in an existing spectrograph is not sufficient. To make effective use of available 2k-pixel detectors, a new spectrograph design is needed.

We developed a new spectrograph specifically for Raman applications, with a novel optical design that provides optical performance sufficient for obtaining near-theoretical resolution performance from a 2k-pixel detector, while allowing for operation with multiple gratings.

Historically, spectrograph performance for Raman instruments has been based on measured peak widths for an emission source such as neon. The overall instrument resolution involves additional factors such as the bandwidth of the laser, and should be quoted at somewhat greater than 4 cm⁻¹ for full range collection.

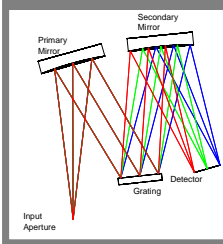
Overview of Design

Precursor: Czerny-Turner Spectrograph

The design overview begins with an analysis of the Czerny-Turner spectrograph, which is the mainstay of Raman spectroscopy. As shown in Figure 1, C-T spectrograph has a single concave primary mirror, and a single concave secondary mirror. Since they are off-axis elements, the dominant aberration contributed by each element is off-axis coma. The off-axis effects of the primary and secondary are allowed to approximately cancel one another, by optimizing the tilt angle of the secondary.

However, the optimal tilt angle of the secondary depends on both the tilt angle of the primary, and the tilt of the grating. This is because the grating introduces wavelength dependent anamorphic magnification. This effect is simply due to the difference in width of the incident and diffracted beams at any given wavelength.

FIGURE 1. Optical diagram of a typical Czerny-Turner spectrograph



Precursor: Czerny-Turner Spectrograph, cont.

Commercial C-T spectrographs incorporate advanced optical components such as toroids. These elements control the astigmatism of the spectrograph, and to some extent on-axis aberrations, but the dominant aberration remains the off-axis coma, which can only be controlled through optimization of tilt angles. In addition, the extent to which coma can be reduced through optimization of conventional optical surfaces limits the resolution that can be achieved.

Towards a New Design

Our new spectrograph design is based on the observation that the primary and secondary systems should each be independently optimized, in order to eliminate the effect of anamorphic magnification by the grating. Potentially, the primary and secondary systems involve separate design processes.

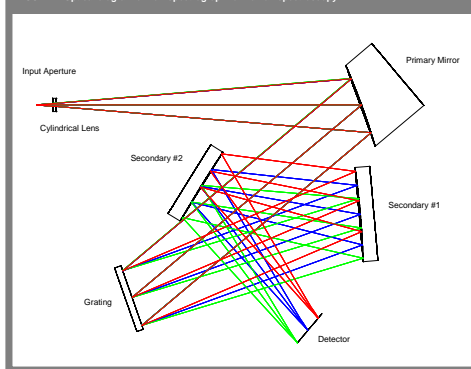
The primary system collimates what is nearly a point source, thus a parabolic primary is aberration free. In contrast, a parabola would not be an obvious choice in a Czerny-Turner design, because of the need to provide off-axis aberration to balance the aberration of the secondary.

While a parabolic mirror is preferred for the primary, it is a poor choice in the secondary system, because it is only corrected for aberrations from a single field point. The secondary system is a more complicated design problem, which must be corrected across a wide field. A single mirror cannot do this. A reflective doublet, i.e., consisting of two secondary mirrors, has a chance of correcting the system.

The “Triplet” Spectrograph Design

Combining a parabolic primary with a two-mirror secondary completes the spectrograph design. Figure 2 shows the layout.

FIGURE 2. Optical diagram of new spectrograph for Raman spectroscopy



The “Triplet” Spectrograph Design, cont.

Combining a parabolic primary with a two-mirror secondary completes the spectrograph design. Figure 2 shows the layout. Crossing the beams affords a compact geometry, and provides space for the cooled detector housing, as well as for the grating mount.

It should be noted that unlike the Czerny-Turner case, the incident beam on the grating is essentially aberration free, as is the diffracted beam, thus the grating does not modify the distribution of aberrations, as it does in the Czerny-Turner.

The input beam is collimated by a primary mirror, which is an off-axis parabola. A pair of spherical mirrors focuses the diffracted rays from the grating to a tilted plane. In reality, the tilted “plane” is a chord of a curved focal plane, but the overall radius of curvature is large.

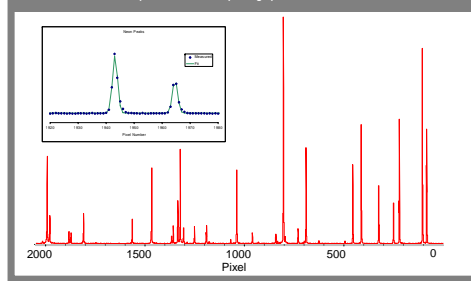
A compound secondary system offers benefits unavailable to the Czerny-Turner design: The two mirrors can be of different focal length, and their spacing can be varied, thus affording two additional degrees of freedom for optimization. As a result, optimization of the compound secondary results in a spread function that is superior to a Czerny-Turner. The result is the improvement in optical performance needed to make meaningful use of a 2k-pixel detector.

Like all off-axis designs, the triplet spectrograph is astigmatic. A cylindrical lens is added in the primary system for partial correction of this aberration. From a practical standpoint, the cylindrical lens eliminates the need for one or both of the secondary mirrors to be toroidal. This in turn allows the use of inexpensive spherical mirrors of high surface accuracy, without the need for tedious rotational adjustment.

Results

Figure 3 shows a neon emission spectrum from the DXR spectrograph with a 2k-pixel detector. The inset shows two peaks, with a Gaussian fitting curve, to demonstrate that spectral resolution approaches 2 pixels FWHM.

FIGURE 3. Neon emission spectrum from DXR spectrograph



Results, cont.

Spectral quality from the triplet spectrograph can be studied in two additional ways. Figure 3 shows the FWHM of neon peaks as a function of their center channel number on the detector, with two gratings that differ in incident angle by 12 degrees. The figure shows two benefits of the triplet design. First, resolution is very nearly constant across the field. Second, it is independent of grating angle, thus allowing a single spectrograph to deliver high Raman performance with multiple laser wavelengths.

FIGURE 3. FWHM of neon peaks vs. peak center channel number, with two diffraction gratings

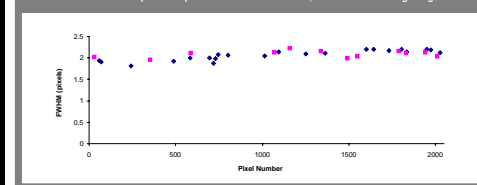
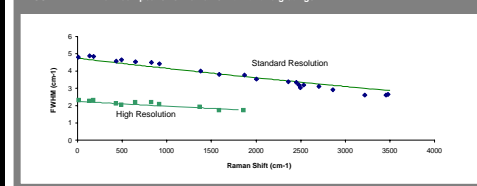


Figure 4 shows the same data, translated into Raman shift units in the horizontal axis for two gratings that cover the full spectral range, and the “fingerprint” range with a 633 nm laser. Again, this graph illustrates the predictable resolution performance of the spectrograph, while illustrating that resolution is a roughly linear function of Raman shift when displayed in wavenumber units.

FIGURE 4. FWHM of neon peaks vs. Raman shift with two gratings



Conclusions

A new spectrograph design meets the needs of a routine-use Raman instrument. Though it may seem ironic at first glance, the requirements for “routine use” translate into the need for higher spectral performance in order to eliminate inconvenient aspects of mainstream lab Raman instruments, including the need for a rotating grating mount.