High Resolution Raman Spectroscopy Using an Echelle Spectrograph

Introduction

The measurement of Raman spectra is straightforward in concept: a laser beam is directed at the sample of interest, the scattered light is collected, the polychromatic beam of light is dispersed, and the intensities at individual frequencies are measured. The optical components required can be summarized into four parts: a laser, a sampling device, a spectrograph, and a detector. For all intensive purposes, the same type of laser and detector are common in modern commercial Raman instrumentation. Although gas lasers in the visible region are still widely used, they are rapidly being replaced by solid-state laser technology. These latter lasers are available at several wavelengths in the visible and near-IR regions and offer stable ouput with minimum external requirements. Current instrumentation almost exclusively employ a CCD as the detection device. These offer extremely high quantum efficiency and are available in various chip sizes to accommodate different spectrograph designs.

The heart of a Raman system, and where there remains a variety of differences in commercial instrumentation, is the dispersive spectrograph. The simplest type of dispersion is accomplished by using a grating. In this manner, light is spread out in one dimension and then directed at the CCD chip. The compromise of this technique rests between spectral range and resolution. For example, a 3500 cm^{-1} range spread over a one inch CCD chip with 1024 elements can only provide 7 cm^{-1} spectral resolution (i.e.

3.5 cm^{-1} per pixel). Alternatively, the light can be dispersed even greater to increase resolution with the trade-off of losing spectral range. Greater spectral range can be achieved by moving the grating to two or more positions and splicing the CCD images together. While a moving grating is a reasonable solution, any dispersive spectrometer with moving parts is subject to calibration shifts as well as being less feasible for applications requiring portability.

The Echelle Spectrograph

An echelle spectrograph is a unique solution to combining wide spectral range coverage at high resolution. In essence, light is dispersed in two dimensions to make

use of a larger area of the CCD chip. An echelle spectrograph incorporates a prism (or prisms) and a grating arranged to disperse light in directions orthogonal to each other. With this configuration, light is dispersed into "orders" or "tracks" by the grating which each contain a small spectral region dispersed in roughly a perpendicular direction. The multiple diffracted orders are spatially overlapping, and careful analysis is required to reassemble the data into a single spectrum. As an end result, the echelle spectrograph provides high resolution and wide spectral range coverage in a single CCD chip exposure, negating the need for moving optics.

The optical arrangement inside InPhotonics' echelle spectrograph. The prism(s) and grating disperse the light in orthogonal directions.
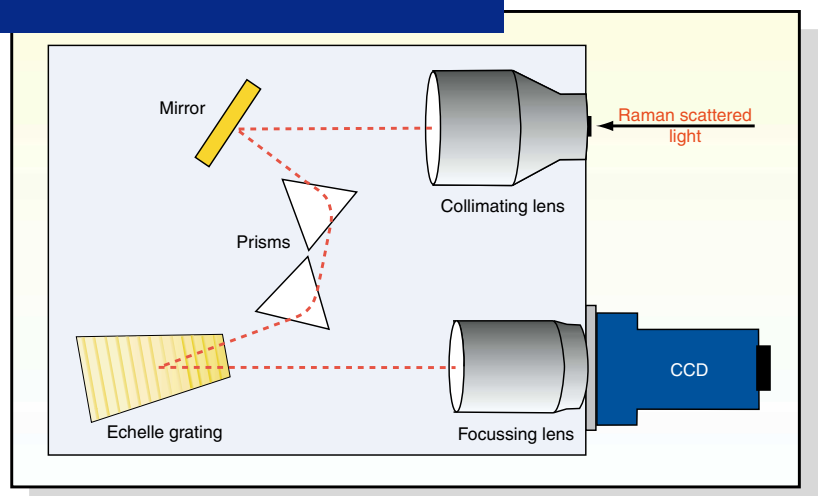
Resolution and Linewidths

Raman spectroscopy can be used to identify and quantitate chemical species. In order to analyze mixtures of compounds, it is critical that the bands of each substance be observed as clearly as possible. This is particularly true if a compound of low concentration is found mixed with a similar species at much higher concentration. The clearest Raman spectrum is one which ensures that observed linewidths are not broadened by the spectrometer; i.e. the spectral resolution of the instrument should be better than the natural linewidths of the measured species.

The natural linewidths of Raman bands vary according to the degree of interaction between neighboring molecules. Vibrational bands are broadened as molecular interaction increases. Phases that have more ordered structures also give rise to narrower vibrational bands. Amongst condensed phases, crystalline solids have fairly narrow lines, typically 1 - 4 cm^{-1} due to their ordered structure. Amorphous solids such as polymers have broader Raman bands, typically 4 - 8 cm^{-1} wide. Liquids also tend to have broader lines (4 -8 cm^{-1}) especially if hydrogen bonding occurs. For example, the OH stretching band in an alcohol has a linewidth >> 16 cm^{-1}. Spectra measured at low temperature show increasingly narrower linewidths due to the decreased kinetic energy in each vibrating molecule.

The figure at right shows a Raman spectrum of an aqueous mixture measured with an echelle spectrograph. This system can provide 1 cm^{-1} resolution (< 0.5 cm^{-1} per pixel) without the use of entrance and exit slits that limit throughput.* The upper curve of the figure shows the same substance measured at lower resolution (roughly 4 cm^{-1} and 8 cm^{-1} resolution). Clearly,

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*With the standard fiber optic input, the spectral resolution (shown in the figure) measured as FWHH is roughly 4 cm^{-1}.
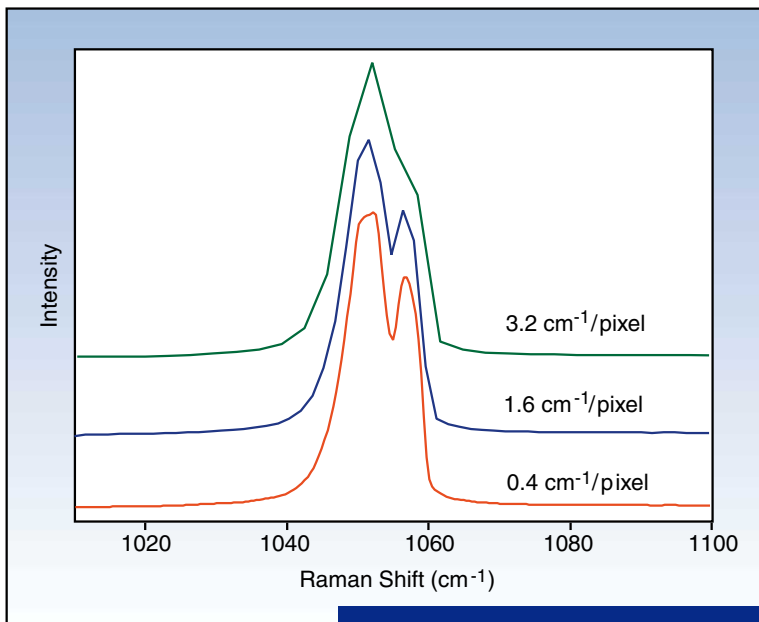
Raman spectra of two dissolved nitrate salts at different spectral resolution.

the high-resolution echelle spectrum is able to discriminate the two species much better, facilitating identification and quantitation.

Permanent Calibration

Due to the stationary optics in an echelle spectrograph, the system has the added benefit of permanent calibration. Calibration in the frequency domain is important particularly for quantitative analysis. Spectroscopic calibration curves are performed on band intensities, and it is critical that band positions remain fixed at the same frequency for every measurement. Any spectrometer design with a moving optic is subject to calibration errors. Although modern spectrographs can usually be recalibrated, this is undesirable, or even impossible, in many industrial applications.

Conclusion

The InPhotonics echelle spectrometer provides high resolution, full spectral range, high throughput, and permanent calibration. In short, it is the ideal Raman system for industrial applications that require high discrimination between chemical species while maintaining rugged instrument design.

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