Blink and you miss it - Catching fleeting catalytic intermediates by high speed 785 nm NIR Raman spectroscopy

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The “inelastic scattering of light”, or Raman effect, was observed in practice for the first time in 1928 by C.V. Raman for which he was awarded the Nobel Prize in 1930. It is only in the last two decades, however, that Raman spectroscopy has begun to realize its potential as an almost universally applicable analytical technique from materials and life sciences applications to point of care analysis. This is primarily thanks to the availability of compact laser sources, high sensitivity cameras and high resolution compact spectrometers.

Catching transient species during catalyst activation

The weakness of detectors in the NIR region (800-1050 nm) with quantum efficiency dropping off over this range from ca. 40% to 0% is a key drawback of 785 nm Raman spectroscopy. Typically long exposure times and spectral averaging are required to achieve a good signal to noise level, however this approach seriously reduces the time resolution achieved (to mins) and means that weak signals for compounds that are present for only a few 100s of milliseconds cannot be observed. Using more efficient NIR detectors (e.g. back thinned CCDs) does not usually solve this problem due to etaloning that can be difficult to suppress. This drawback can be circumvented by a combination of efficient collection optical arrangements and above all high laser light fluxes. With a stable high powered laser (500 mW at sample) and a large confocal volume for collection to limit sample damage, time resolutions as low as 100 ms per spectrum can easily be achieved.

As an example, an oxidation reaction in which H$_2$O$_2$ is added to a solution containing a precatalyst is chosen. In this reaction only 0.25 mM precatalyst is present (far below that which can be detected by Raman spectroscopy but its absorption at 785 nm means that its spectrum is resonantly enhanced) and H$_2$O$_2$ is added to give a final concentration of 250 mM which decreases slowly over time.

Within 1 s of addition of H$_2$O$_2$, however, the precatalyst becomes activated with an intermediate that is present only with a maximum concentration of 0.05 mM for 0.5 s and has an absorption band near 785 nm which results in enhancement of its Raman spectrum by ca. 10 000 times through resonance. However, it is observed only because high signal to noise spectra can be recorded at 200 ms intervals.

Lasers for Raman spectroscopy

By far the most popular wavelength used for Raman spectroscopy is 785 nm, as it offers the best balance between avoiding fluorescence, absorption of the laser light (and Raman scattering) by the sample and therefore heating effects, and the limits to detector sensitivity. However, the choice of wavelength depends heavily on the specific application. In general, shorter wavelengths mean fluorescence is encountered more often but the intensity of Raman scattering increases quadratically (intensity shows a $1/\lambda^4$ dependence), and longer wavelengths means less fluorescence but a weaker signal. Furthermore, 785 nm lies at the edge of the detectors sensitivity (Silicon) before more expensive detectors need to be considered (InGaAs based with excitation at 1064 nm for example), which together with light absorption in the NIR by water itself, reduces somewhat the advantage of using yet longer excitation wavelengths. Hence selecting the correct laser excitation wavelength is critical to increase the chance of collecting a usable Raman spectrum.

The lasers available at 785 nm are diode lasers, however, a narrow line width (<3 cm$^{-1}$ for condensed phases such as solids and solutions and even narrower for gases) is essential for Raman spectroscopy in order to resolve individual Raman bands.
This narrowness is achieved in a 785 nm diode laser by using extra components, such as a volume Bragg grating (VBG). Linewidths of <40 pm (<0.65 cm⁻¹) can be achieved using VBGs and a laser output power of up to 500 mW.

In addition, since the Raman spectrum is dependent on the exact excitation wavelength, i.e. Raman spectra are recorded as a wavelength dispersed spectrum and then converted to Raman shift (Δcm⁻¹ from excitation line) wavelength stability is crucial to ensure the Raman spectrum does not change during or between measurements.

Finally, potentially fatal back reflections need to be avoided, which is achieved by using an optical isolator and spectral clean up filters are required to remove weak additional lines that would interfere with the Raman spectrum. The Cobolt 08-NLD 785 nm laser addresses all of these important performance features in a compact footprint and ensures reliability thanks to the proprietary manufacturing technique called HTCure™.

Conclusions

The use of a stable high power NIR laser is essential to achieving high time resolution and high signal to noise ratios allowing for both fast and slow processes to be captured simultaneously.

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About Cobolt AB
Cobolt supplies high performance CW and Q-switched lasers, for stand-alone use or OEM integration in equipment for fluorescence analysis, Raman spectroscopy, interferometric metrology, micromachining and environmental monitoring. Using proprietary HTCure™ manufacturing technology, the lasers display outstandingly tolerance to demanding environmental conditions and ensured lifetime. Cobolt is based in Stockholm, Sweden.