

UV resonance Raman spectroscopy for micromolar detection of fluorescent compounds

Application Note

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Introduction

Raman analysis of fluorescent materials and compounds is a challenging task experimentally due to the overlap of fluorescence which, even when very weak, can overwhelm the inherently weak Raman scattering signal. Several approaches can be implemented to circumvent this problem including NIR (785 nm or even 1064 nm) excitation. For example, although highly fluorescent even at 785 nm a good S/N (signal to noise ratio) spectrum of 9-methylanthracene can be obtained (see figure 1).

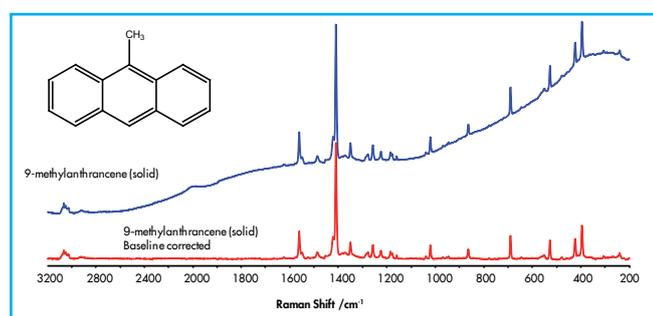


Figure 1 Raman spectrum of a solid sample 9-methylanthracene (at λ_{exc} 785 nm) i) before (blue) and after (red) baseline correction to remove the contribution from fluorescence

The challenge however is to obtain Raman spectra which are free of fluorescence and in solution at low concentrations. There are two approaches to this. The first is surface enhanced Raman spectroscopy using gold or silver colloids which has proven highly effective in analysis of trace contaminants such as dipicolinic acid. [1]

However for on-line analysis, e.g. reaction monitoring, process control etc, such an approach is not feasible. An alternative therefore is resonance Raman spectroscopy in which the Raman signal is enhanced by using a laser wavelength that is coincident with an optical absorption band. Such an approach has been used extensively to characterise compounds and materials that absorb visible light due to the ready availability of detectors with high efficiency sensors between 400 and 1100 nm and relatively low cost CW solid state and gas lasers.

For more general application excitation in the UV region is preferable as the majority of compounds absorb light at wavelengths below 300 nm. In addition fluorescence/auto-fluorescence and room lights do not contribute significantly at wavelengths below 300 nm. Furthermore because of the $1/\lambda^4$ dependence of Raman scattering intensity on wavelength, low laser powers (and hence less heating) are needed in the UV.

Experimental Setup

A challenge however to the application of UV Raman is the sensitivity of the CCD detectors available since quantum efficiency below 300 nm is typically less than 10%. Using a backthinned CCD (e.g. the Andor iDus DV420A-BU2 CCD detector) however increases quantum efficiency in the UV to over 50% allowing for high S/N spectra to be obtained with low laser power and with low acquisition times using a frequency quadrupled Nd-YAG pulsed laser (266 nm) and a Shamrock SR-303i-B spectrograph (holographic 2400 l/mm grating blazed at 300 nm). A standard 180° backscattering geometry and quartz optics were employed. An alternative approach to signal enhancement is to use a wavelength shifting phosphor coating (UVB) on the CCD however backthining of the CCD (BU2) increases the long term stability of the spectral sensitivity.

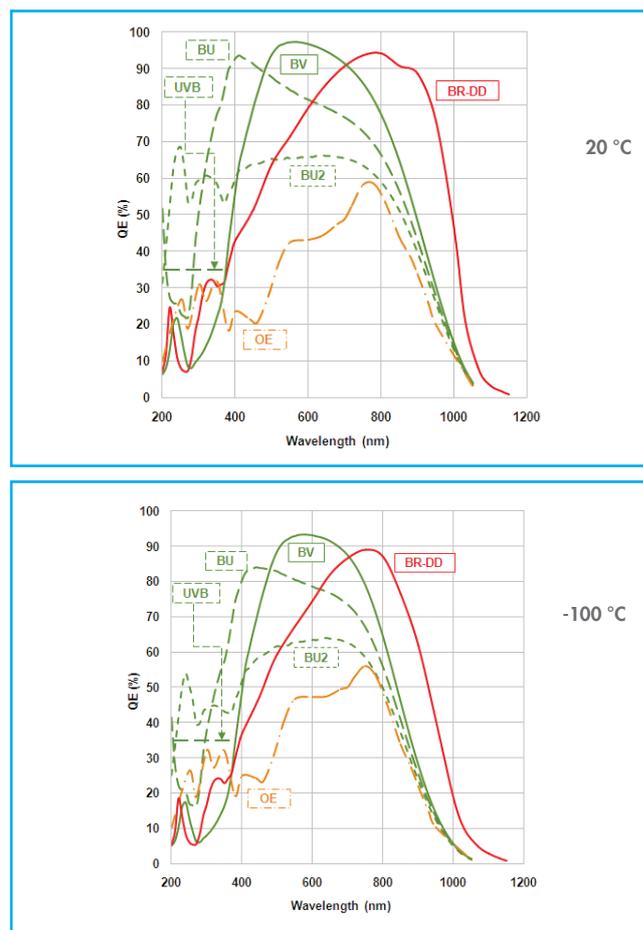


Figure 2 Quantum efficiency curves for various detector options

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Results

The UV Raman spectrum of a 10 μ M solution of 9-methylantracene in cyclohexane is shown in figure 3. Importantly the spectra are free from contributions from fluorescence which swamps the Raman spectrum at 355 nm excitation. In this example the excitation laser is resonant with the second absorption band of 9-methylantracene (figure 4) and hence although the compound is present in very low amounts relative to the solvent, resonant enhancement means that the Raman scattering from 9-methylantracene is of comparable intensity to the solvent scattering. It is also important to note that the relative intensity of the individual bands in the spectrum change somewhat but band position does not. Furthermore the spectra are virtually free of contributions from components that do not absorb light at 266 nm at <100 mM concentrations, which allows for reaction monitoring in complex reaction media.

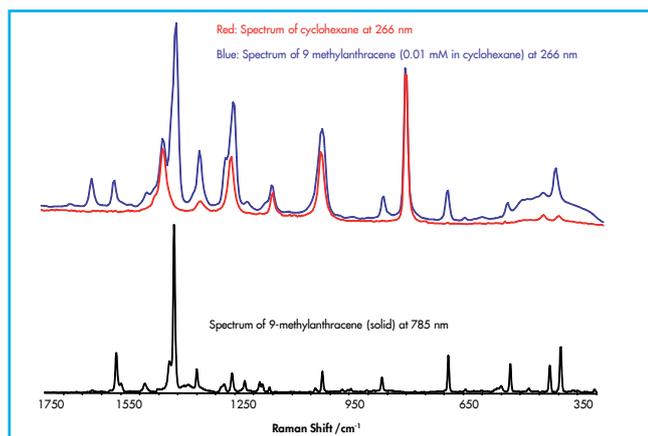


Figure 3 Spectrum of 9-methylantracene i) (black, baseline corrected) recorded as a solid sample at λ_{exc} 785 nm and ii) as a 10 μ M solution in cyclohexane (blue spectrum) with the spectrum of cyclohexane shown in red for comparison. Excitation at λ_{exc} 266 nm from a Nd-YAG laser (5 ns FWHM, 10 Hz, < 1 mW (estimated at 500-800 μ J per pulse 100 accumulations of 4 s exposures). No spectral processing has been applied to the data.

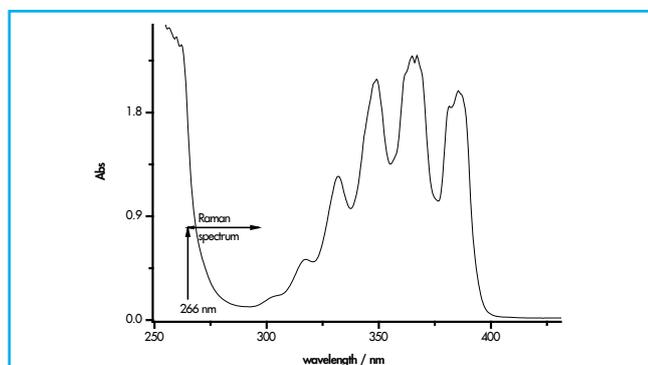


Figure 4 UV-Vis absorption spectrum of 9-methylantracene in cyclohexane. The excitation wavelength and region where Raman scattering is obtained is shown.

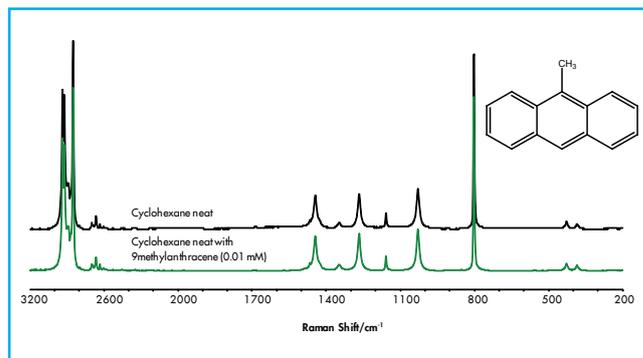


Figure 5 Raman spectra of the same solutions used in figure 3 obtained at 785 nm excitation. At this wavelength the signals from the 9-methylantracene are below the detection limit.

Outlook

The availability of CCD detectors with high UV quantum efficiency and low lost UV laser sources holds considerable promise in the development of UV Raman spectroscopy for materials and catalyst characterisation and in reaction monitoring in complex media.

References

- [1] Quantitative surface-enhanced Raman spectroscopy, Steven E. J. Bell and Narayana M. S. Sirimuthu, Chem. Soc. Rev., 2008, 37, 1012-1024

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