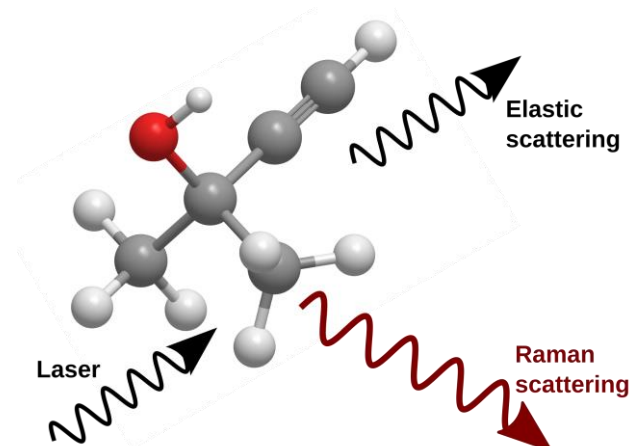


Raman Spectroscopy for online analysis: parameters you cannot find in the textbooks

We study the capabilities of Raman spectroscopy for online analysis of hydrogenation processes and investigate the effects of environmental and instrumental parameters. These parameters are fundamental in producing reliable data but cannot easily be found in literature.

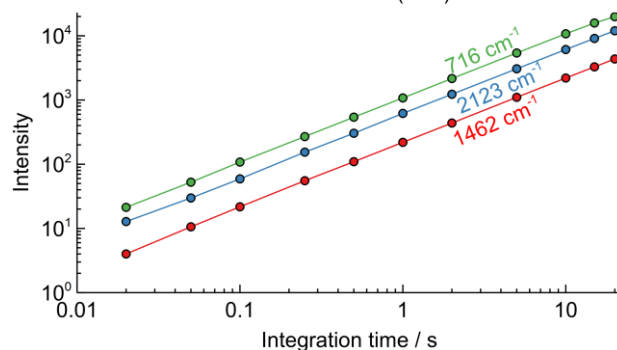
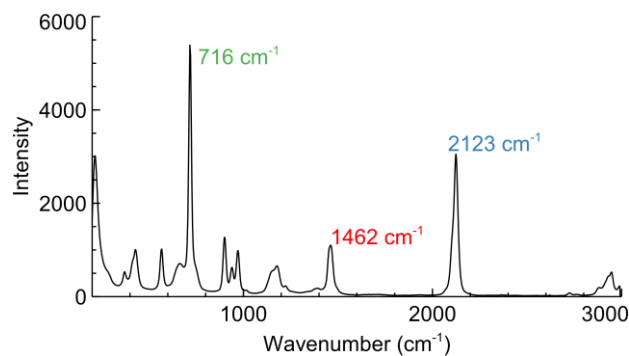


Background

Raman spectroscopy is a valuable technique for “molecular fingerprinting”. It probes molecular vibrations and provides a non-destructive way to determine chemical structure, phase, crystallinity, and molecular interactions.

The process works by shining laser light at a sample and analysing the way it scatters that light back. The majority of light is scattered back at the same energy, known as elastic or Rayleigh scattering. However, some of the light is scattered back at a different energy than that put in, also known as inelastic or Raman scattering. The reason for this is because the molecule absorbs some of that input energy in the form of bond vibrations, producing a distinct chemical fingerprint that allows us to ascertain what the structure is.

The particular compound we chose for this study was 2-methyl-3-butyn-2-ol, as it serves as a model molecule for hydrogenation reactions. The results we discuss are specific to software and the instrument, but the overall conclusions will be broadly applicable.

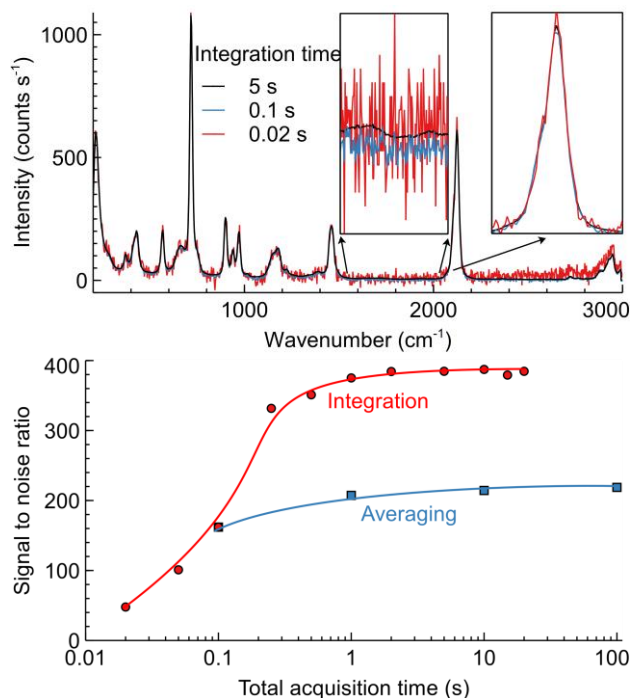


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Integration time and averaging

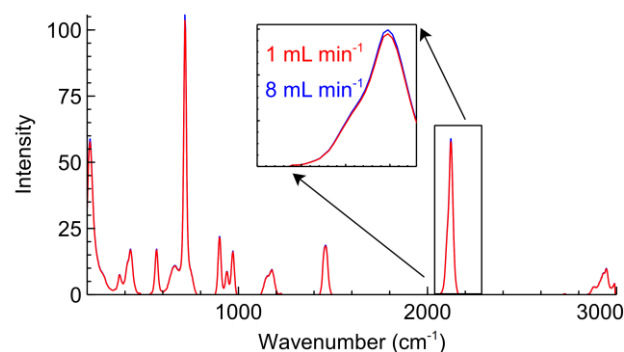
The integration time of a spectrum is the measure of how long the scattered light is exposed to the detector. Longer integration time means more signal can be collected, and thus a stronger spectrum with a better signal-to-noise ratio. With increasing integration time, we observe that the intensity of peaks increases linearly. However, in the plot of peak intensity versus time, when we extrapolate the lines, we can see that they do not go fully to zero at “zero” integration time. This result highlights the effect of background noise and also the effect of fluorescence.

An alternative way to increase the signal-to-noise ratio is averaging multiple spectra. In theory, averaging several spectra reduces noise; the results were modest in practice though. Hence, increasing the integration time provides a much higher signal-to-noise ratio.



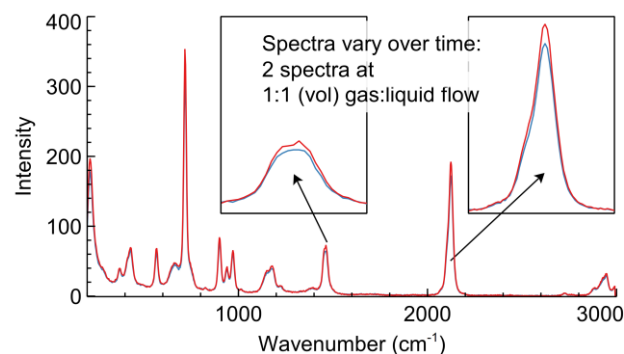
Liquid flow rate

If a liquid is homogenous, then its velocity through the flow cell should not make any difference to the spectrum. As expected, varying the liquid flow rate had no effect on the Raman scattering.



Introduction of gas

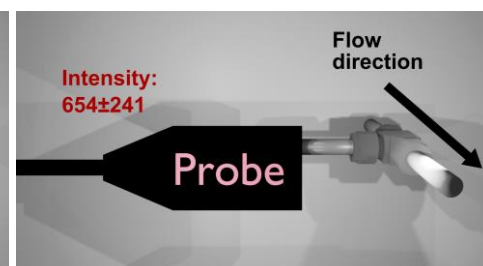
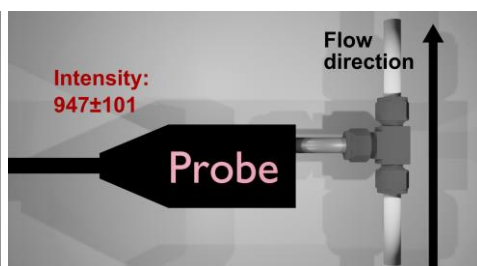
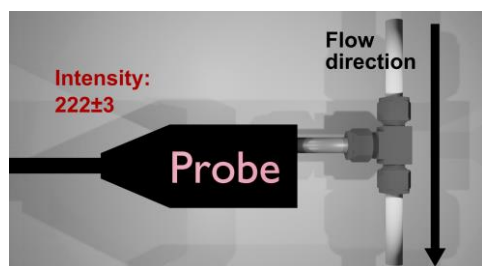
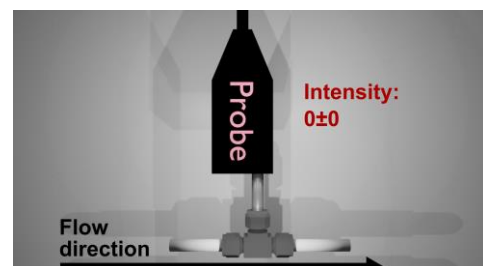
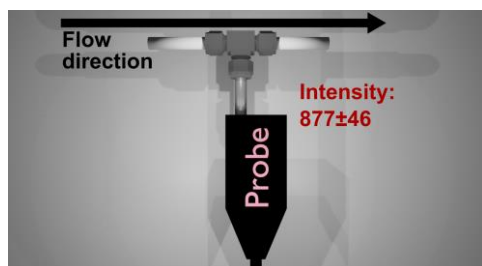
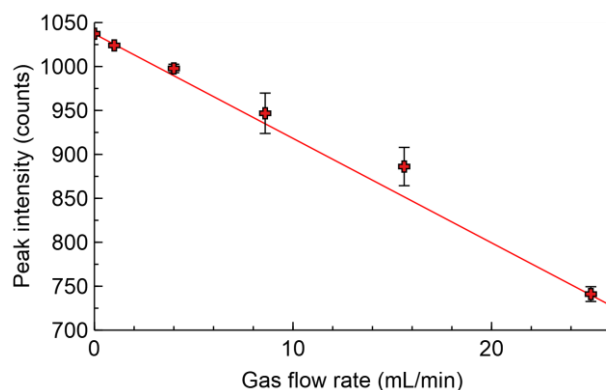
In hydrogenation reactions, we will use Raman spectroscopy to monitor processes with both gas and liquid phases. What happens to the Raman scattering if gas enters the flow cell? In order to answer this question, different amounts of nitrogen gas were introduced into the flow cell along with the liquid.



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The intensity of all the peaks decreased proportionally to the gas flow rate (liquid flow - 8 mL min⁻¹) because the gas bubbles produced no Raman signal. As the flow rate of gas increased, more bubbles entered the cell causing a variation of the signal. The ratio of the peaks stays constant with a relative standard deviation within 2.8%.

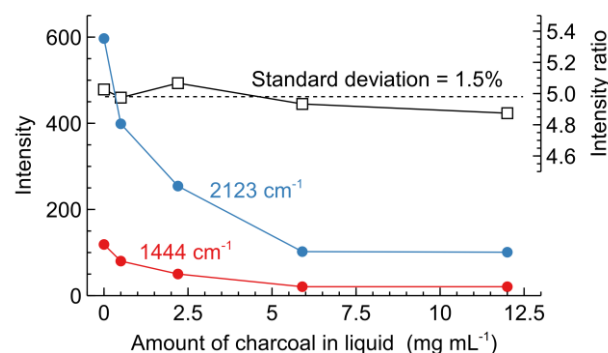
Another interesting facet of this experiment is that the orientation of the Raman probe has a distinct effect on the intensity of the peaks in the Raman spectra. The probe position above the gas-liquid flow produced no signal because no liquid was in the focus of the laser beam. Positioning the Raman probe below the flow resulted in the most stable readings because gas was always above the flow. However, the highest absolute signal was observed when the gas-liquid flow was going upwards due to the gas bubbles rising faster than the liquid.



Presence of solids

Batch reactions often involve the use of suspensions and slurries, particularly in heterogeneously catalysed reactions. We therefore studied the effect of solids entering the Raman cell. To do this, varying amounts of charcoal powder was suspended in the alkyne and spectra were recorded.

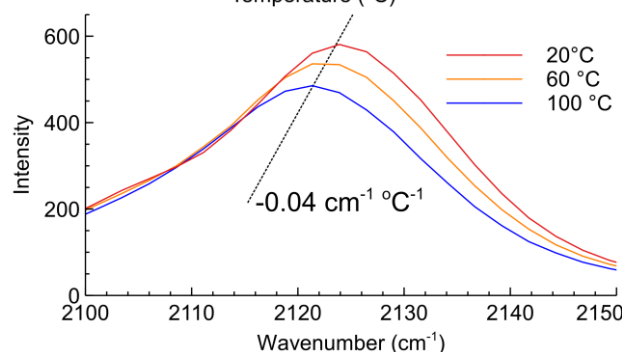
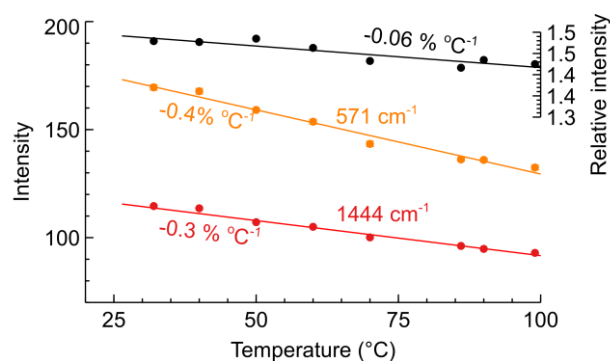
The intensity of peaks decreases exponentially with the mass of suspended solid. However, the decrease levelled out at concentrations higher than 5.9 mg/mL. Importantly, the peak ratio was constant with a deviation of only 1.5%.



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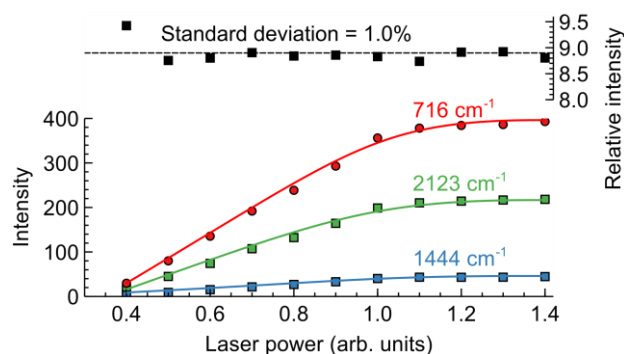
The effect of temperature

As temperature increases, peak intensity decreases, and the peaks shift to a lower wavenumber. Yet, the effect was moderate. We concluded that temperature must be controlled at ± 1.5 °C to maintain peak intensity within an accuracy of 1%; and ± 5 °C for an accuracy of 3%. Fortunately, however, relative peak intensity is far less sensitive to temperature allowing temperature control of as much as ± 8 °C to stay within 1% accuracy.



Laser power

Intensity of peaks in the Raman spectra remain constant between 1.0-1.4 arbitrary units of power. Relative intensities between peaks also remain within 1.0% in the event of a decrease in laser power.



Conclusion

The main technical aspects of Raman spectroscopy for online analysis were studied. Raman is shown to be an excellent tool for monitoring reactions such as alkyne or alkene hydrogenation because of their unique spectral handles. The high signal-to-noise ratio achievable at integration times above 1s provides analytical accuracy better than 0.3%.

Our results show that if gases or solids enter the cell, the absolute peak intensity decreases. However, the relative peak intensity (the ratio of peak intensities) remains stable and allows the determination of concentration of components to an accuracy within a few percent. The same approach of relative peak intensities could also be used to compensate for temperature variations in the process, with relative intensities requiring temperature stability of only ± 8 °C to maintain the accuracy at around 1%.