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Queen's University Belfast

CASE STUDY

The Effect of Crystal Orientation on Raman Spectra

This case study highlights the large spectral differences that can arise between the Raman Spectra collected with different orientation of the excitation beam and crystallographic axes.

BACKGROUND

Over recent years, Raman spectroscopy has proved to be a very effective tool for polymorph screening, especially when combined with multivariate analytical programs such as Principal Component Analysis PCA. PCA is designed to highlight hidden trends within a data set by describing the variance present through factor loadings. However, in screening experiments it is important to distinguish between spectral differences due to polymorphism and those from other sources. Here we show data highlighting the large spectral differences that can arise between the Raman spectra collected with different orientation of the excitation beam and crystallographic axes.

A Simple Example

If a random layer of sucrose crystals are Raman mapped the spectra collected (see below) show large differences. Since sucrose is a known monomorph these effects are not due to different polymorphs - although they do give the same types of spectral changes.

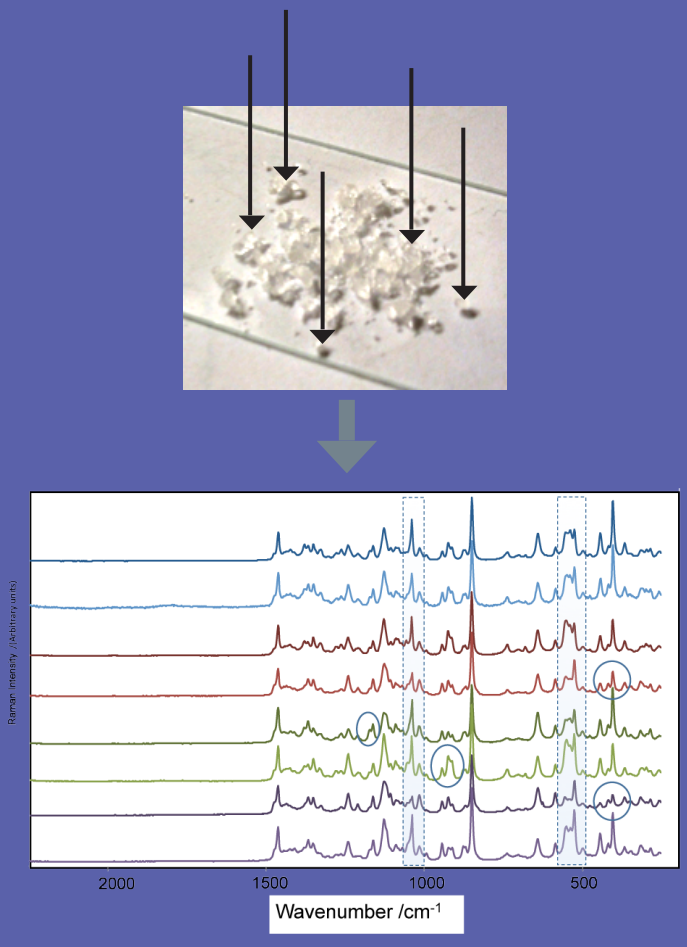
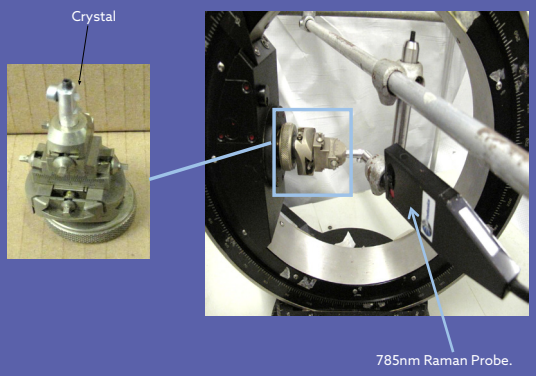


Figure 1. Simple Raman spectra collected during a mapping experiment of a sample of crystalline sucrose. Some of the differences, such as the apparent disappearance of banks and very large changes in band profiles are highlighted.

Experimental Method



To investigate the effect of crystal orientation on the Raman spectrum a goniometer system which allowed the crystal to be rotated around 3 independent orthogonal axes was constructed. This allowed control of the orientation of the crystal with respect to a 785 nm Raman probe. PCA was used to analyze the spectra and identify any variance present.

Crystal Rotation Experiments

A sucrose crystal was mounted at an arbitrary orientation and Raman spectra were collected as it was rotated in increments of 5°. The changes were similar to those found between the spectra of different random crystallites shown above.

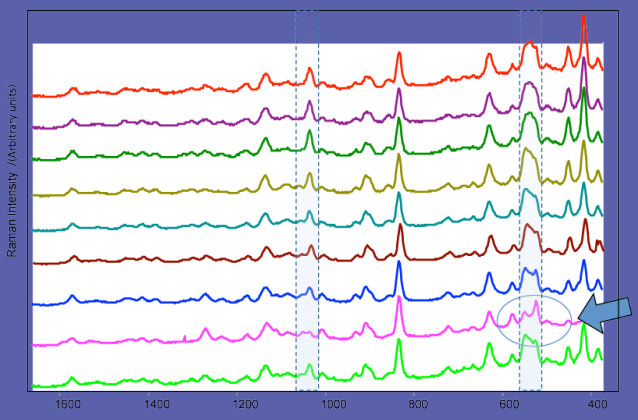


Figure 2. Raman spectra collected during initial rotation experiment.

PCA of the data above showed that the variance could be explained by the three factors shown as loading plots in figure 3.

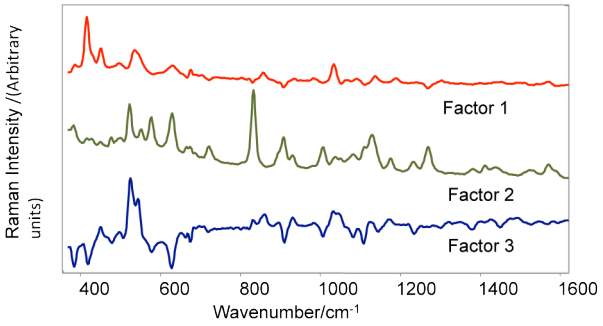


Figure 3. Factor loading plot.

By examining the PCA score plot (fig 4), the path of the crystal can be tracked. This indicates that the position of the crystal within the laser beam directly relates to the variance seen within the spectra.

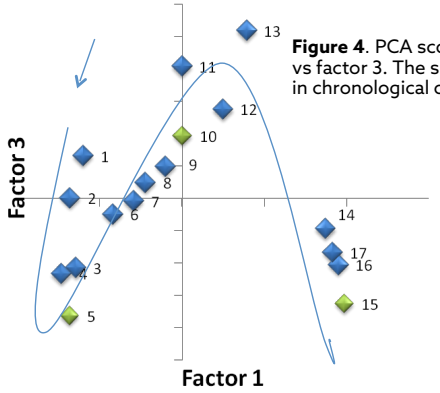


Figure 4. PCA score plot of factor 1 vs factor 3. The spectra are numbered in chronological order.

The score plot of the 2 principal factors (fig 5) can be used to identify the spectra which are the most dissimilar. The differences within these spectra (fig 6) are again similar to those highlighted above.

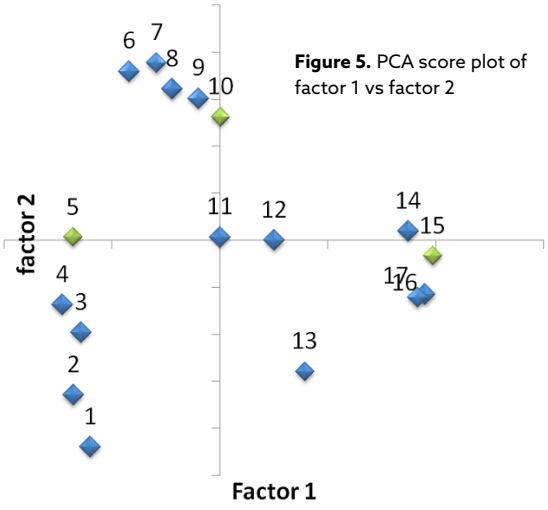


Figure 5. PCA score plot of factor 1 vs factor 2

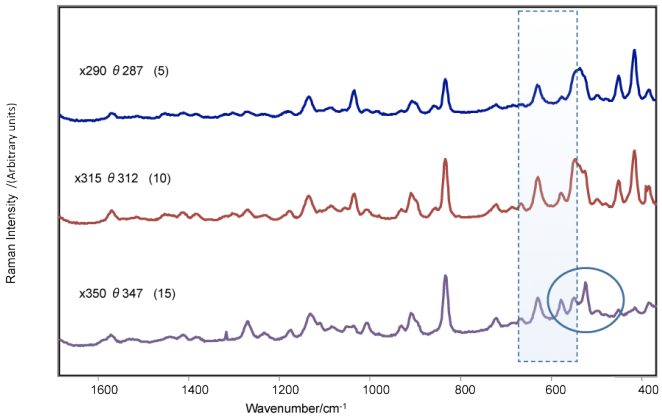


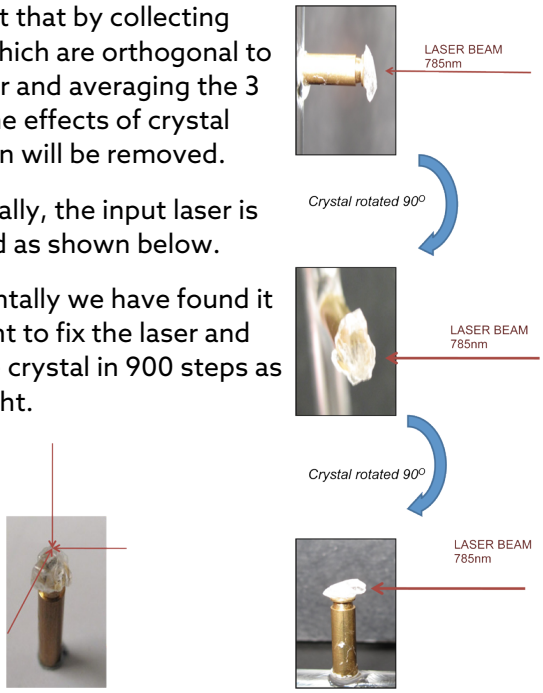
Figure 6. Representative Raman spectra selected using score plot to find those with the largest differences from the mean. The Spectra shown are highlighted in green in the score plot.

Orthogonal Spectra

We expect that by collecting spectra which are orthogonal to each other and averaging the 3 spectra the effects of crystal orientation will be removed.

Conceptually, the input laser is orientated as shown below.

Experimentally we have found it convenient to fix the laser and rotate the crystal in 900 steps as shown right.



The data for two different sets of orthogonal spectra are shown in figure 7. In each of the sets, the spectra are different from each other. Averaging them gives a resultant spectrum which is equivalent to sampling at all 3 possible cartesian orientations. This means that the resultant spectra are identical, irrespective of the initial orientation of the sucrose crystal.

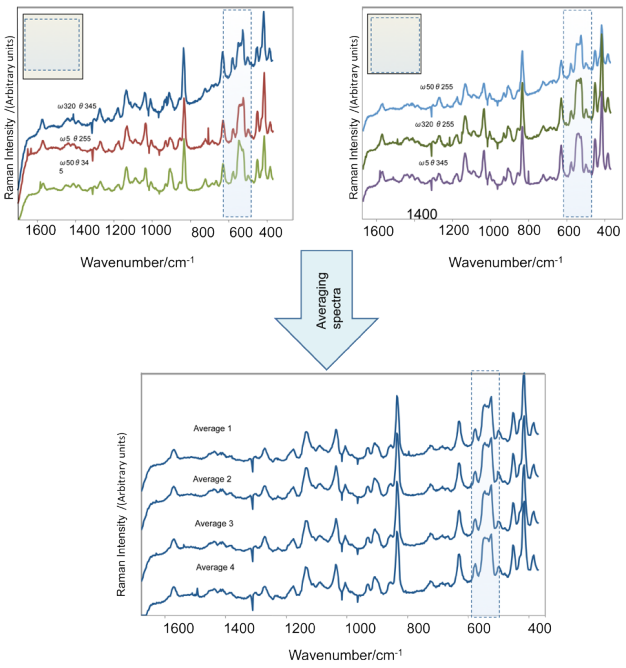


Figure 7. Averaged spectra record for 4 arbitrary initial orientations of sucrose crystal with respect to the laser probe. Note the similarity between these resultant spectra compared to spectra recorded at a single orientation which are shown in figure 6.

Conclusion

Orthogonal excitation suppresses the orientation effects which have the potential to cause confusion in poymorph screening experiements. In these preliminary studies, the crystal was reorientated with respect to a fixed laser direction. Future studies will be carried out with fixed crystal positions.

Acknowledgements

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C.E Greenan [1], Dr. S.E.J. Bell [2], L. McCausland [1]

[1] Almac Sciences, 20 Seagoe Industrial Estate, Craigavon, Northern Ireland, BT63 5QD

[2] School of Chemistry and Chemical Engineering, Queen's University Belfast, UK

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GET IN TOUCH

UK
Almac Group
(Global Headquarters)
20 Seagoe Industrial Estate
Craigavon
BT63 5QD
United Kingdom

sciences@almacgroup.com
+44 28 3833 2200

US
Almac Group
(US Headquarters)
25 Fretz Road
Souderton, PA 18964
United States of America

sciences@almacgroup.com
+1 215 660 8500