

Application of confocal Raman spectroscopy to thin polymer layers on highly scattering substrates: a case study of synthetic adhesives on historic textiles

A. M. Macdonald,^{1*} A. S. Vaughan² and P. Wyeth³

¹ Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK

² Department of Electronics and Computer Science, University of Southampton, Highfield, Southampton SO17 1BJ, UK

³ Textile Conservation Centre University of Southampton Winchester Campus, Park Avenue, Winchester SO23 8DL, UK

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This study considers confocal Raman spectroscopy as a means of identifying a range of synthetic polymeric adhesives used in textile conservation. Many of the synthetic adhesives applied to support fragile textiles in the 1970s are now showing signs of ageing and the textiles are therefore being presented for retreatment. With no record of the adhesive used, conservators are unsure of the appropriate protocol to remove the original adhesive prior to retreatment. We have shown that Raman spectroscopy lends itself to the analysis of these thin polymer layers as it is inherently non-destructive and can be applied *in situ*. We also found that, for particularly thin polymer layers ($\sim 20\ \mu\text{m}$), the underlying textile often scatters far more efficiently than the overlying polymer and therefore the polymer cannot always be identified unambiguously *in situ*. Although thick, transparent polymer samples are known to produce maximum Raman peak intensity when the laser is focused a few microns below the sample surface, focusing on or just above (0–5 μm) the polymer layer is shown to maximize the ratio of polymer peak intensity to textile substrate peak intensity, thus facilitating identification of the polymer. Defocusing further to a point 20 μm above the upper surface is shown to reintroduce interference from the substrate spectrum to a level comparable to that acquired when focused within the thin polymer layer, closer to the textile substrate. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: confocal Raman spectroscopy; thin polymer films; adhesives; substrate interference; textile conservation

INTRODUCTION

Raman spectroscopy has found increasing application in the worlds of art and archaeology,^{1–6} in particular for the analysis of pigments. Specific examples include pigments in fine art,⁷ wall paintings,⁸ wall coverings,⁹ polychromes,¹⁰ icons,¹¹ papyri and manuscripts^{12–19} and pottery.^{20,21} We have recently developed a protocol for applying Raman spectroscopy to the identification of pigments on historic painted textiles, in order to aid conservation of these culturally important artifacts.²² Raman spectroscopy has also been used to identify degradation and decomposition products on historic artifacts to inform chosen conservation procedures.^{13–15} This paper considers another contribution that Raman spectroscopy can make to aid the work of textile conservators, that

of identifying synthetic materials applied during previous conservation treatments.

Painted textiles present a particular challenge to conservators because of the damage they typically suffer in use. For example, only part of the supporting fabric is painted and, not being stretched on a frame, it remains flexible. This flexing can result in severe damage to the painted areas, including flaking, and the fabric may tear or, in the case of silk, shatter. Conservation of historic painted textiles often involves supporting the fragile textile, for example, by heat-sealing a fine mesh silk crepe-line to the reverse of the textile using a vinyl acetate or an acrylic adhesive.^{23–26} However, textile conservators are now finding that previously treated artifacts are now being presented for re-conservation, as the polymeric adhesives age and fail, become tacky, brittle or discoloured.^{26,27} Indeed, some of the early vinyl acetate adhesives are now showing evidence of changing pH or are generating acetic acid, which is damaging the very artifact the adhesive was originally intended to conserve.²⁷

*Correspondence to: A. M. Macdonald, Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, UK. E-mail: amm4@soton.ac.uk

Identification of these previously applied adhesives is therefore an essential element in informing the approach taken by conservators to remove them. Infrared spectroscopy is appropriate, but only when sampling of the adhesive is possible. However, it is not generally acceptable to remove any part of an historical artifact for analysis and, therefore, a direct method for the comprehensive and non-destructive identification of the adhesive on a textile is required. Raman spectroscopy has great potential in this context. While the use of coatings, as is required for surface-enhanced Raman scattering (SERS), spectroscopy may be considered unethical, confocal Raman spectroscopy does seem to lend itself readily to the *in situ* study of these thin adhesive layers. However, the underlying substrate frequently scatters far more efficiently than the thin overlying adhesive layer and, therefore, the spectra obtained may not always permit unambiguous identification of the polymer.

The objectives of this study were, therefore, (i) to determine whether Raman spectroscopy is sufficiently discriminating to distinguish between the different, yet chemically similar, adhesives routinely used in textile conservation and (ii) to identify the appropriate protocol for identifying, *in situ*, a polymer adhesive layer previously applied to an historic textile.

EXPERIMENTAL

A range of synthetic adhesives was studied during the course of this investigation. These systems included ethylene–vinyl acetate (EVA) copolymers (Vinamul 3252, Vinapas EP1, Evacon R, BEVA371, Mowilith DMC2) and acrylics (Lascaux 360HV and Paraloid 72B). Most of the adhesives were supplied as concentrated solutions and were cast directly on to glass slides. BEVA371 and Paraloid 72B were supplied as a waxy solid and as pellets, respectively; these were gently heated and pressed on to glass slides, whereupon the material softened to give specimens with a flat surface. Despite the usual assertion that samples used for Raman microspectroscopic analysis require little or no preparation,^{28,29} it has been reported that different pellet shapes often cause variations in the baseline signal.²⁹ Conversely, flat surfaces have been shown to be ideal for Raman interrogation.³⁰ Samples prepared as above were then oriented with their flat surface uppermost and placed on microscope slides for analysis. The slides were routinely covered with aluminium foil, to eliminate potential problems associated with fluorescence from the underlying glass microscope slide, as has been reported elsewhere.³¹

To create model polymer–textile laminate systems, comprising silk crepe line heat-sealed with adhesive to silk, as used to support fragile textiles during conservation, the adhesives listed above were first diluted as follows. The EVA copolymers Vinamul 3252, Vinapas EP1, Evacon R and Mowilith DMC2 were each mixed with deionized water in a ratio of 1:7 by volume; BEVA371 was dissolved in

white spirit in a ratio of 1:4 by volume; Lascaux 360HV was dissolved in a ratio of 1:2 in a solvent composed of 1 part acetone to 1 part water and Paraloid 72B solid pellets were dissolved in acetone to form a 5% (w/v) solution. The diluted adhesive solutions described above were then painted on pieces of fine silk crepe line and were left to dry, before being heat-sealed to silk fabric at 60 °C using an iron, to simulate the process typically used in conservation.²⁶

Raman spectroscopy was performed on all samples using a Leica microscope coupled to a Renishaw RM1000 Raman microprobe systems with a 780 nm diode laser. A laser power of 25 mW was used throughout this study. The spectrometer has a Peltier-cooled charge-coupled device (CCD) detector and a holographic grating of 1800 grooves mm⁻¹. A holographic (notch) filter prevents backscattered (Rayleigh) radiation from entering the detector. The spectrometer was routinely set up in confocal mode, with a slit width of 15 µm and a CCD area of 4 pixels (image height) × 574 pixels (spectrometer range), which acts as a virtual confocal pinhole. These settings are in line with Renishaw's recommendations for confocal operation of the instrument.³² A microscope objective of 50× (NA 0.75) was used to acquire Raman spectra and all data were processed using a combination of GRAMS/32 and Sigmaplot 2000 software. For analysis of the adhesives, the laser was focused on the perfectly flat surface of the polymer and then the microscope stage was raised 20 µm; this has been shown to provide maximum Raman scattered signal from these transparent materials.³⁰ One hundred accumulations of 10 s extended scans were used to provide high-quality spectra of the solid polymeric adhesives.

The model laminate samples were oriented so that the side to which the crepe line was attached was uppermost, in order to obtain spectra of the polymer adhesive layer through the netting. The laser was focused initially on the surface of the polymer and, again, spectra were obtained from the adhesives by integrating 100 accumulations of 10 s extended scans. Reference spectra were also acquired from silk fibres at different orientations, in the absence of an adhesive, for comparative purposes. Finally, a depth profile of the polymer–textile laminate system was obtained with the laser focused at points below the silk surface, within the adhesive layer and above the composite sample.

RESULTS

Synthetic adhesives

Figure 1 shows spectra obtained from the five EVA adhesives. Although the precise formulation of each of these polymers varies with manufacturer, there are certain peaks that clearly confirm the presence of ethylene and vinyl acetate units. For example, the peaks at 629 cm⁻¹ (O–C=O deformation) and 1730 cm⁻¹ (C=O stretch) are both due to the vinyl acetate component, the peaks at 1373 cm⁻¹ (CH₂ wag), 1349 cm⁻¹ (CH₂ wag), 1126 cm⁻¹ (C–C symmetric stretch of

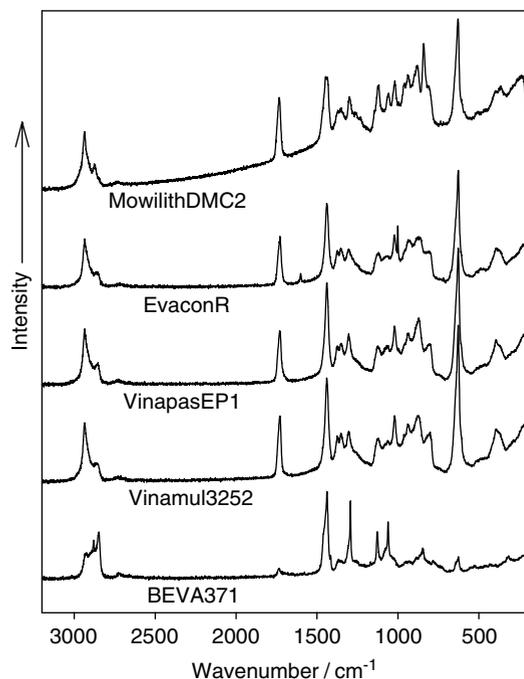


Figure 1. Raman spectra of EVA copolymer adhesives.

ethylene), 1061 cm^{-1} (C–C asymmetric stretch of ethylene)²⁹ all indicate ethylene, and the 1018 cm^{-1} peak is due to the C–C stretch of the vinyl component.³³ The strong peak at 1439 cm^{-1} is assigned to a CH_2 scissors mode involving both the vinyl acetate and ethylene components.²⁹

It is notable, however, that the BEVA371 sample shows a distinctly different spectrum from those of the other EVA adhesives, with a relatively weak peak at 629 cm^{-1} and very weak peaks at 1739 and 1018 cm^{-1} (that is, peaks relating to the vinyl acetate component of the polymer). However, BEVA371 has stronger peaks at 1063 and 1126 cm^{-1} (both assigned to C–C stretch from the ethylene) and a particularly strong peak at 1298 cm^{-1} ; this is assigned to the CH_2 twist and, again, is attributed to the ethylene units. Hence the above data all serve to imply that BEVA371 has a much higher proportion of ethylene, relative to vinyl acetate, than the other EVA adhesives considered here. Indeed, it is known that the properties of EVA polymers change with the content of vinyl acetate incorporated into the copolymer during polymerization,^{29,33} and this is borne out by the fact that BEVA371 is not soluble in water and has a waxy appearance when cast into a film. This adhesive is rarely used in the conservation of fine textiles, being considered more appropriate for lining heavier works of art on canvas.

For conservators to distinguish between the various, very similar formulations, note has to be taken of additional prominent peaks, which may be due to the inclusion of additives during manufacture. Vinamul 3252 and Vinapas EP1, from their Raman spectra, have identical formulations

and both have been referred to in the literature as ‘copolymers of vinyl acetate and ethylene dispersions’.²⁴ Manufacturer’s information indicates that Evacon R is also a copolymer of vinyl acetate and ethylene. However this material has an additional strong peak at 1000 cm^{-1} and a weak peak at 1595 cm^{-1} , possibly from the inclusion of additives, which serve to distinguish it from Vinamul 3252 and Vinapas EP1.

Mowilith DMC2 is listed as a ‘copolymer of vinyl acetate and dibutylmaleate dispersion’.²⁴ The additional strong 842 cm^{-1} peak, the relative strength of the 1058 cm^{-1} ethylene peak and the existence of the 1296 cm^{-1} ethylene peak distinguish Mowilith from the other EVA copolymer adhesives. The notable fluorescence in this spectrum is due to the age of the sample, which had a pronounced yellow appearance. Mowilith is no longer manufactured, having been found to exude acetic acid; it is therefore imperative to be able to identify this adhesive unambiguously so that it can be removed before causing damage to the fabrics to which it has been applied in the past.

Figure 2 shows spectra of the acrylic adhesives Paraloid 72B and Lascaux 360HV. Paraloid 72B is claimed in the literature to be a copolymer of ethyl methacrylate and methyl acrylate (PEMA-co-MA), with a molar ratio of 70:30, having previously been reported to be poly(methyl methacrylate-co-ethyl acrylate) (PMMA-co-EA).³⁴ Comparison with the spectrum published by Willis *et al.*³⁵ confirms that it is indeed a PEMA-co-MA, as does comparison with spectra that we have obtained from a range of model acrylic systems.³⁶ The peak assignments by Willis *et al.* indicate that the 843 cm^{-1} peak is attributable to the C–O–C symmetric stretch and

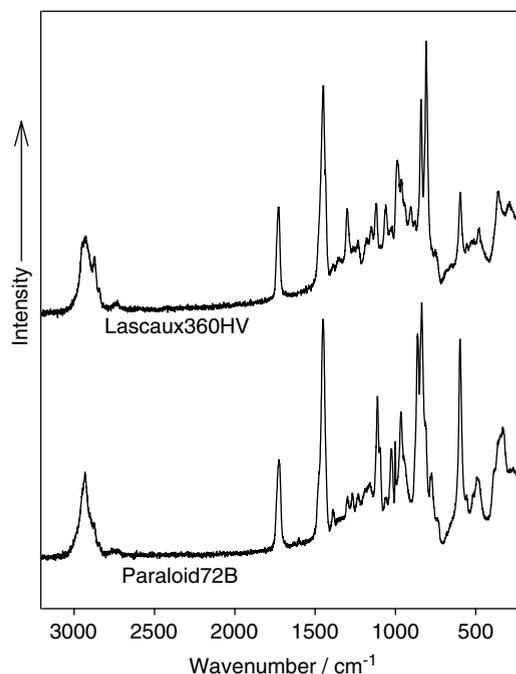


Figure 2. Raman spectra of acrylic adhesives.

595 cm^{-1} to the C–C–O symmetric stretch.³⁵ Comparison with peak assignments made for a poly(ethyl acrylate) system indicate that the 1450 cm^{-1} peak may be assigned to CH_2 wag and 1100 cm^{-1} to the C–C asymmetric stretch.³⁷ The spectrum of Lascaux 360HV is significantly different from that of Paraloid 72B and comparison with the spectrum from a model sample of poly(butyl methacrylate) (PBMA)³⁶ confirms it to be, as described in the literature, a 'poly(butyl methacrylate) dispersion'.²⁴

In summary, we have shown that Raman spectroscopy of synthetic polymeric adhesives used in textile conservation can discriminate between chemically similar EVA formulations and identify unambiguously the precise constituents of acrylic copolymers.

Analysis of adhesive/textile laminates

Figure 3 shows a reflected light optical image of the model adhesive–textile laminate specimen, which was reconstructed from a through-focus sequence of images covering a total stage displacement of 100 μm . In this, the three components of the sample can be seen to varying extents at different positions within the image, because of differing degrees of reflection from the different interfaces. The most easily identified component is the coarse silk crepe line, which is clearly visible as dark horizontal and diagonal fibres ($\sim 100 \mu\text{m}$ in diameter) that are superimposed upon the rest of the sample. The woven silk textile can be seen at the points marked A and B, where the constituent fibres are oriented vertically and horizontally, respectively. In this micrograph, the bright, rather granular regions (for example, at C) correspond to portions of the sample where the incident illumination is being reflected specularly back into the microscope objective from the thin adhesive film. Where specular reflection does not occur, it is extremely difficult to see the adhesive.

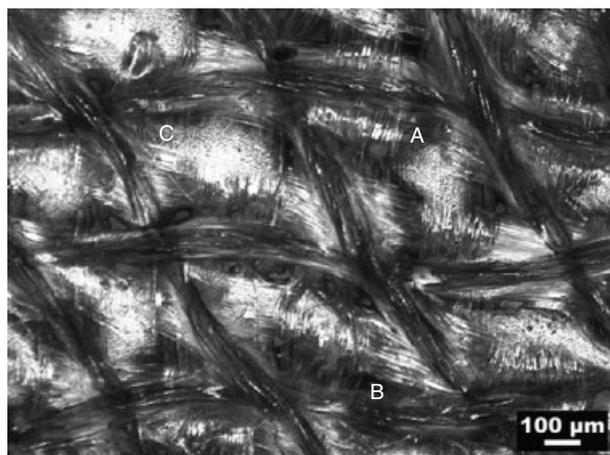


Figure 3. Reflected light optical image of a model adhesive–textile laminate specimen, reconstructed from a through-focus sequence of images covering a total stage displacement of 100 μm .

In applying confocal Raman spectroscopy to model systems such as that described above, it became clear that the technique could readily identify a relatively thick layer ($>50 \mu\text{m}$) of vinyl acetate or acrylic adhesive *in situ*. Confocal Raman spectroscopy has long been used to identify layers in polymer laminates, for example, as illustrated by Sacristan *et al.*³⁸

Figure 4 shows four offset Raman spectra. Although the bottom two spectra were both obtained from the same sample of silk, notable differences exist between the two spectra. For example, in the spectrum labelled Silk 1, the most intense Raman peak occurs at 1226 cm^{-1} whereas in Silk 2 it is the line at 1663 cm^{-1} which is most prominent. Hence, although the same peaks can be identified in both spectra, significant differences in relative intensity occur between the two traces; this is related to the relative orientation of the silk fibres and the axis of polarization of the exciting laser. In this figure the uppermost spectrum was obtained when focused on the surface of the polymer *in situ* on the silk substrate. Comparison of this with the Vinamul spectrum shown below it demonstrates the practical problems associated with any analysis of a thin polymer film which is located above a relatively strongly Raman scattering substrate. Here it is evident that the thin adhesive layer ($\sim 20 \mu\text{m}$ in thickness) cannot be immediately identified, owing to significant interference from the silk substrate. The Vinamul and silk spectra shown in Fig. 4 reveal how both these components contribute to the composite spectrum obtained from the polymer–textile laminate system. Although it is relatively

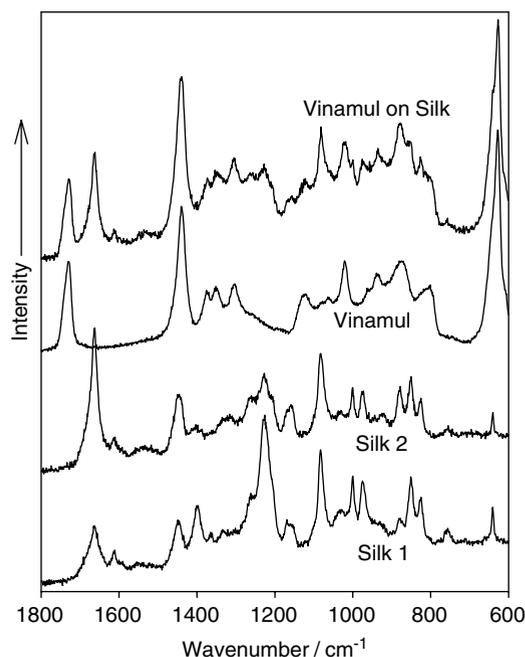


Figure 4. Raman spectrum obtained from adhesive *in situ* on silk substrate showing interference from underlying silk. Silk and adhesive spectra shown for comparison.

straightforward to deconvolute the spectrum obtained from the laminate sample into contributions from the Vinamul and the silk when, as here, each spectrum is known, this may not be so easy when dealing with unknown materials, particularly when they have degraded and the orientation of the silk fibres is unknown.

Doubt has often been cast on the depth resolution claimed for the confocal Raman technique.^{39–42} In particular, difficulty has been reported in characterizing a thin polymer layer on a highly scattering substrate,³¹ hence the spectral interference found here is not unexpected. The extent to which the underlying silk substrate spectrum interferes with the adhesive spectrum was therefore investigated further by undertaking a complete depth profile from a single spot on the polymer–textile laminate sample. Figure 5 shows a sequence of spectra obtained in this way. It is evident that the relative intensity of the silk and polymer peaks changes with stage position but, more significantly, it is clear that both elements of the system contribute to the composite spectrum at all points over a stage position range of 40 μm .

This variation in relative peak intensities is presented quantitatively in Fig. 6, which shows the ratio of the peak intensities from selected pairs of polymer and silk Raman bands as a function of stage position. The upper trace shows data indicating the ratio of the 1729 cm^{-1} Vinamul peak to that of the 1663 cm^{-1} silk peak; the lower trace similarly represents the ratio of a Vinamul to a silk band but, this time, the plot was generated using the 1440 cm^{-1} peak from the adhesive and the 1082 cm^{-1} peak from silk. In both cases,

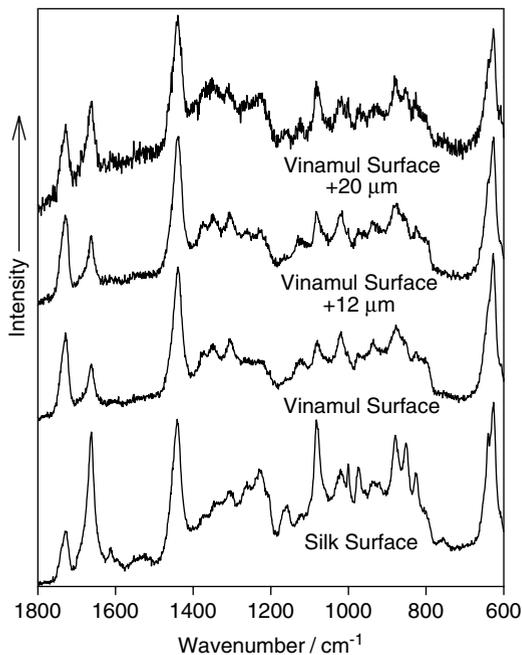


Figure 5. Raman spectra obtained from depth profile of polymer–textile laminate showing changes in relative peak intensities with focal depth.

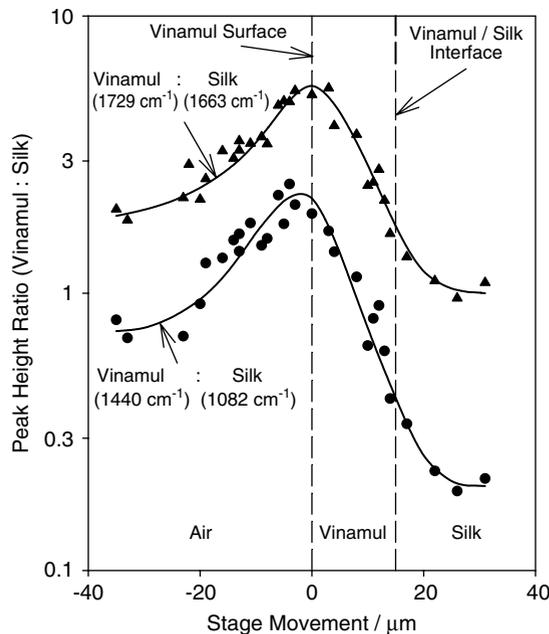


Figure 6. Plot of peak-height ratios obtained at various stage positions, such that the laser is focused within and above polymer. The upper trace shows the ratio of the 1729 cm^{-1} Vinamul peak to the 1663 cm^{-1} silk peak, and the lower trace shows the ratio of the 1440 cm^{-1} Vinamul peak to the 1082 cm^{-1} silk peak.

the numerical values shown were generated by dividing the absolute height of the appropriate Vinamul peak by that of the silk peak. Similar traces were generated using other pairs of peaks and equivalent behaviour was observed.

From Fig. 6, it is evident that, despite the fact that maximum peak intensity of a homogeneous transparent material is obtained when focused within the sample,³⁰ in this case the relative intensity of the vinyl acetate peaks to the silk peaks is maximized when focused at or slightly above (0–5 μm) the polymer surface. This is, of course, dependent on the absolute scattering intensity upon defocusing for both the polymer and the underlying silk. Defocusing further, to a point 20 μm above the adhesive surface in this sample, reintroduces the interference from the silk to a level where the relative peak intensities are comparable to those obtained when focused $\sim 12 \mu\text{m}$ below the adhesive surface ($\sim 3 \mu\text{m}$ above the silk surface). In the uppermost trace in Fig. 5, the low count rate that results from defocusing to this extent above the sample has been compensated by increasing the sampling time by an order of magnitude. The spectrum obtained when focused 20 μm above the adhesive surface was obtained using 1000 scans compared with 100 scans for the spectrum from the silk surface. Nevertheless, Fig. 5 does demonstrate that useful spectra can be acquired when focusing $\sim 20 \mu\text{m}$ above the sample surface. This indicates that, even with this degree of defocusing, a considerable number of Raman scattered photons passes through the

instrument's confocal optics and contribute to the detected signal. This result, initially, appears contrary to existing theoretical understanding of confocal spectroscopy, which would require the plane of interest to be located at the focal point of the exciting radiation, as it is here that the maximum Raman scatter is considered to take place. We are not aware of any other studies that have considered the possibility of obtaining useful Raman spectra with the sample located so far *below* the nominal point of focus.

DISCUSSION

The true resolution of confocal Raman spectroscopy along the optical axis of the instrument is a topic that has attracted considerable attention, both theoretically⁴³ and in terms of how experimental results should really be interpreted.^{39–42} Although it is not our intention here to provide any quantitative analysis of the data shown in Fig. 6, we feel that these results do require some qualitative discussion, even if, without supporting mathematics, any model must be somewhat speculative. For the discussion that follows, we will define the origin of a coordinate system to be the focal point of the exciting radiation and the positive z -direction to correspond to the direction of the incoming laser beam along the optical axis.

It is accepted that the confocal volume, or 'waist' of the laser beam at the focal plane, is the point from which most useful Raman scatter takes place; as measured by the FWHM criterion applied to silicon in air, this is typically of the order of $2\ \mu\text{m}$ in extent. However, Tabaksblat *et al.*⁴³ predicted that, within a thick transparent sample, 'more than 20% of the total amount of light passing through the (confocal) pinhole comes from planes more than $5\ \mu\text{m}$ away from focus'. Other authors^{29,40–46} have also noted that useful Raman scattered photons are obtained from an *extended region* (named variously the confocal volume,³⁰ the illuminated region,^{40,41} the laser field,⁴¹ the focal spread,⁴² the scattering volume or sampled volume⁴⁴ and the focal volume^{44–46}). Progressively immersing this extended region into a transparent sample is reported as giving a linear increase in Raman peak intensity; that is, if the focal point were, initially, located a distance z_d above the surface, the detected signal would, presumably, then correspond to the integral of all the Raman radiation that could contribute to the final signal from $z = z_d$ to $z = +\infty$ in the coordinate system defined above. Raising the stage and thereby reducing z_d would then increase the detected signal, up to a maximum when the stage is raised some distance above the focal point^{29,41–44} ($z_d < 0$). Although this extended region has been attributed to optical effects such as refraction and diffraction at the surface of the transparent sample,^{40–42,44–46} clearly this cannot be the case when the focal point lies above the sample surface. Further raising the stage and, thereby, immersing the extended excitation volume into the transparent sample has been reported to result in a fall-off in Raman peak

intensity^{41,43,46} and this has been attributed to the emerging Raman photons being scattered by the material.³⁰

From the above description, lowering the plane corresponding to the surface of the adhesive below the standard focal point of the laser would result in the polymer layer being located in the lower portion of the extended excitation volume, while the silk is located lower still. The Raman scattered photon intensity is understandably greatly reduced in this configuration, as the confocal optical set-up would then result in a low, but non-zero, collection efficiency for Raman scattered photons. Nevertheless, sampling over an extended time compensates for this and allows a useful spectrum to be obtained; all elements of the sample scatter enough Raman photons for them to be detected such that the combined spectrum is formed.

In summary, it would seem that, even in confocal mode, significant numbers of Raman scattered photons can be collected from a sample placed at any point within the extended volume, if sufficient sampling time is allowed, and in fact, the sample surface is not, necessarily, best located at the focus of the laser beam. For a homogeneous transparent sample, maximum Raman peak intensity is obtained by focusing the laser up to $20\ \mu\text{m}$ into the sample, depending on its degree of transparency. However, interference from an underlying substrate *may* be reduced by locating the sample slightly below the laser focal point, depending on the precise optical set-up of the system, the thickness of the overlying sample and the nature of the substrate. This extended sampling volume is not, we suggest, a product of optical effects such as refraction, at the surface of the sample, as has been suggested elsewhere^{40–42,44–46} but is inherent in the system, as such optical effects are clearly not present when the focal point lies above the sample surface.

CONCLUSION

The initial intention of this work was to provide a practical framework to aid in the conservation of historic textile artifacts. To this end, we characterized a range of synthetic adhesives routinely used in textile conservation, using Raman spectroscopy, and showed that it is possible to differentiate between them *in situ*. In the case of composite samples, as would practically be encountered in conservation work, the sample often takes the form of a thin, weakly Raman scattering polymer layer upon an underlying substrate. Then, adopting the confocal mode and defocusing the laser to a point on or just above ($0–5\ \mu\text{m}$) the polymer reduces interference from the substrate such that an unambiguous identification may be made. The form of our defocus results seem difficult to reconcile with current theoretical models of the confocal Raman technique, which are based largely on ray tracing concepts. Rather, our results seem to imply that all points in the extended sampling volume, both above and below the point of focus, contribute to the Raman response, albeit to varying degrees, and that this z -dependence can then

be practically exploited to reduce the relative contribution of Raman scattered photons from an underlying substrate, in order to identify thin, poorly scattering, overlying layers.

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