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*Development of nanoparticle catalysts and total internal reflection (TIR) Raman spectroscopy for improved understanding of heterogeneous catalysis*

BINGHAM, LAURA, MARIA

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## Appendix: Chapter 1

The calculation of probing distances for infrared (IR) and Raman spectroscopy. The relationship between probing distance ( $d$ ) and wavelength ( $\lambda$ ) is given by Equation 1A.1. Values of  $\theta=73^\circ$ , and  $n_1= 1.461$  (the refractive index for silicon) and  $n_2= 1$  (the refractive index for air) were used (representative of conditions used within our system). This allowed for the plotting of probing depth as a function of wavelength (Figure 1A.1). A linear trend was seen. Typical Raman excitation wavelengths (such as 532 nm) gave lower probing depths (in the region of 40 nm), than for the higher wavelengths associated with IR spectroscopy.

$$d = \frac{\lambda_0}{4\pi} (n_1^2 \sin^2(\theta) - n_2^2)^{-\frac{1}{2}} \quad \text{Equation 1A.1}$$

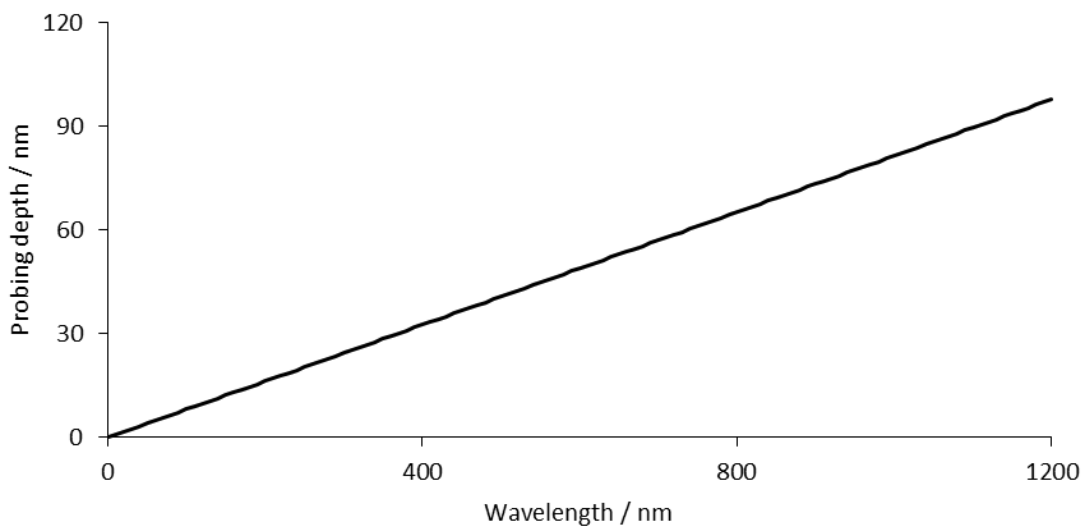


Figure 1A.1. Graph showing the linear relation of probing depth against excitation wavelength for spectroscopic techniques.