

## Raman atomic force microscopy – a feasibility study

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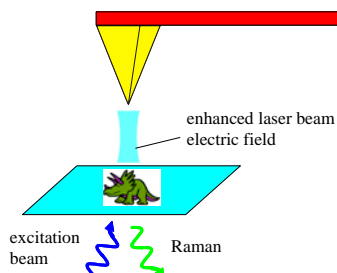
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### Introduction

The provision of simultaneous molecular specificity and nanoscale spatial resolution is key to understanding structure and molecular function in materials, interface sciences, nano-devices, molecular wires, cell biology and medicinal chemistry. To date there are several methods capable of nanoscale spatial resolution including electron microscopy and scanning probe microscopies such as near-field aperture scanning optical microscopy (NSOM) and Atomic Force Microscopy (AFM). However, none of these techniques can provide detailed molecule specific, spectroscopic information with spatial resolution on the tens of nanometre scale. For example, apertures with diameter  $\phi < 50$  nm are available, however, the poor transmission efficiencies in either excitation or collection modes limit the practicality of NSOM for Raman imaging. Recent work of several groups has demonstrated the feasibility of an entirely new approach to meet this critical requirement for a truly chemically specific imaging technique with nanoscale resolution<sup>1</sup>.



**Figure 1.** Schematic diagram of the setup: A laser beam illuminates the AFM tip for chemical specific analysis with sub-diffraction limit (nanoscale) spatial resolution.

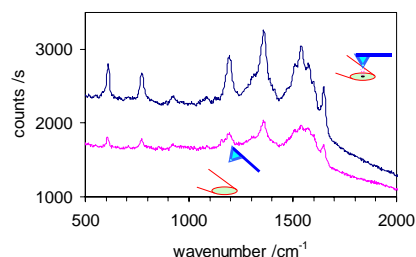
In this apertureless Raman-AFM technique a metallised AFM tip mimics the effect of a single, noble metal nanoparticle used in the surface enhanced (resonance) Raman scattering technique, SE(R)RS that is much exploited for its high (single molecule) sensitivity. The enhanced electric field of the laser beam increases Raman scattering efficiency in this same region leading, for example, to reported enhancements of 4000 in Raman scattering<sup>1</sup>.

The methodology is still in its infancy but a number of exceptionally promising pilot experiments have already been performed demonstrating spatial resolution down to 35 nm with carefully chosen samples and conditions<sup>2</sup>.

### Experimental Study

As the first step in a long term programme leading ultimately to the establishment of a facility at RAL, we have demonstrated the Raman AFM enhancement effect with existing laser and detection instrumentation available at RAL. The experiment was performed on a silver coated substrate thinly coated with Rh6G, using 514.5 nm excitation beam (2 mW). This beam was focused to an estimated spot size of  $\sim 0.5$   $\mu$ m diameter using a microscope objective lens. Spectra obtained with and without the tip are shown in Figure 2. The observed enhancement of the collected Raman signal with the tip was 2.7. The Raman

spectrum from the enhanced zone alone is obtained by subtracting the two spectra from each other. Taking into account the difference in the size of the enhanced zone of diameter  $\sim 200$  nm, which is approximately equal to the dimensions of the AFM tip, and the size of the illuminated zone this corresponds to the local enhancement factor of  $\sim 20$  under the AFM tip. This enhancement is commensurate with the radius ('sharpness') of the tip. A large enhancement is expected from smaller radius tips. Such tips will be required for achieving higher spatial resolution. The AFM tip, manufactured by Nanonics, consisted of a gold sphere of 200 nm diameter attached to a silicon AFM cantilever. The sample was mounted on a manual x,y-micropositioner used for coarse placement, whilst the tip was separately mounted on a computer controlled x,y,z-nanopositioner of accuracy 5 nm. The silver substrate was prepared using a method described in Reference 3 with thickness of a few nanometres to ensure partial optical transparency for the transmission of the probe and Raman signals. The spectra were collected at the backscattering geometry from below the sample using a Leica DM-IRB microscope and objective lens with numerical aperture of 1.2. The AFM tip was carefully positioned above the sample and gradually lowered to bring the enhanced electric field towards the sample surface. The spectra were collected using a liquid nitrogen cooled CCD camera and a single stage spectrometer.



**Figure 2.** Raman spectrum (SERRS) of Rh6G with (top) and without (bottom) AFM tip. The acquisition time for each spectrum was 2 s.

### Conclusion

The results demonstrate the viability of developing a prototype of the Raman AFM device based around existing laser and detection technology at RAL. The new concept holds promise to advance research across many areas including a study of macrostructure and molecular dynamics in photosynthetic membranes, membrane protein identification, design of new drugs, material sciences and direct DNA/protein sequencing.

### References

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