The effects of probe boundary conditions and propagation on nano-Raman spectroscopy

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Summary

Raman spectra obtained in the near-field, with collection of the Raman-shifted light in reflection, show selective enhancement of vibrational modes. We show that the boundary conditions for an electric field near a metal surface affect propagation of the reflected signal and lead to this selection. The enhancement of certain Raman forbidden vibrations is explained by the presence of an electric field gradient near the metal-apertured fibre probe.

Introduction

The metal aperture at the apex of a near-field scanning optical microscope (NSOM) probe locally concentrates the electric field. The electric field near the probe is enhanced, and one would expect to see corresponding enhancement of the Raman signal. As these evanescent fields decay on a nanometre-length scale, both a strong surface enhancement of all components of the electric field and strong field gradients are produced. These gradients have profound effects on the Raman spectra of samples within them, leading to a gradient-field Raman (GFR) effect. This leads to new selection rules for surface-enhanced Raman spectroscopy (SERS) (e.g. see Moskovits, 1985; Creighton, 1988 and references therein), and also to differences between far- and near-field Raman spectroscopy measured with a near-field optical microscope (Hallen *et al.*, 1995; Ayars *et al.*, 2000). Because all components of the electric field are enhanced (Fig. 1) one expects a larger signal from all Raman-like modes, including those coupling to the field via the classic Raman effect and those coupling by field gradient effects such as GFR. This is not observed, and we discuss the reasons here. We first

present the experimental data, then show the expectations, and finally discuss the role of propagation around the probe tip.

In the near-field, the electric field is enhanced. This can be seen in Bethe–Boukamp calculations as shown in Fig. 1 (Bethe, 1944; Boukamp, 1950). In this calculation, the electric field is polarized in the *x* direction and is incident on a subwavelength aperture. There is tremendous enhancement of the *x*-, *y*- and *z*-polarizations close to the aperture. We would expect, therefore, to see enhancement of all the Raman peaks as we move the probe close to the surface. If we recall that these spectra are obtained in a backscattering geometry, the lack of enhancement can be understood. The fibre is coated with metal and boundary conditions imposed by Maxwell's equations dictate that the electric field must be perpendicular to the metal. This is illustrated nicely in Fig. 1. The E_x field is centred under the aperture (silica) and spreads with distance from the tip. The E_z component lies under the metal, where it matches the boundary condition to the metal while providing the continuity required for the electric field.

In NSOM, a sharpened optical fibre is coated with aluminium to form an aperture. The probe is positioned near the surface under lateral force feedback. NSOM is used in illumination mode, with 514 nm Ar ion laser light coupled into the fibre probe. Reflected light is collimated with a 0.50 NA lens, passed through a holographic filter, focused into a Czerny-Turner spectrometer, and finally collected onto a cooled ($-45°$C) couple charged device camera. Elliptically polarized light is incident through the probe in the *z*-direction and light is collected in reflection (*z*-direction) without an analyser. Lines from vibration modes not observed in the far-field spectra are observed as the probe approaches the surface. The differences in the spectra as the probe approaches the surface are highlighted by subtracting a 'far-field' spectra taken with the probe relatively far ($\approx 1 \mu$m) from the sample surface. Figure 2 (Jahncke *et al.*, 2002) shows the Raman signal in dark grey and

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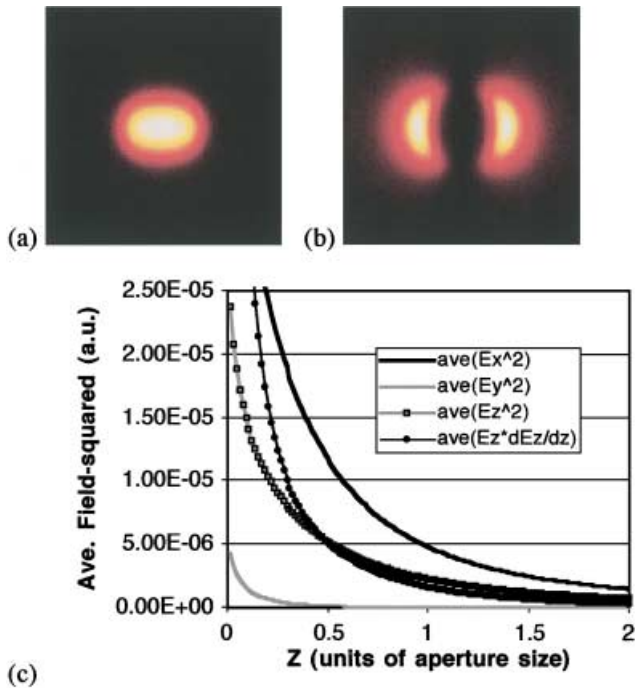
(a)   (b)

(c)

Fig. 1. Bethe–Boukamp model calculations of the electric field magnitude squared as a function of position. (a) and (b) show the x- and z-component, respectively, of the electric field in a plane 0.2 aperture sizes below the tip over a region 3 aperture sizes on a side with the tip centred. For the calculation, 514 nm light was used with a 100-nm aperture, and the colour scale on (a) is four times that of (b). The integral over planes as in (a) and (b) is shown in (c). The average electric field is shown for the different electric field components as a function of distance from the aperture in units of aperture size. In all cases, the electric field is enhanced near the aperture.
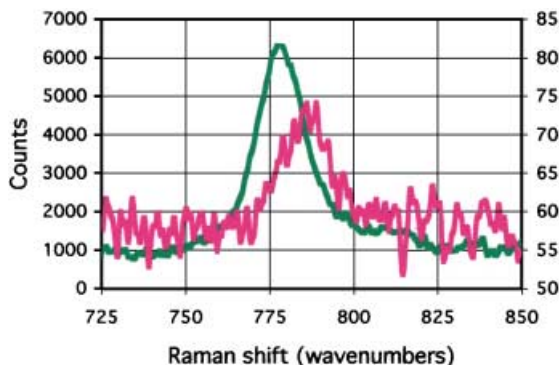

Fig. 2. Raman spectra obtained with a metal-coated fibre probe. The dark grey spectrum is obtained with the fibre tip ≈ 40 nm from the sample surface. The light grey spectrum is the difference between the dark grey spectrum and a spectrum obtained far from the sample surface.

the difference between the near- and far-field spectra in light grey (noisier peak) when the near field tip is ≈ 40 nm from the surface. The difference spectrum shows a new peak near 787 cm^{-1}, not an enhancement of the same far-field peak
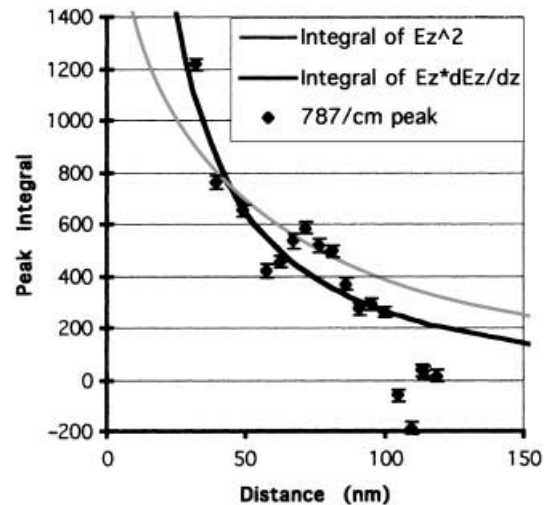

Fig. 3. The probe–sample distance dependence of the NSOM–Raman difference spectra compared with standard Raman and GFR models.

(the A1767 cm^{-1} mode of Yang *et al.*, 1986) observed here at 778 cm^{-1}, as the probe moves towards the surface. The shift in the peak energy is far too large to be explained by surface stresses or interaction with the metal of the probe. We identify it as the B1 peak of KTP (Ayars & Hallen, 2000), that has been observed at 783 cm^{-1} (Yang *et al.*, 1986), but is not Raman-allowed in the geometry of our far-field (tip retracted) experiment. We also observe the strong infrared absorption mode at 712 cm^{-1} (Jacco, 1986), as a new peak when the tip approaches the surface. Both peaks show the same behaviour as a function of distance, including a strong derivative-like feature near 90 nm probe–sample separation (Ayars & Hallen, 2000). The explanation for our observation of these peaks derives from the strong electric-field gradients near the probe. This permits a different coupling mechanism between the optical electric field and the vibration, which we call GFR in Ayars *et al.* (2000). Heuristically, the field gradient causes the Coulomb force on an atom to vary during the vibration when that atom has been partially charged by a polarized bond. The selection rules for this process differ markedly from the usual Raman selection rules, and the prefactors favour Raman-like observation of strong infrared (not normally Raman) vibrations. The probe–sample distance dependence of the B1 peak is shown in Fig. 3 (Jahncke *et al.*, 2002), along with the best-fit Raman and GFR models. The experimental data in the figure are obtained by integrating the peak in the difference spectra (such as that in Fig. 2 and others in Fig. 2 of Ayars & Hallen, 2000) at different distances. The model curves are from Fig. 1. The GFR describes the data quite well except for the derivative-like variation near 90 nm, which we attribute to coupling with plasmons on the Al probe coating (Hallen & Ayars, unpublished). The negative values of the experimental curve in the lower part of the derivative-like feature are due to our
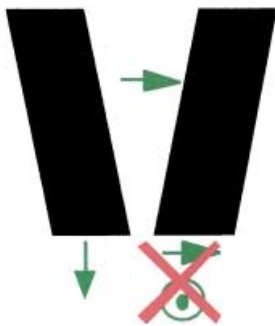
Fig. 4. A metal-coated probe with arrows indicating the direction of the electric field.

'far-field' spectra being too close to the surface, so that some B1 line intensity is present in them. If the 'far-field' reference spectra had been taken further from the surface, those experimental points would be reduced, but not negative.

Light that propagates around the aperture to be collected in the reflection geometry must also satisfy the boundary condition near the metal: only electric field normal to the surface is allowed. This is shown in Fig. 4. These boundary conditions apply to any conductor, and because conductors are required to confine or locally enhance the electric field in any nano-optical system, apertured or not, such considerations apply quite generally. Light that is not polarized in the z-direction cannot propagate laterally near the tip, so instead is reflected downwards where it can be collected in transmission. This explains the somewhat complementary nature of 'far-field' Raman spectra, taken with the probe relatively far from the surface, compared with the difference spectra, which show the near-field contribution. Because the far-field peaks are excited with light polarized in the xy plane, they tend to emit light with x- or y-polarization. This is of course not true in general as the bonds may be tilted < 90° from the z-axis, so will emit both z- and xy-polarized components, but will be true if the crystal has sufficient symmetry and is properly orientated with respect to the surface, as appears to be the case here. One would expect to see an enhancement of the xy vibrational modes in a geometry that would allow it, such as in transmission rather than in reflection. In fact, such an enhancement has been observed by Anderson (2000), who brought a gold-coated atomic force microscopy cantilever into the near-field of a sulfur film on quartz. He observed an enhancement of the xy-polarized Raman modes when the signal was collected from the tip side of the cantilever. Note that the xy Raman lines observed in the reflection geometry are generated in the sample away from the probe, so that their light can propagate to the spectrometer. Therefore, their source region is not expected to be confined well laterally or enhanced near the surface, so does not benefit from the NSOM measurement. This underlines the initial apprehension for spectroscopy with NSOM: the source of spectroscopy exists wherever the light travels, and it must travel through the 'far-field' before it is collected.

Even Raman scattering in the silica tapered probe can be detected (Jahncke & Hallen 1996). It is only through surface enhancement, new modes of coupling and propagation, all of which we describe here, that the resolution benefits may be extracted.

In conclusion, we have shown that propagation of light around a near-field probe can have dramatic effects on the observed spectroscopic lines. This allows selection of certain Raman forbidden vibrational modes that are excited in the near-field due to the presence of an electric field gradient near the metal aperture. Constraints due to propagation with a given geometry can prohibit the (near-field enhanced) far-field-allowed Raman lines from being detected. This implies that they cannot obscure the observation of new near-field-only allowed Raman-like signals, such as z-polarized modes and GFR modes. Such techniques can be used to localize NSOM spectroscopy so that the resolution benefits of NSOM can apply to spectra and not just image contrast.

Acknowledgements

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