H.D. Hallen, E.J. Ayars and C.L. Jahncke, "The effects of probe boundary conditions and
propagation on nano-Raman spectroscopy," J. Microsc. 210, 252 - 4, 2003
NFO-7, Rochester, NY, August 11-15, 2002

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

H. D. Hallen, E. J. Ayars** and C. L. Jahncke****

** Physics Department, North Carolina State University, Raleigh, NC 27695-8202*
*** Physics Department, Walla Walla College, College Place, WA 99324*
**** Physics Department, St. Lawrence University, Canton, NY 13617*

Abstract
Raman spectra obtained in the near-field, with collection of the Raman shifted light in reflection, show a selective enhancement of vibrational modes. We show that the boundary conditions for 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 fiber probe.

Keywords
Near-field scanning optical microscopy, NSOM, Near-field Raman Spectroscopy, Nano-Raman, light propagation in the near-field, electric field enhancement, resolution, KTP, gradient-field Raman, boundary conditions near a metal

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 a corresponding enhancement of the Raman signal. As these evanescent fields decay on a nanometer 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), for example see Moskovits (1985), Creighton (1988) and references within, and also to differences between far-field and near-field Raman spectroscopy measured with a near-field optical microscope Hallen et al. (1995), Ayars et al. (2000). Since all components of the electric field are enhanced, figure 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 in this paper. 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, Bethe (1944), Bouwkamp (1950) calculations as shown in figure 1. In this calculation, the electric field is polarized in the x direction and is incident on a subwavelength aperture. There is a tremendous enhancement of the x, y and z polarizations close to the aperture. We would expect, therefore, to see an enhancement of all of 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 fiber 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 centered 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.

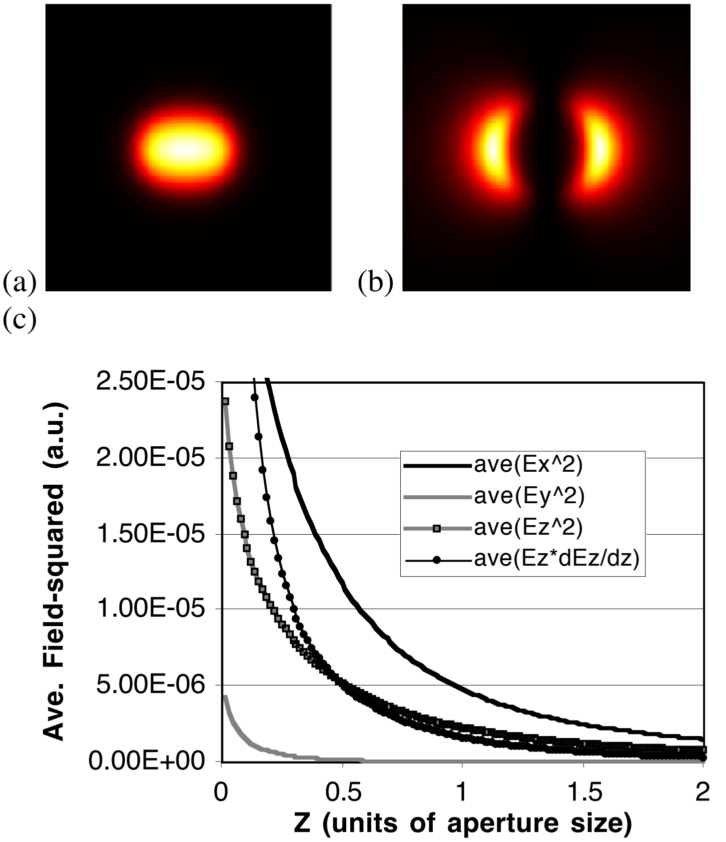

Figure 1. Bethe-Boukamp model calculations of the electric field magnitude squared as a function of position. (a) and (b) show the x-component and z-component respectively of the electric field in a plane 0.2 aperture sizes below the tip over a region 3 aperture sizes on a side with the tip centered. For the calculation, 514 nm light was used with a 100 nm aperture, and the color scale on (a) is 4 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.

In NSOM, a sharpened optical fiber is coated with aluminum to form an aperture. The probe is positioned near the surface under lateral force feedback. The NSOM is used in illumination mode, with 514 nm Ar ion laser light coupled into the fiber 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) CCD camera. Elliptically-polarized light is incident through the probe in the z-direction and light is collected in reflection (z-direction) without an analyzer. 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 (approximately a micron) from the sample surface. Figure 2, Jahncke et al. (2002), shows the Raman signal, dark gray, and the difference between the near and far field spectra in light gray (noisier peak) when the near field tip is about 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 (the A1 767 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

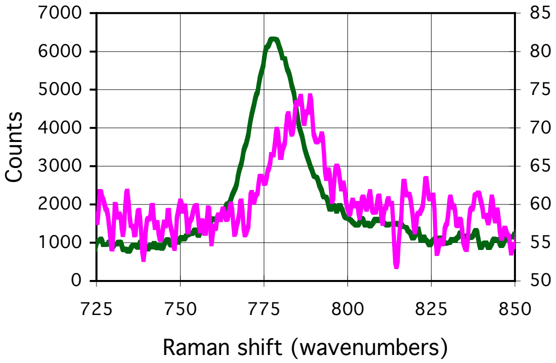

Figure 2. Raman spectra obtained with a metal coated fiber probe. The dark gray spectrum is obtained with the fiber tip about 40 nm from the sample surface. The light gray spectrum is the difference between the dark gray spectrum and a spectrum obtained far from the sample surface.

the probe. We identify it as the a 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 IR absorption mode at 712 cm^{-1}, Jacco (1986), as a new peak when the tip approaches the surface. Both peaks show the same behavior as a function of distance, including a strong derivative-like feature near 90 nm probe-sample separation, Ayars & Hallen (2000). The explanation of 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 favor Raman-like observation of strong IR (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 is obtained by integrating the peak in the difference spectra (such as that in Fig. 2 and others in Fig. 2 of Ayars ad 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 and Ayars (in preparation). The negative values of the experimental curve in the lower part of the derivative-like feature are due to our '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 in allowed. This is sketched in Fig. 4. These boundary conditions apply to any conductor, and since conductors are required to confine or locally enhance the electric field in any nano-optical system, apertured or not, such considerations apply quite generally. The 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 to the difference spectra, which show the near-field contribution. Since 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 since the bonds may be tilted less than 90 degrees 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 oriented 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

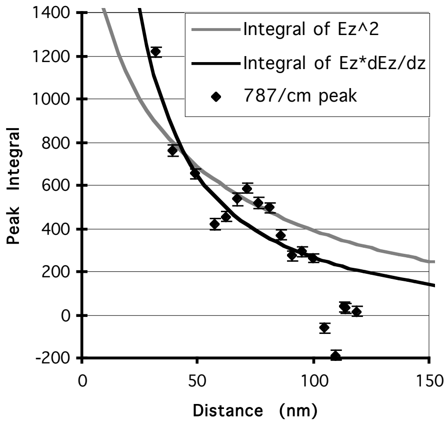

Figure 3. The probe-sample distance-dependence of the NSOM-Raman difference spectra is compared to the standard Raman and GFR models.

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 AFM 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 do 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 and Hallen (1996). It is only through the 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 the 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. This work was supported by the National Science Foundation through grant DMR-9975543 and the Research Corporation through grant CC5342.

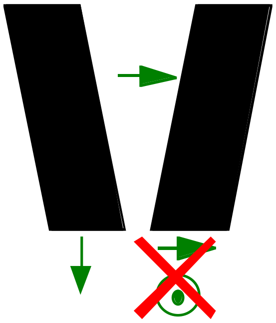

Figure 4. A metal coated probe with arrows indicating the direction of the electric field.

References

Anderson, Appl. Phys. Lett., **76**, 3130 (2000).

Ayars, E. J., H. D. Hallen and C. L. Jahncke, "Electric field gradient effects in Raman spectroscopy," Phys. Rev. Lett. **85**, 4180 (2000).

Ayars, E. J. and H.D. Hallen, "Surface enhancement in near-field Raman spectroscopy," Appl. Phys. Lett. **76** (26) 3911-13 (2000).

Bethe, H.A., Physical Review **66**, 163 (1944).

Bouwkamp, C.J., Phillips Research Report **5**, 401

(1950).

Creighton, J. A., "The selection rules for surface-enhanced Raman spectroscopy," in *Spectroscopy of Surfaces*, Edited by R. J. H. Clark and R. E. Hester (John Wiley & Sons, New York, 1988) 37.

Hallen, H. D., A. H. La Rosa and C. L. Jahncke, "Near-field scanning optical microscopy and spectroscopy for semiconductor characterization," Phys. Stat. Sol. (a) **152**, 257 (1995).

Hallen, H. D. and E. J. Ayars, (in preparation).

Jacco, J. C., Materials Research Bulletin **21**, 1189 (1986).

Jahncke, C.L. and H. D. Hallen."Near-field Raman Spectra: surface enhancement, z-polarization, fiber Raman background, and Rayleigh scattering", 9th annual meeting of IEEE Lasers and Electro-Optics Society (LEOS) 96 conference proceedings volume 1, pp. 176-177.

Jahncke, C.L., E.J. Ayars, and H.D. Hallen, proceedings of 2002 Microscopy and Microanalysis, Quebec City, Quebec.

Moskovits, Martin, "Surface-enhanced spectroscopy," Rev. Mod. Phys. **57**, 783 (1985).

Yang, Hua-guang, Ben-yuan Gu, Yan-yun Wang, Huang Cheng-en and De-zhong Shen, Guangxue Xuebac **6**, 1071 (1986).