Gradient-Field Raman: Selection Rules in the Near Field

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The metal aperture at the apex of a near-field scanning optical microscope (NSOM) probe locally concentrates the electric field. As these evanescent fields decay on a nanometer length-scale, 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. It leads to new selection rules for surface enhanced Raman spectroscopy (SERS), for example see [1,2] and references within, and also to differences between far-field and near-field Raman spectroscopy measured with a near-field optical microscope. [3,4] We describe how a strong gradient of the electric field can alter the Raman spectra, and investigate its implications on selection rules. Heuristically, the field gradient causes the Coulomb force on a polarized bond to vary during the vibration, providing a new coupling mechanism between the field and the vibration. These selection rules differ markedly from the usual Raman selection rules, and allow Raman-like observation of strong IR (not normally Raman) vibrations.

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. New peaks not observed in the far-field spectra observed as the probe approaches the surface. Using difference spectra to highlight the changes, we find the distance dependence for the B1 peak of KTP. This vibration is the strong IR absorption mode at 712 cm^{-1} [5] but is not Raman-allowed in the geometry of our far-field experiment. The probe-sample distance dependence of the peaks is shown in Fig. 1, along with the best-fit Raman and GFR models. 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. [6]

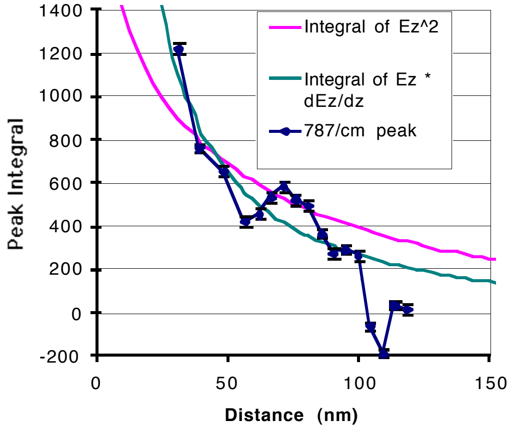

Figure 1. The probe-sample distance-dependence of the NSOM-Raman difference spectra is compared to the standard Raman and GFR models.

References

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

[2] J. A. Creighton, "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.

[3] H. D. Hallen, 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).

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

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

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