

Near-field Raman spectroscopy: electric field gradient effects

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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. 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. [3-5]

A strong gradient of the electric field alters the Raman spectra. When an electric field varies over the length of a bond, a Raman signal can be generated that depends upon the polarizability times the field gradient rather than the field times the polarizability gradient. This results from accounting for variations in both the polarizability and electric field with vibration coordinate [6] in the derivation of Raman spectra. Selection rules for this process, which we term gradient-field Raman (GFR), resemble surface selection rules, so differ from usual Raman selection rules, and relative intensities follow those of infrared spectroscopy.

Strong electric field gradients are generated near metal surfaces. Most of the Raman work (except NSOM) performed near metal surfaces has been concerned with SERS. Consideration of SERS peaks not normally seen in Raman yields good evidence for GFR observation on several materials, [6] including benzene, pyrazine, several cyanides, and C_{60} .

Near-field scanning optical microscopy (NSOM), using a metal aperture at the probe tip to limit the illuminated area, provides another experimental configuration where GFR effects, including those of solid materials rather than molecules, may be observed. The metal that forms the aperture creates the strong field gradients that are required. This configuration has the advantage that the metal can be moved with high precision in all three dimensions, including retraction from the surface to effectively 'turn off' the GFR effect.

The changes observed as the probe approaches the surface are rather small, so we resort to comparative spectra. Several spectra taken far from the surface were averaged, to improve signal-to-noise, and subtracted from single spectra acquired closer to the surface. One result is shown in Figure 1. Two peaks at different energies than the original two peaks are observed. The intensity of these peaks changes at a roughly exponential rate with distance from the surface. [7] This is what would be expected for the evanescent decay of electric field modes near the metal surface, and reflects the expected distance behavior for the GFR. The bigger peak, at 787 cm^{-1} , can be attributed to the B1 vibration reported

previously. [8] The B1 symmetry requires electric field normal to the surface, so for our geometry, this peak appears only in the near-field. The smaller peak, at 712 cm^{-1} , likely derives from the GFR effect. There are no Raman lines previously observed that are strong enough, even considering alternative polarization states. Most studies have not reported any line at this energy, except other NSOM-Raman studies of this system. [3, 9] There is a strong IR absorption mode at 712 cm^{-1} . [10] Thus, as noted above, we expect a strong GFR peak at this energy.

In summary, we have described a new mechanism by which a strong gradient of the electric field can cause normally forbidden vibration modes to appear in Raman spectra. Since infrared and Raman modes are complementary in many materials, this gradient-field Raman spectroscopy should help to provide a full vibrational analysis of a sample in a single measurement, especially when combined with an NSOM measurement, which allows the GFR terms to be preferentially reduced for positive identification of modes.

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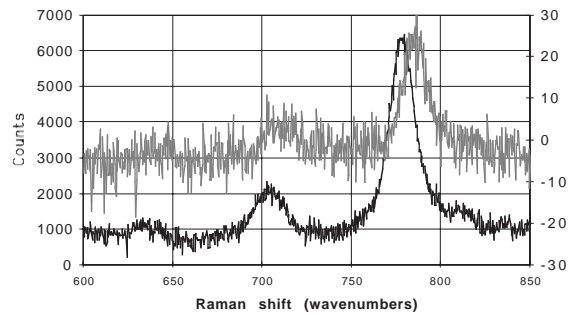


Fig. 2: A NSOM-Raman spectra taken with the probe nearly in contact with the surface, (darker, left axis) is compared to a near-far difference spectra. (lighter, right axis)