

Near-field Raman Spectra: surface enhancement, z-polarization, fiber Raman background and Rayleigh scattering

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We present evidence for a z-polarization component and a surface-enhancement effect in near-field Raman data. Observation of Raman scattering from the fiber and Rayleigh scattering may be used to determine probe quality.

Near-field optical microscopy (NSOM) is a technique that offers several advantages over conventional optical microscopy. Increased spatial resolution and simultaneous topographic images are the best known gains resulting from using NSOM. However, there are other differences between near and far-field techniques which may be used to advantage. We present some of these differences observed between near-field and far-field Raman spectra. The principle difficulty in using NSOM is the low signal levels resulting from the probe shape. When combined with the low quantum efficiency of Raman spectroscopy, a challenging experiment results. It is necessary to have a relatively high signal throughput in order to observe the Raman scattering from the sample. However, in attempting to obtain more light through the probe, the probe is often destroyed. That is, the metal coating near the aperture diffuses away due to heating effects leaving a larger aperture than the one originally fabricated.[1] We indicate how Raman scattering from the probe may be used to determine probe quality during near-field Raman experiments.

The experiment used to obtain the spectra presented here can be found in detail elsewhere.[2] We use an argon ion laser as the excitation source. The NSOM is operated in an

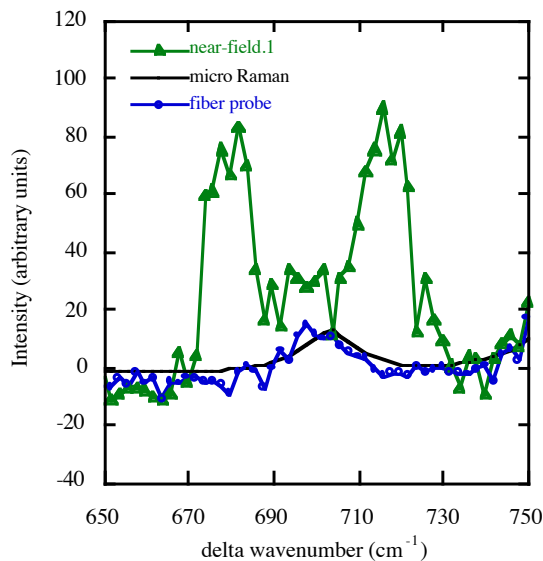


Figure 1. Three normalized Raman spectra are shown. The spectrum obtained in the near-field contains two peaks not found in the far-field micro-Raman spectrum or in a far-field spectrum obtained through a fiber probe.

illumination mode and the backscattered radiation is collected and focused into a one meter double spectrometer with a resolution of 4 cm^{-1} . A cooled PMT in the photon counting mode is used as a detector with a background of 5 dark counts/sec. The far-field micro-Raman spectra that are presented here are obtained using the same spectrometer and detector as in the near-field case only a microscope with a 40X objective is used instead of the NSOM. The sample studied is KTiOPO_4 (KTP), a non-linear optical material. The near-field data is obtained with a probe whose aperture size is approximately 250 nm.

A comparison of near-field and far-field spectra on KTP can be seen in figure 1. The two features at 667 cm^{-1} and 715 cm^{-1} are not present in the micro-Raman spectrum or in a far-field spectrum obtained through a fiber probe. We present this data as evidence of a near-field surface enhancement. These peaks are not explained by a z-polarization component in the near-field.

Polarization studies on KTP do not indicate peaks in these positions that can be fully explained by a z-polarization component.[3]

However, other indicate the presence of a z-polarization component of the light in the near-field. In figure 2 we present three Raman spectra which have been normalized. We expect to see a peak at 215 cm^{-1} due to the backscattering geometry. This peak is present in both the micro-Raman spectrum and in the spectrum obtained through the optical fiber which is removed from the near-field. The near-field spectrum contains a peak in this region, but it is shifted, broadened and of higher intensity than the peaks in the other two spectra. This can be explained by a Raman peak at 220 cm^{-1} which has been observed for other scattering geometries [4], and would only be present if there were a z-polarization component of the light in the near-field. While the presence of a z-polarization component explains the data, there is an alternative, although less likely, explanation. The near-field measurements are more sensitive to the surface and therefore surface stresses may be causing a shift and a broadening of the Raman signal.

Another difference between the near and far-field techniques is that little or no Rayleigh tail can be seen in the near field spectra. In figure 2, one can see a background offset due to the Rayleigh scattering between the near-field data and the micro-Raman and far-field fiber probe data. This is most likely due to the small sampling volume in the near-field measurements.

A useful technique for determining the quality of near-field Raman spectra and of the fiber probe may be found in the Raman spectra itself. Quartz is a Raman active material with a broad peak in the region of $300 - 500\text{ cm}^{-1}$ as seen in middle spectrum in figure 3. The bottom spectrum in figure 3 was obtained using a fiber probe with an aperture larger than the wavelength of the light. The Raman signal from the fiber is present in this data. The top spectrum in figure 3 is the near-field data, and no fiber background is observed. In fact, in each of the Raman spectra we obtained on KTP that indicated surface enhancement, no fiber background Raman signal was present. The presence of Rayleigh scattering and of a Raman fiber background may be used as indications of poor quality near-field Raman measurements.

Near-field nanoRaman is different from its far-field counterpart. Surface enhancement and light polarized normally to the probed surface are two qualities of the near-field measurements which may be exploited. Rayleigh scattering in the near-field is insignificant and both Rayleigh and Raman scattering from the fiber probe may be used to determine probe quality.

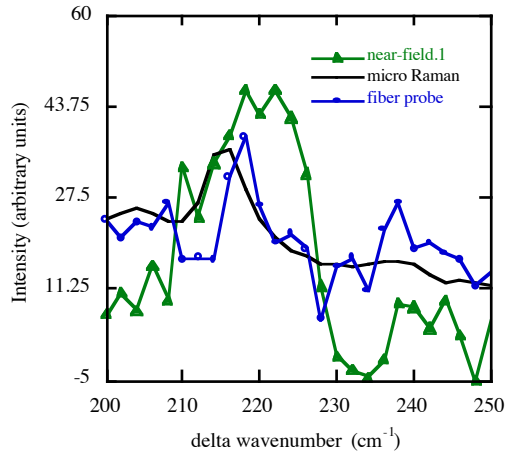


Figure 2. A shifting and broadening of the peak in the region of 220 cm⁻¹ is seen in the near-field spectrum when compared with the two far-field spectra

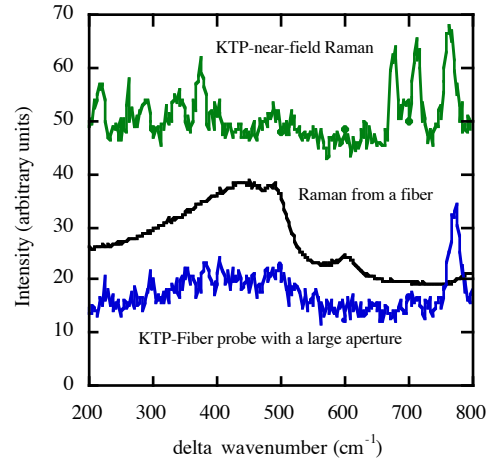


Figure 3. Raman scattering from the quartz fiber is observed in a large aperture probe, but not in the near-field spectrum indicating a surface enhancement.

References

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