

Raman Spectroscopy: Probing the Border Between Near-Field and Far-Field Spectroscopy

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ABSTRACT

We have performed Raman spectroscopy using a near-field scanning optical microscope. The small sample volume coupled with the light-starved nature of the Raman effect makes nano-Raman studies difficult. We present results showing near-field effects in an investigation of Rb-doped KTP. These effects include a change in selection rules due to the presence of a z-polarization component in the near-field, a surface-enhancement effect in near-field Raman data, a reduced Rayleigh tail, and simultaneous topography with the near-field probe. An image taken within a Raman feature demonstrates that nano-Raman imaging is indeed possible if the near-field instrument has considerable long-term stability.

1. INTRODUCTION

Raman spectroscopy with a Near-field optical microscope (NSOM) and an apertured probe has proven to be an insightful technique for elucidating the differences between near-field and far-field spectroscopy. From its first report^{1, 2} and through subsequent papers,³⁻⁵ several distinctions have become apparent. Perhaps the most obvious difference is the topographic image provided by the NSOM measurement as a byproduct of keeping the aperture close to the surface. The simultaneous topography is useful as complementary data from the same region. Increased spatial resolution is perhaps the best known advantage of 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 including a change in selection rules, reduced Rayleigh tail, and strong surface enhancement. We also indicate how Raman scattering from the probe may be used to determine probe quality during near-field Raman experiments.

2. EXPERIMENT

The experiment used to obtain the spectra presented here can be found in detail elsewhere.^{3, 4, 6} We use an argon ion laser as the excitation source. The NSOM is operated in an 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.

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.⁷ This effect, and our use of a photon-counting PMT rather than a parallel detector limited performance, and we are currently upgrading our system. Another recent advance which should make the Raman measurements much easier and hence more widely applicable is the recent demonstration of much higher throughput probes.⁸⁻¹¹ In any case, the measurements presented here

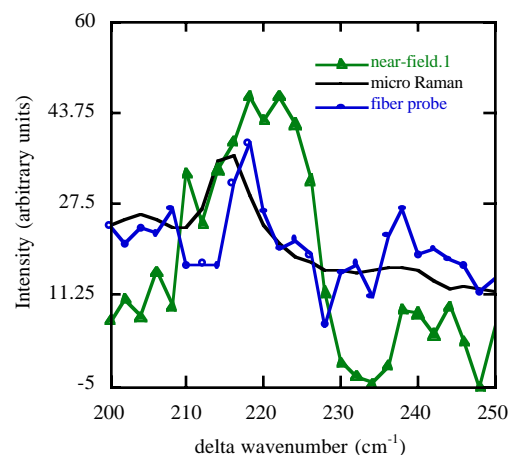


Figure 1. A shifting and broadening of the peak in the region of 220 cm^{-1} is seen in the near-field spectrum when compared with the two far-field spectra

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illustrate that the near-field Raman spectroscopy measurements are of much more interest than increased resolution alone.

3. DATA AND COMPARISON

A comparison of near-field and far-field spectra on KTP can be seen in figure 1. This figure indicates a change in selection rules in the near field and a decrease in the Rayleigh tail. We present three Raman spectra which have been normalized. We expect to see a peak at 215 cm^{-1} due to excitation with the electric field vector in the plane of the surface (transverse) in this 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. The larger area under the peak can be explained by a change in selection rules so that the Raman peak at 220 cm^{-1} , which has been observed for other scattering geometries¹², is active. This peak would only be present if there were a z-polarization component of the light in the near-field. This z-polarized light, present only near the metallic aperture with the probe in the near field, is the origin of the selection rule change and permits analysis of the vibration modes in three dimensions at high spatial resolution.

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 1, 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. The Rayleigh tail is due to elastic scattering from sample inhomogeneities, and is expected to be reduced due to the small sampling volume in the near-field measurements.

The two features at 667 cm^{-1} and 715 cm^{-1} in figure 2 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.⁴

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.

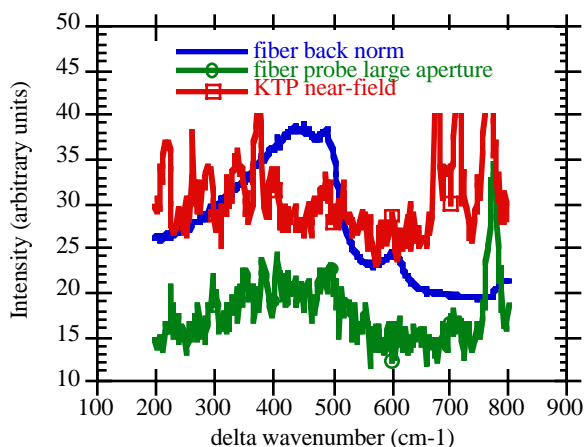


Figure 3. Raman scattering from the quartz fiber is observed in a large aperture probe, but not in the near-field spectrum indicating a surface enhancement.

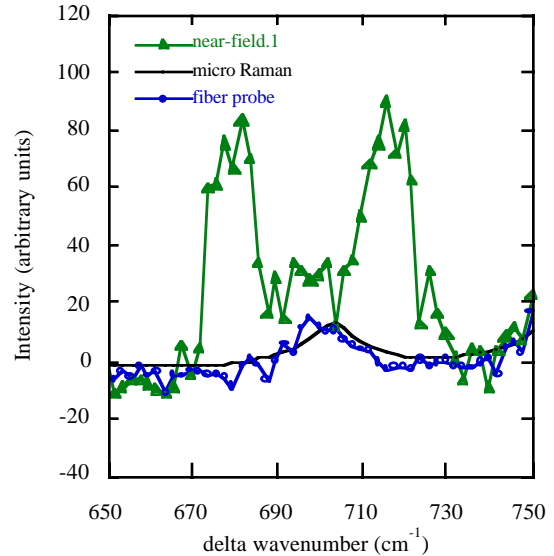


Figure 2. Three normalized Raman spectra are shown. The spectrum obtained in the near-field contains two peaks not found in the far-field micro-Raman spectrum or in a far-field spectrum obtained through a fiber probe.

4. CONCLUSIONS

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.

5. ACKNOWLEDGEMENTS

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