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## **Fundamental differences between micro- and nano-Raman spectroscopy**

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### **Summary**

Electric field polarization orientations and gradients in the near-field of near-field scanning optical microscope (NSOM) probes render nano-Raman fundamentally different from micro-Raman spectroscopy. With  $x$ -polarized light incident through an NSOM aperture, transmitted light has  $x$ ,  $y$  and  $z$  components allowing nano-Raman investigators to probe a variety of polarization configurations. In addition, the strong field gradients in the near-field of an NSOM probe lead to a breakdown of the assumption of micro-Raman spectroscopy that the field is constant over molecular dimensions. Thus for nano-Raman spectroscopy with an NSOM, selection rules allow for the detection of active modes with intensity dependent on the field gradient. These modes can have similar activity as infra-red (IR) absorption modes. The mechanism can also explain the origin and intensity of some Raman modes observed in Surface Enhanced Raman Spectroscopy, or SERS.

### **Introduction**

When micro-Raman spectroscopy became a viable technique, there was some question as to whether there were fundamental differences between it and conventional Raman spectroscopy (Delhaye & Dhamelincourt, 1975; Rosasco *et al.* 1975). As it turned out, the introduction of a microscope objective in micro-Raman spectroscopy introduced no fundamental changes in the technique. Thus micro-Raman is now viewed as a conventional Raman technique simply with enhanced resolution that is bounded by the far-field diffraction limit.

As near-field techniques have matured, spectral analysis coupled with nanometric resolution has become a reality (Paesler & Moyer, 1996), and a new question has emerged: Are there fundamental differences between micro- and nano-Raman spectroscopy? This time the question is answered resoundingly in the affirmative. There *are* fundamental differences that lead to new capabilities and new interpretations of Raman data.

The electric field in the vicinity of an NSOM probe is distinct in three very important ways from the field of a spot focussed as tightly as possible on a small region of space. First, in the near-field evanescent fields contribute considerably and intensities are often much stronger than those that can be obtained in conventional far-field configurations. In NSOM, the large majority of this enhanced intensity is localized to a region directly in front of the aperture. Since this region is normally obscured from the collection optics in reflection-mode nano-Raman configurations, this difference is of little consequence. Second, for  $x$ -polarized light passing towards the NSOM probe, light with  $x$ -,  $y$ - and  $z$ -components will be present in a small sample volume near the output of the probe. This allows for excitation of a variety of modes without requiring reorientation of the sample. A third effect in nano-Raman spectroscopy results from the strong electric field gradients in the vicinity of the NSOM probe. In the standard derivation of the Raman effect, one assumes a constant electric field. Even for confocal Raman spectroscopy, this is an excellent approximation; the electric field intensity does not change measurably over molecular distances. In nano-Raman spectroscopy, on the other hand, the presence of a non-negligible field gradient affects the measurement in a fundamental way.

In the following section, Raman spectroscopy is briefly outlined to give a framework for the following two sections on polarization and gradient effects. Then, following a brief section on experimental design, results of nano-Raman measurements provide demonstrations of both the polarization and the gradient field effects.

## Raman spectroscopy

The polarization  $P$  of the material depends on the polarizability  $\alpha$  of the material and on the electric field  $E$  of the incident light at frequency  $\nu_o$  (Ferraro and Nakamoto, 1994).

$$P = aE_o \cos(2\pi\nu_o t).$$

Charges in the material may oscillate at some frequency  $\nu_m$  about their equilibrium positions:

$$q = q_o \cos(2\pi\nu_m t).$$

Usually the electric field magnitude  $E_o$  is presumed to be constant over the dimensions of the oscillations. This is an excellent approximation for visible light in far-field configurations. The oscillations may, however, induce a change in the polarizability of the material, which can be approximated by a Taylor expansion of  $\alpha$ :

$$a = a_o + \left. \frac{\partial a}{\partial q} \right|_{q_o} q + O(q^2).$$

Combining these and simplifying gives, to first order in  $q$ ,

$$P = \alpha_o E_o \cos(2\pi\nu_o t) + \frac{1}{2} q_o \left( \frac{\partial \alpha}{\partial q} \right)_o E_o \left[ \cos\{2\pi(\nu_o - \nu_m)t\} + \cos\{2\pi(\nu_o + \nu_m)t\} \right] + O(q^2)$$

The first of these terms is the Rayleigh scattering, and the second is the Raman scattering. The existence of Raman-scattered light depends on the Raman activity,  $\partial\alpha/\partial q$ . If there is no change in the polarizability for a given vibrational transition then  $\partial\alpha/\partial q = 0$ , and the transition is not Raman-active. In three dimensions, change in the polarizability tensor determines the activity, and the vibration is Raman-active if any one of the polarizability tensor components is changed during the vibration.

## Polarization effects

Whether one appeals to the more idealistic analytical results of Bethe (1944) and Bouwkamp (1950) or any of the more recent realistic numerical work such as that of Martin (1999), theoretical work suggests that with  $x$ -polarized light incident on an aperture, the transmitted light has  $x$ ,  $y$  and  $z$  components. The total intensity of the transmitted radiation varies strongly with distance from the tip, as do each of the components.

In conventional normal incidence Raman spectroscopy, vibrational modes with  $x$  or  $y$  components are excited by the incident light, which is necessarily polarized in the  $xy$  plane. Modes with purely  $z$  components require an electric field in the  $z$  direction for excitation. The  $z$  modes are usually measured by reorienting the crystal so that the incident light has a polarization component along the desired axis. In near-field Raman, there is a  $z$  component of the field which provides excitation of these modes without reorientation of the crystal. Theoretical studies show that the integrated  $z$  polarization intensity in the very near field is actually stronger than the *total* field in the far-field.

## Field gradient effects

Classically, the effect of the field gradient can be explored by taking a Taylor expansion of the electric field

$$E = E_o + \frac{\nabla E}{\nabla q} q + O(q^2)$$

and including it in the above derivation. This results in a polarization given by

$$\begin{aligned} P &= a_o E_o \cos(2pu_o t) \\ &+ \frac{1}{2} q_o \frac{\nabla a}{\nabla q} E_o [\cos\{2P(u_o - u_m)t\} + \cos\{2P(u_o + u_m)t\}] \\ &+ \frac{1}{2} q_o \frac{\nabla E}{\nabla q} a_o [\cos\{2P(u_o - u_m)t\} + \cos\{2P(u_o + u_m)t\}] + O(q^2) \end{aligned}$$

The first two terms of are the same as before. The third describes a scattering with the Stokes and anti-Stokes frequency shifts similar to the Raman lines. Instead of a dependence on activity  $\partial\alpha/\partial q$ , however, this scattering term is dependent on the field gradient and the polarizability. Selection rules for this term depend on the characteristics of  $\alpha$ , and so would have similar activity as IR absorption spectroscopy. This is the gradient field Raman - or GFR - term.

An identical result follows quantum mechanically. In this case, transitions in vibration levels due to coupling with a radiation field are described by the perturbation Hamiltonian:

$$H = \mathbf{m} \cdot \mathbf{E}$$

where  $\mathbf{m}$  is the dipole moment and  $\mathbf{E}$  is the electric field. The electric dipole moment can be written as

$$\mu_a = \mu_a^p + \alpha_{ab} E_b + \frac{1}{3} A_{abc} \frac{\partial E_b}{\partial c} + \dots$$

where the  $\{a,b,c\}$  are a permutation of the coordinates  $\{x,y,z\}$  and summing over repeated indices is implied.  $B$  is the magnetic field;  $\alpha$  and  $A$  are given by: (Sass, *et al.*, 1981)

$$\alpha_{ab} = \frac{1}{\hbar} \sum_j H(\omega) \langle i | \mu_a^p | j \rangle \langle j | \mu_b^p | f \rangle$$

$$A_{abc} = \frac{1}{\hbar} \sum_j H(\omega) \langle i | \mu_a^p | j \rangle \langle j | \theta_{bc} | f \rangle$$

where  $H(\omega) = \frac{W_{ji}}{\omega_{ji}^2 - \omega^2}$ ; and where  $\mu^p$  and  $\theta$ ,  $m$  are the permanent electric dipole and the quadrupole operator, respectively, and  $\langle i |$  and  $| f \rangle$  are the initial and final states of the system, respectively.

The derivation of the spectroscopic signals originates with a first-order expansion of  $\mu$  in the coordinate of vibration  $q$ . Terms without  $q$  dependence may be discarded since they will not couple adjacent vibration states. Upon removal of high order terms that are small even in the case of large field gradients, the relevant dipole terms can be written as:

$$m_a \approx \frac{\partial \mu_a^p}{\partial q} + \frac{1}{2} \frac{\partial^2 \mu_a^p}{\partial q^2} E_b + \frac{1}{6} \frac{\partial^3 \mu_a^p}{\partial q^3} E_b E_c + \frac{1}{24} \frac{\partial^4 \mu_a^p}{\partial q^4} E_b E_c E_d$$

These four terms result in IR absorption, Raman, gradient field Raman (GFR), and quadrupole-Raman, respectively.

The ratio of the GFR term to the Raman term depends upon the field gradient and the polarizability gradient. We approximate the polarizability gradient by  $\alpha/a$ , where  $a$  is close to an atomic dimension. This gives us a ratio of GFR to Raman of:

$$\frac{G}{R} \approx \frac{a}{E} \frac{\partial E}{\partial q}$$

In vacuum, the field gradient yields terms of the order  $(2\pi/l)E_b$ . The ratio of the GFR term to the Raman term is then (for 500 nm light and  $a = 0.2$  nm)

$$\frac{G}{R} \approx \frac{a}{E} \frac{2\pi}{l} E_b = \frac{2\pi a}{l} \approx 3 \cdot 10^{-3}$$

Thus, any GFR contribution is insignificant in vacuum.

Near a metal surface, the jellium approximation (Feibelman, 1975) indicates that the normal component of the electric field varies by nearly its full amplitude over a distance of 0.2 nm. The field gradient is then approximately  $E_b/0.2$  nm, and

$$\frac{G}{R} \approx \frac{a}{E} \frac{E_b}{0.2 \text{ nm}} \gg 1$$

One thus could expect to find a measurable GFR signal near metal surfaces.

The GFR differs appreciably from Raman spectroscopy in selection rules. These rules result from the requirement that  $\langle Y_f | \mathbf{m} \cdot \mathbf{E} | Y_i \rangle$  be nonzero. The  $q$  dependence of  $\mu$  means that this expectation will be nonzero if the  $\psi$  differ by one vibrational quantum. In addition, the coefficient of  $q$  must be nonzero. The Raman selection rules are determined by the requirement

$$\frac{\partial \mu}{\partial q} \neq 0$$

This is equivalent to the condition that  $\alpha$  and the vibration belong to the same symmetry species (Ferraro & Nakamoto, 1994). Conversely, the GFR selection rules require that  $\mathbf{E}$  belong to the same symmetry species as the vibration, or

$$\frac{\partial \mathbf{E}}{\partial x_{q=0}} \neq 0$$

This will be true if the vibration has a component normal to the surface, since that is the direction in which  $\mathbf{E}$  varies most rapidly. The polarizability must also be nonzero. For example, if  $z$  is normal to the surface, then  $\alpha_{az}$  and  $E_a$  must be non-zero. This is the case for NSOM, in which the largest components of  $\mathbf{E}$  are near the probe (Betzig & Trautman, 1992), but it is certainly not the case in far-field measurements. The GFR effect should scale with polarizability, and should thus be stronger for ionic systems. This is in contrast to Raman spectroscopy, which typically is stronger for covalent bonding. The GFR effects should also be strongest for the vibration modes for which infrared absorption is strong. That is, the GFR spectra will complement the Raman spectra in many materials, particularly centro-symmetric materials. The extra requirement for observation of the GFR effect is a strong field gradient along the vibrating bond.

The effects of a strong electric field gradient on Raman spectra has been discussed previously as a mechanism for some of the observed spectral lines in SERS (Sass, *et al.*, 1981). As there is no good, controllable method of regulating distance or field gradient in SERS, NSOM-Raman offers the first opportunity to test the distance dependence of this effect. The GFR effect was also predicted as an effect in the Raman spectra of microparticles suspended in laser traps (Knoll, *et al.*, 1988).

### Experimental set-up

Aluminum coated etched fiber tips were positioned near the surface of samples under investigation, and spectra were taken with the tip near the surface under lateral force feedback. The NSOM was used in the illumination mode with 514 nm laser light. Reflected light is collimated with a 0.50 NA lens and is passed through a holographic filter, focussed into a single stage 1 meter spectrometer, and collected onto a cooled CCD camera. Light reflected from the filter is simultaneously gathered to provide a reflection image and to verify that observed effects are not attributable to laser power fluctuations.

The tip mounting assembly eliminates problems associated with high mechanical Q and allows for large collection efficiency, see Fig. 1. By gluing one leg of the tuning fork to the base, the symmetry of the oscillator is destroyed and the resonator changes from a low-loss tuning fork to a high-loss vibrating beam with a resonance of 35-37 kHz. With one arm of the fork fixed, higher level harmonics in the fork do not cancel and are used for feedback. At the second cantilever beam mode around 90 kHz the Q is reduced by a factor of ten and the mechanical limit on bandwidth is reduced by a factor of 30 or more. Scanning of the sample is accomplished with a standard four-quadrant piezo tube, and the coarse approach mainframe consists of a monolithic double-compound flexure. The collection optics, scan tube/sample holder, and tip mount are all affixed to the flexure which is firmly mounted inside a copper thermal isolation box. The material studied is  $\text{KTiOPO}_4$  (KTP) a non-linear optical material used for second harmonic generation.

## Results and discussion

A Raman spectrum taken with the tip held in the far-field of the sample is shown in Fig. 2. The  $767\text{ cm}^{-1}$  peak is the symmetric A1 vibration reported in both near- and far-field measurements (Kugel, *et al.*, 1988; Jahncke *et al.*, 1995). Features at  $698\text{ cm}^{-1}$  and at  $631\text{ cm}^{-1}$  can be identified as an A2 vibration and a weaker A1 vibration, respectively. The shoulder at roughly  $800\text{ cm}^{-1}$  could be associated with a vibration at  $789\text{ cm}^{-1}$  reported by Yang, *et al.* (1986).

As the tip is brought into the near-field of the sample, the features change subtly. Difference spectra allow one to focus on the changes in the spectrum as the near-field effects come into play. Thus, a series of spectra were obtained as the tip approached the sample, and each spectrum was subtracted from a far-field NSOM spectrum such as that of Fig. 2. Each spectrum took several minutes to obtain. These difference spectra are shown in Fig. 3. From the top to the bottom, the spectra correspond to the following positions: (a) in contact with the surface, (b) just out of contact, (c)  $47\text{ nm}$  further than the b spectrum, (d)  $70\text{ nm}$  further than the b spectrum, (e)  $108\text{ nm}$  further than the b spectrum, and (f)  $127\text{ nm}$  further than the b spectrum. Reading from bottom to top, it is clear that a large feature at  $785\text{ cm}^{-1}$  appears as the tip is brought into the near-field of the sample. This peak can be identified as that reported by Yang *et al.* (1986) at  $783\text{ cm}^{-1}$  which possesses B1 symmetry. The B1 symmetry requires a polarization component in the z-direction, normal to the surface. The data of Fig. 3 thus provide a demonstration of the fact that varying polarization states may be sampled in an NSOM Raman experiment merely by adjusting the distance between the tip and the sample. This capability is unique to nano-Raman.

As further evidence that the feature at  $785\text{ cm}^{-1}$  is indeed a z-sensitive Raman mode, the distance dependence of this feature is plotted in fig. 4. Also shown is the distance-dependence of the squared z-component of the electric field as calculated by the Bethe-Bouwkamp model (Bouwkamp, 1950). One arbitrary scale factor is used to shift the data along the ordinate. This scaling is equivalent to assuming a certain aperture size. (The single point on the ordinate represents the contact spectrum. Its coordinate on the abscissa is somewhat arbitrary since the tip flexes on contact.) Agreement between the data and the theoretical fit of Fig. 4 suggest that the  $785\text{ cm}^{-1}$  mode is indeed attributable to a z-sensitive Raman mode. In these NSOM nano-Raman spectra, therefore, clear sensitivity to z-polarization Raman activity is evident.

In a spectrum taken over several hours in a similar NSOM configuration, a peak emerges that cannot be attributed to a Raman active mode of any orientation - including z-polarization. This peak appears at  $712\text{ cm}^{-1}$  as can be seen in Fig. 5. In this raw (unfiltered non-difference) spectrum, several Raman peaks can be identified. The left peak at  $683\text{ cm}^{-1}$  is a B1 vibrational mode. The hump at  $695\text{ cm}^{-1}$  is the A2 vibration, and the familiar peak at  $676\text{ cm}^{-1}$  is the A2 symmetrical vibration. The peak at  $712\text{ cm}^{-1}$  is not explained by conventional Raman or z-polarization effects. Once again, the distance dependence of the peak is instructional. In figure 6, the near-field enhancement of the  $712\text{ cm}^{-1}$  peak is plotted as a function of distance. According to the theory developed above, if the peak does indeed represent the GFR effect, its height should scale with the magnitude of the z-component of the electric field times its gradient. This dependence is shown as the dashed line in the figure. Given the noise in the data, the fit can be said to

be semi-quantitatively correct. The peak may therefore be identified as the well-known IR active mode at  $712\text{ cm}^{-1}$ . It is rendered observable in this Raman spectrum by the presence of the large electric field gradient in the near-field of the NSOM probe.

## Conclusion

Nano-Raman spectroscopy is fundamentally different from micro-Raman spectroscopy. In NSOM-based nano-Raman experiments, alternative polarization states may be sampled by adjusting the tip-sample spacing. In particular, z-polarization active modes become observable when the tip is in the near-field of a sample surface (in the x-y plane) that is illuminated through a probe excited with x-polarized light. Also, IR active modes can be observed in nano-Raman spectroscopy because of the large field gradients in the near-field of an NSOM probe.

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## Figure Captions

**Fig. 1.** NSOM tip-holder assembly and collection optic. The holder is a one inch long conventional microscope cover slide. The tuning fork is glued to the end of the holder. A slot is cut in the aspheric lens to accommodate the fork and tip.

**Fig. 2.** Typical KTP Raman spectrum. This spectrum was taken with the NSOM configured as shown in Fig. 1.

**Fig. 3.** KTP difference spectra at varying near-field distances. Spectra represent the difference between the spectra taken and the spectrum taken with the tip retracted to the far-field as in Fig. 2. Reading from the top to the bottom, the distances are: (a) in contact with the surface, (b) just out of contact, (c) 47 nm further than the b spectrum, (d) 70 nm further than the b spectrum, (e) 108 nm further than the b spectrum, and (f) 127 nm further than the b spectrum.

**Fig. 4.** Integral of the area under the  $785\text{ cm}^{-1}$  peak versus distance between the sample and the tip. The solid line represents a numerical integration of the Bethe-Boukamp model of the z-component of the electric field.

**Fig. 5.** A nano-Raman scan of KTP with the tip in the near-field of the sample. The peaks at  $683$ ,  $695$ , and  $676\text{ cm}^{-1}$  are identifiable Raman peaks. The peak at  $712\text{ cm}^{-1}$  is not explained by conventional Raman or z-polarization effects. It may be identified as an IR active mode excited by the large electric field gradient inherent in nano-Raman spectroscopy performed with an NSOM.

**Fig. 6.** Near-field enhancement of the  $712\text{ cm}^{-1}$  peak. The dashed line represents a fit to the magnitude of the z-component of the electric field times the gradient of that field.