

Chapter 4

Tip-sample distance dependence

The tip-sample distance dependence of TER scattering of guanine and ClO_4^- ions adsorbed on a atomically flat Au(111) surface has been studied. The intensities of the discrete Raman bands of the adsorbates decrease steeply by almost two orders of magnitude upon retracting the tip by only about 20 nm. Together with the lateral resolution, which was estimated to be about 30 nm,[53] this elucidates the high spatial resolution of TERS not only parallel, but also perpendicular to the surface. The measurement of the TER intensity over more than 20 nm of tip-surface distance enabled the quantitative comparison with recent theoretical calculations by Notingher *et al.*[35] The rapid decay of the band intensities is attributed to the fast decrease of the near-field enhancement of excited LSP in the tip-substrate cavity with increasing tip-sample distance z , following an z^{-10} behaviour.

In addition to studies on the dependence of TER band intensity on the tip-sample distance, the behaviour of the TER background was investigated. It was attributed to tip-enhanced fluorescence-like emission from the adsorbate (or an adsorbate-metal complex). The background intensity shows a similar steep decrease with increasing tip-sample distance as the Raman bands. As expected, the enhanced field acts equally on both Raman and luminescence scattering. Our experimental results were compared to several theoretical studies on the distance dependence of enhanced luminescence.

In contrast to the adsorbate bands, the background shifts significantly towards lower frequencies during the retraction of the tip. This provides direct experimental evidence

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for the frequency shift of LSP resonances in the tip-substrate cavity upon changing the tip-sample distance, and, therefore, strongly underlines the electromagnetic nature of the tip-enhancement mechanism. Such a blue shift with increasing distance had long since been predicted by theory, but up to now never proven experimentally.

Our experimental data remarkably well resemble theoretical data published by Käll *et al.*,[64] as seen in Fig. 4.1. See following text for a detailed discussion.

4.1 Experimental part

The experiments are performed on an atomically smooth Au(111) single crystal surface prepared by flame-annealing, as described in Chapter 3. To coadsorb guanine and perchlorate, the Au crystal is immersed into an ethanolic solution of 10^{-3} M guanine and 10^{-1} M HClO₄ for one hour. Afterwards, the sample is rinsed with ethanol to remove multiple adlayers.

To measure the tip-sample distance dependence of the TER signal, the feed-back loop of the STM is gated and the z-position of the tip controlled by a programmable voltage-ramp generator. Tip retraction with constant speed is started 5 to 10 s after gating the feed-back loop. During the retraction of the tip, a series of Raman spectra (1 s integration time) is recorded at intervals of about 1.5 s.

Three different measurement series of different retraction speeds, 0.16 nm/s (8 nm retraction distance z_{retr}), 0.32 nm/s ($z_{retr} = 16$ nm) and 1.6 nm/s ($z_{retr} = 80$ nm), are reported and analyzed. All spectra were normalized by subtracting the one recorded without tip ($z = 1 \mu\text{m}$) to eliminate possible contribution from far-field illumination or light scattering by the metal substrate.

4.2 Raman band decrease with increasing z

Our experimental set-up employing an STM leads to much more reliable data than AFM-TERS studies on the band intensities versus distance behaviour found in the literature:[55, 65–68] An STM-tip is held stable at a well-defined distance above the sample, in contrast to an AFM-tip that oscillates with an amplitude of several tens of

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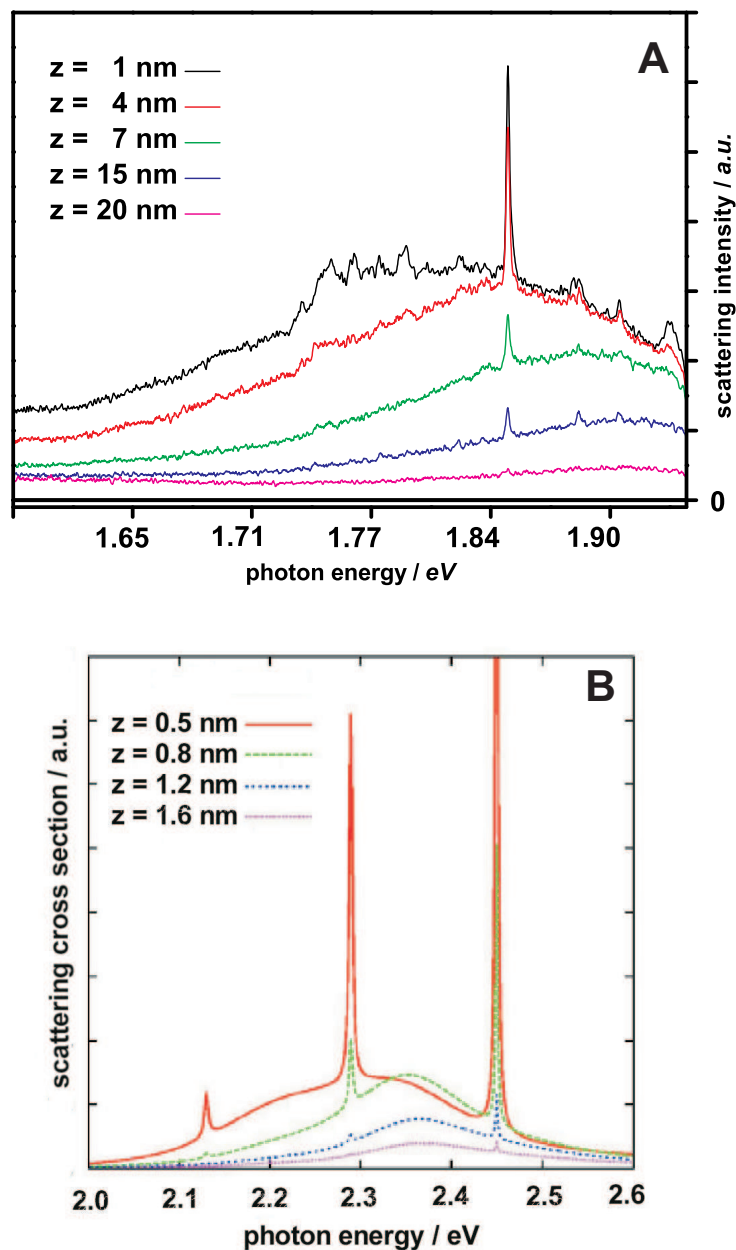


Figure 4.1: A theoretical calculation by Käll and coworkers for a dye molecule "floating" between two Ag spheres (B) produces spectra that show a remarkable similarity to our experimental ones (A) if one takes into account the different energies for surface plasmons in Ag and in Au. Figure B reproduced from Ref. [64].

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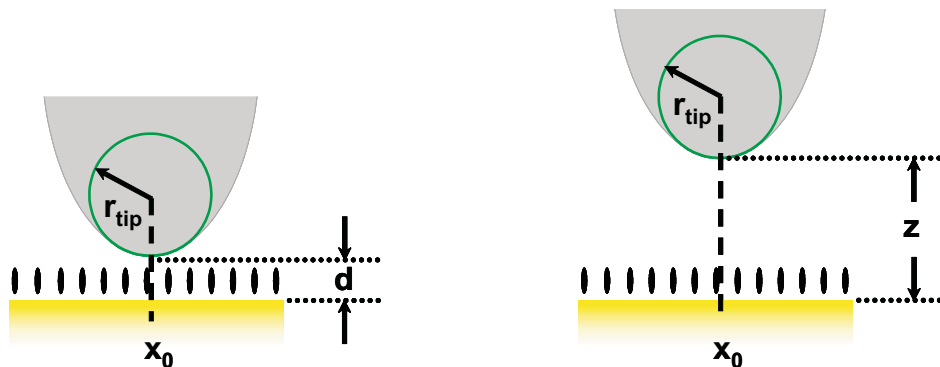


Figure 4.2: In tunneling contact, the tip is located approximately 1 nm above the sample surface. By the use of an external voltage ramp generator, the tip is retracted further over a retraction distance z_{retr} during the experiment, so that the overall tip-sample distance $z = d + z_{retr}$.

nanometres.[67, 68] For correct determination of the near-field distribution underneath a metal tip, especially at smallest tip-sample separations of 1-5 nm, where the field enhancement is maximal, such oscillations are an unsurmountable hindrance to data interpretation as they inevitably lead to a nonlinear average of the Raman signal for each data point. Therefore, we employ an STM-tip controlled by piezo crystals to gain a much more precise insight into the band and background behaviour, i.e. the vertical near-field distribution, with varying gap length.

Both adsorbed species, guanine and perchlorate, show TER scattering. With the tip in tunneling position ($d = 1$ nm), a number of characteristic guanine bands appear very weak in intensity, while perchlorate shows a characteristic, intense band at 930 cm^{-1} , assigned to its A_1 breathing mode.[69] In contrast to the guanine bands that decrease slowly with proceeding illumination without tip retraction due to bleaching, the ClO_4^- -band intensity remains unaffected. Therefore, for quantitative TER intensity versus distance profiles, the intensity of this band was evaluated (compare Fig. 4.3). It should be emphasized that the bands of coadsorbed guanine molecules decrease similarly with increasing tip-sample distance.

The integral intensity of the Raman line at 930 cm^{-1} is plotted versus the tip-surface distance in Fig. 4.4. The data are extracted from three series of TER spectra with total retraction lengths of 6 nm, 12 nm and 50 nm (retraction speeds of 0.16 nm/s,

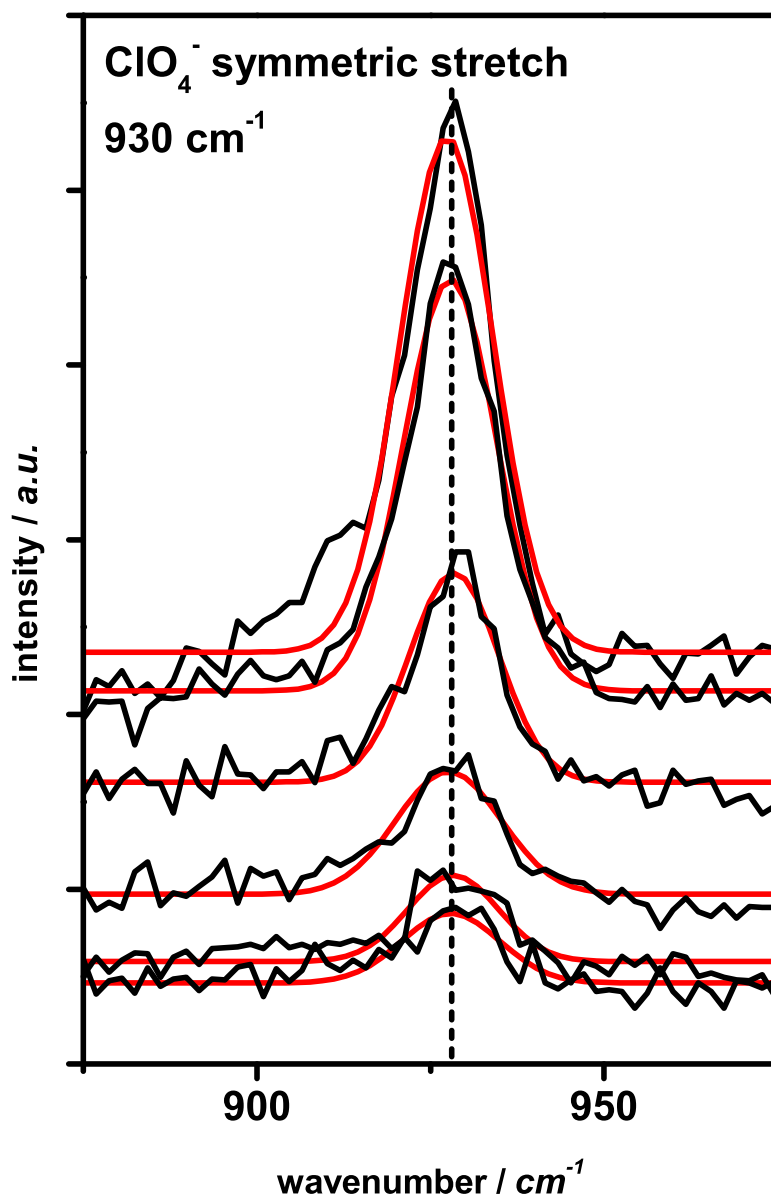


Figure 4.3: The time series of TER spectra recorded during tip retraction shows the decrease of the ClO₄⁻ band intensity and of the background with increasing tip-sample distance. The spectrum is found to be stable over time if the tip is kept in tunneling position.

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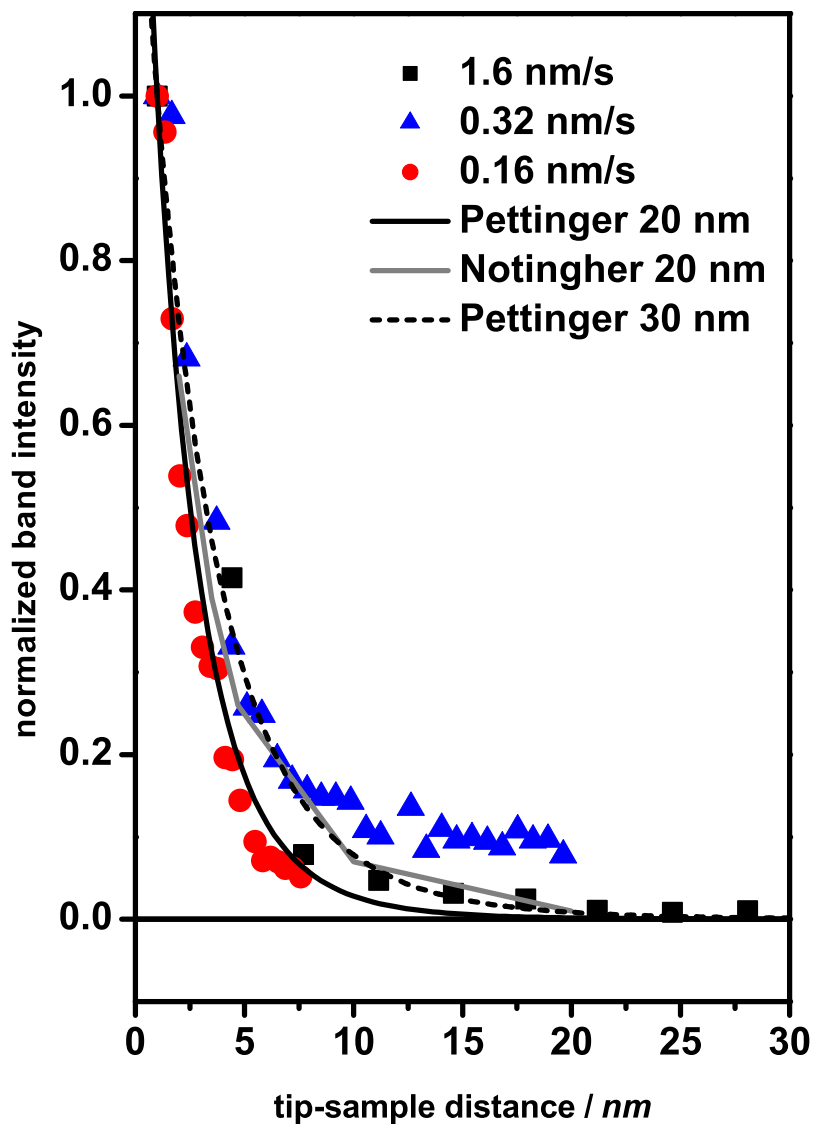


Figure 4.4: The ClO_4^- band intensity vs tip-sample distance z is plotted. It shows that hardly any Raman signal can be detected when $z \geq 15$ nm, following a $1/z^{10}$ -distance dependence (see text for details). Squares: experimental data; solid line: fit according to Eq. 2.1.

4.2 Raman band decrease with increasing z

0.32 nm/s and 1.6 nm/s, respectively). For accurate determination of the integral intensities, particularly for the weak band intensities at large tip-sample distances, the 930 cm^{-1} band was fitted by two Gaussian curves and a linear background (Fig. 4.3). The integral band intensity was normalized to 1 at $z = d = 1\text{ nm}$, which is the approximate tip-surface distance in tunneling mode. The TER intensities from all three series exhibit the same steep decrease with increasing tip-surface distance, reaching about one percent of the initial intensities at around 20 to 30 nm tip-sample distance. This behaviour is independent of the retraction speed, as expected.

Applying Eqn 2.1,[53] the experimental data from Fig. 4.4 could be very well fitted for $r_{tip} = 30\text{ nm}$, which is in reasonable agreement with the measured radius of the tip of approximately 20 nm. Within the framework of the sphere-substrate model, the extended body of a real tip is accounted for by an effective sphere radius somewhat larger than the real radius of the tip. Recent finite element calculations by Notinger *et al.* (compare Chapter 2.5.2) on the distance dependence of the Raman enhancement underneath a tip with $r_{tip} = 20\text{ nm}$ are also included in Fig. 4.4. Since in those calculations the minimum tip-surface distance was 2 nm, Notinger's theoretical data was normalized to Pettinger's theoretical intensity values (according to Eqn 2.1) at 2 nm distance, which also agrees well with the experimental average at this point.

Apparently, the experimental data match both calculations over two orders of magnitude. However, in Notinger's calculations, no metal substrate surface is taken into account, and the Raman enhancement refers only to the position directly beneath the tip apex, not considering the lateral extension of the near-field. The actions of these two differences are likely to cancel each other. The general behaviour of the TER intensity with increasing tip-sample distance is in agreement with the observations by Raschke *et al.* for the tip-sample coupling upon elastic light scattering in AFM-aSNOM. For very sharp metal tips, the scattered near-field signal was found to decay strongly within 5 nm.[70] However, as our TERS apparatus is based on an STM, it allows a much more precise positioning of the tip by piezo control than in the case of AFM-TERS, where the tip is oscillating above the surface, which results in a smaller error in our measurements.

4.3 Background decrease with increasing z

Integration over the entire spectral range reveals that the background continuum actually represents the major part of the inelastic scattering. The very pronounced Raman peaks that stick out from the background only contribute a minor part to the overall scattering intensity. The origin of the background, which is commonly observed in TE(R)R and SE(R)R spectra, but absent in normal Raman (NR) spectra, is still under discussion, and spectra are therefore often presented after background correction in the literature (e.g. Refs [32, 33, 53, 71]).

In 1979, it was proposed by Gersten *et al.* that the background is caused by luminescence from an electron-hole pair combination of an adsorbate-metal complex.[72] Otto *et al.* explained it similarly as a by-product of a non-radiative charge transfer between surface and molecule, an electron-hole pair formation and recombination.[73] In a more recent publication, Le Ru and Etchegoin present theoretical calculations in which they assign the background to a "broad emission from all possible virtual states".[74]

It is highly unlikely that the background scattering stems from the metal alone, because the enhanced Raman intensity is found to be roughly proportional to the background intensity,[75] and no emission was found for a perfectly clean substrate.[76] The background is undoubtedly connected to the adsorbate or an adsorbate-metal complex.[77–80] Weiss and Haran report a connection between background and Raman band intensity in their spectra.[81] They show that the background exists only in the presence of the spectrum and vice versa. A similar association of SER scattering and background continuum was found by Moore *et al.*[82]

Among the various theories on the origin of the broad continuum, one has recently regained a lot of attraction: surface-enhanced luminescence.[83–86] Already in the 1980s, theoretical and experimental SERS papers dealt with the apparent concurrence of quenching and enhancement at rough Ag surfaces.[87, 88] Pettinger and Gerolymatou showed that, in fact, the background intensity in a SER spectrum is comparable to the fluorescence spectrum from solution, although the quantum yield of surface-enhanced fluorescence lies only around 10^{-4} because of metal damping effects.[89]

Käll *et al.* carried out a density matrix calculation of surface-enhanced resonant

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Raman scattering and fluorescence of a molecule trapped between two silver spheres, discussing the influence of the field enhancement on these processes. Both are surface-enhanced, but to a different degree, which results in a structured fluorescence background underneath the Raman bands (see Fig. 4.1).[64, 90]

Neither guanine nor perchlorate molecules show fluorescence in the visible in NR spectroscopy. However, in the recorded TER spectra, a significant background is found. Weitz *et al.* compared Raman band and background (fluorescence) intensity of resonant and nonresonant molecules.[23] Interestingly, they found that the lower the fluorescence quantum yield of the free molecule is, the higher enhanced the fluorescence, in spite of the reduced emission via additional decay channels in the metal surface. Therefore, we assume that the continuum is due to a fluorescent-like enhanced emission from the adsorbate or an adsorbate-metal complex. The mechanism for particle-enhanced luminescence, however, is not quite understood yet: Part of the effect might be due to the coupling of surface plasmons and either excitation light, fluorescent radiation or both.[91] We have examined the background behaviour during tip-retraction and compared it to experiment and theory in the literature.

In Fig. 4.5, the spectral changes during tip retraction are shown. At tunneling distance, a very intense background continuum (in addition to the pronounced Raman bands) is recorded that is slightly asymmetric with respect to the examined wavenumber region, exhibiting a maximum at around 1300 cm^{-1} . With increasing tip-sample distance, the background alters its shape to an even less symmetric one, decreasing in integral intensity and blue-shifting its maximum. Even at full retraction of the tip (several tens of nanometers) the background is still present. Complete removal of the tip ($z = 1\text{ }\mu\text{m}$) leads to another significant decrease of the signal, but a still measurable intensity. which is attributed to far-field scattering of the adsorbate or of the metal substrate itself: Typical fluorescence/luminescence cross sections (10^{-6} cm^2) are so much larger than typical Raman cross sections that it should be expected to obtain relatively intense luminescence scattering by a monolayer from far-field illumination only, i.e. molecules located in the broad laser focus. The given experimental conditions cannot assure a perfectly clean substrate, and, especially at very low adsorbate coverages (compare Chapter 5.3), part of the background may actually stem from contamination adsorbate. With the current set-up, experiments with a supposedly

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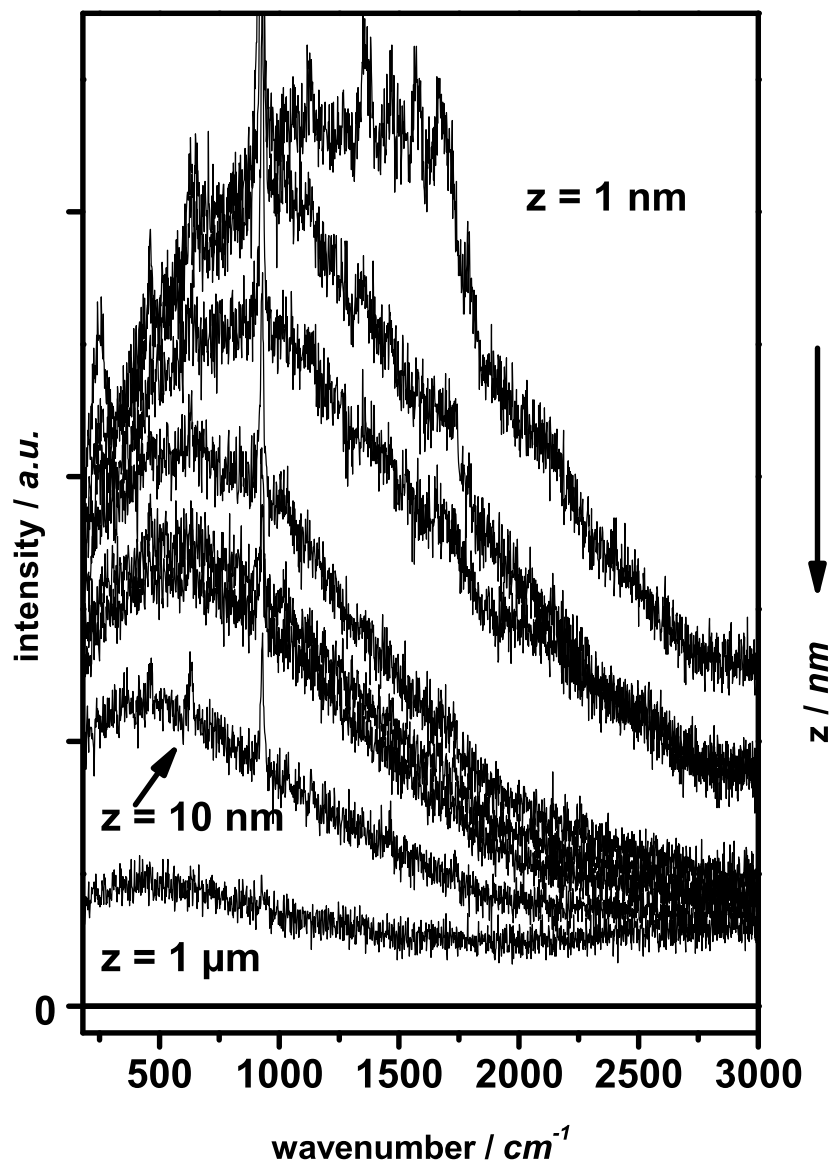


Figure 4.5: In tunneling contact, the TERS spectrum exhibits defined Raman bands on top of a large background. The background decreases when the tip is retracted, but does not cease to zero intensity in contrast to the discrete Raman bands.

4.3 Background decrease with increasing z

”clean” gold substrate will always show Raman bands and a fluorescent-like background continuum resulting from unknown contamination. It would be interesting to carry out TER studies on a pure Au(111) surface working in an inert gas atmosphere to investigate possible spectral contributions from the substrate. The data presented in the following has been corrected for this ”intrinsic” scattering to extract the near-field contribution by subtraction of the TER spectrum recorded after tip removal ($z = 1 \mu\text{m}$).

In Fig. 4.6, the integrated background intensity obtained from a Lorentz fit of the TER spectra after correction is plotted versus the tip-sample distance z for two different retraction speeds. For comparison, the fit curve of the band intensity decrease with increasing z from Fig. 4.4 was added. Up to around $z = 5 \text{ nm}$, band and background intensities decrease similarly. At larger distances, in contrast to the band intensity, the background intensity does not cease to zero, but remains at about 10% of the maximum intensity recorded upon tunneling conditions over the recorded tip-sample distance of 30 nm. This means that there is still a significant amount of luminescence photons when the tip-sample gap is quite large and the Raman enhancement at the sample already negligible.

The observed similarity in behaviour of Raman bands and background scattering at small tip-sample distances up to around 5 nm is explained by the underlying enhancement phenomenon: The resonant excitation of surface plasmons in the tip apex leads to an increase in the local field strength in the tip-sample cavity. Similar to the phenomenon of giant Raman scattering, a significant enhancement of luminescence scattering takes place. De-excitation of the molecule via the LSP mode is preferred over the nonradiative decay channel (excitation of electron-hole pairs) that usually leads to a quenching of the fluorescence of an adsorbate monolayer.[92–94]

The concurrence of quenching and enhancement has often been described in the literature.[95–99] In contrast to enhanced Raman scattering, which is strongest at shortest metal-metal distances, theory predicts an optimal molecule-metal distance of 2-4 nm, when largely enhanced luminescence can be observed, where the enhancement process prevails over the quenching.[64, 94, 100] For a molecule-metal separation $z > 20 \text{ nm}$ quenching is negligible and the electromagnetic field enhancement dominates, whereas the quenching prevails over enhancement for $z < 5 \text{ nm}$.[94] It was found that

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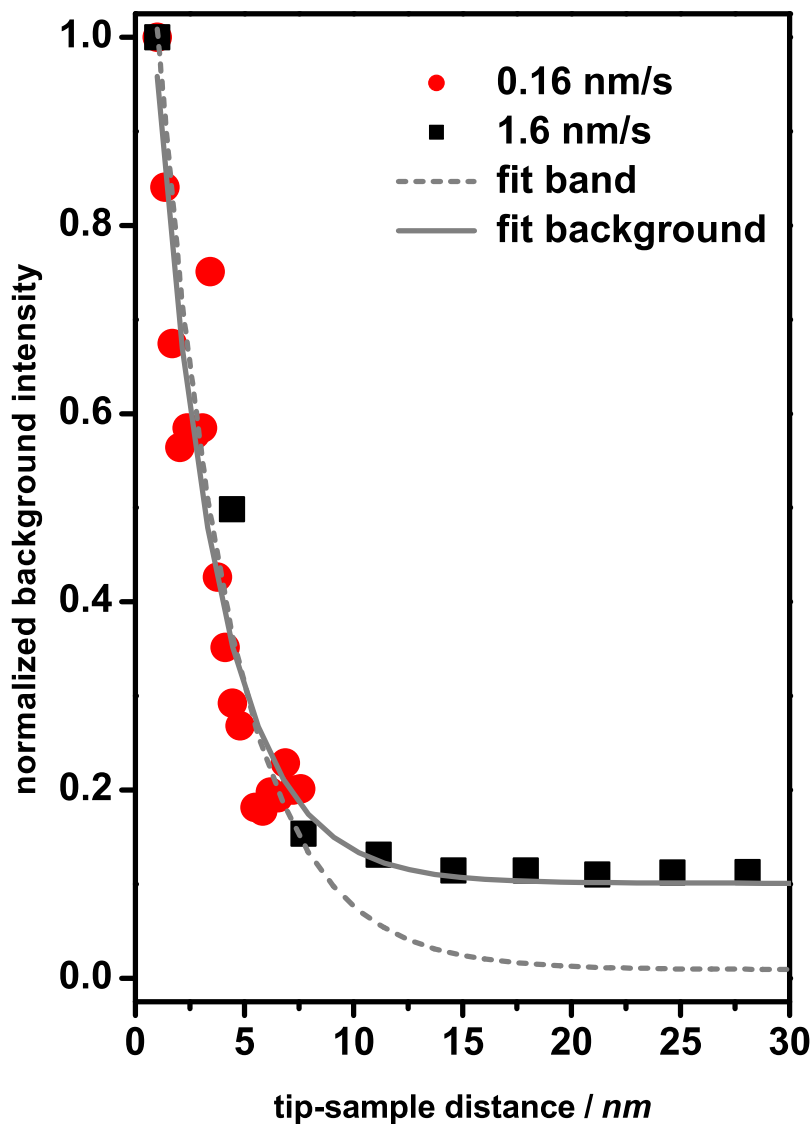


Figure 4.6: The background intensity vs tip-sample distance z is plotted together with a fit to the experimental band and background decrease data. Similarly to the band intensity, the total background intensity shows a decrease when the tip is retracted. It does not cease to zero intensity even at several tens of nanometers tip-sample distance, but reaches a minimum intensity limit of around 20% of the total intensity at $d = 1$ nm. For better comparison of the band and background behaviour, fit curves for both, the Raman band (compare Fig. 4.4) and background decrease are plotted.

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molecules with low quantum yield show more strongly enhanced luminescence at a shorter optimal distance, and vice versa.[100]

Following the argumentation of Käll *et al.*, we explain our spectra with the fact that the quenching effect cannot compete with the strong enhancement in the tip-substrate configuration and is largely suppressed. Therefore, the broad background remains under the Raman peaks at the investigated tip-sample separations.[64] The Raman and luminescence scattering cross sections obtained from theoretical Raman and background spectra of a particle placed between two Ag spheres (Ref. [90], reproduced in Fig. 4.1) show a remarkably similar behaviour with increasing particle separation to our curves in Fig. 4.6.[90] Note that the different background maximum energies are due to the difference in the metal (Au and Ag, respectively) employed.

For a molecule located "floating" in the center between two metal particles, the increasing near-field enhances both, Raman and background scattering when decreasing the particle separation from $z \rightarrow \infty$ to a few nanometers. Approaching the particles further, the molecule in between the particles couples more strongly to the metal and luminescence is quenched. This results in an optimal distance, where luminescence scattering enhancement is maximal and quenching not yet a problem. However, the TERS case is slightly different, as the tip-substrate distance is varied, but the molecule always is located at the metal substrate and not in the center between metal substrate and tip. Thus, the radiationless decay channel via the metal substrate is always present. We expect a steep increase in enhancement of luminescence with decreasing z (increasing near-field strength) without passing through an optimum distance. At larger distances ($z = 10\text{-}50$ nm), the luminescence levels off to about 10% of the initial intensity. From the experimental data at hand, we cannot determine the behaviour of the background intensity until total tip removal, but a slow further decrease approaching the $z = 1$ μm spectrum is expected.

In summary, the omnipresent background continuum in SERS and TERS experiments is attributed to fluorescent-like scattering by the adsorbate or an adsorbate-metal complex. At small tip-metal distances, a tenfold enhancement by the enhanced field created in the tip-sample cavity is monitored. The influence of the strongly enhanced electromagnetic field on the luminescence scattering at small tip-sample distances up to around 5 nm results in a comparable behaviour of the background

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intensity to the Raman scattering intensity. At large tip-metal distances, the far-field spectra still show some background, but no pronounced Raman bands.

4.4 LSP resonance shift

While in NRS the background usually exhibits a flat characteristic, we find a pronounced maximum in the TER spectral background. Itoh *et al.* showed that the maximum energy of the ERS background coincides with the resonance energy of the localized surface plasmons.[80] In other words, the background profile displays the mode structure and energy profiles of LSPs excited in the tip-metal cavity. Hence, the background becomes Lorentzian-shaped like the LSP resonance. By monitoring the shift of the background maximum with varying tip-sample distance, we can directly observe the corresponding changes in the gap resonance.

At $z = d = 1$ nm, the background maximum is located at around 1388 cm^{-1} (1.787 eV). While the positions of the discrete Raman lines remain constant during the retraction of the tip, the background maximum shows a remarkable shift towards higher energy with increasing tip-sample separation. The maximum energy shifts from about 1.787 eV (1388 cm^{-1}) for $z = d = 1$ nm to about 1.885 eV (603 cm^{-1}) for $z = 5.2$ nm (Fig. 4.7). Similar shifts were observed in other experiments with different retraction speeds and increased total retraction distances up to 20 nm. An isolated illuminated tip ($z \rightarrow \infty$) shows a very weak background centered at 1.906 eV (430 cm^{-1}). It is noteworthy that the FWHM of the background remains about constant during tip retraction. Fig. 4.8 summarizes the energy shift by plotting the background maximum energy versus tip-surface distance for three series of Raman spectra up to tip-surface distances of 50 nm.

At larger distances above 5 nm, the experimental maximum frequency levels off and stays about constant for $z > 15\text{-}20$ nm. This indicates that the mutual influence of tip and surface ceases rather abruptly at about 5 nm distance. The observed limit frequency at large distances should therefore represent the LSP of an isolated tip. Indeed, the observed values of 1.89-1.91 eV agree very well with the maximum energy measured for an isolated tip. In addition, this value is in reasonable agreement with the surface plasmon frequency for an ellipsoidal Au particle with dimensions of the

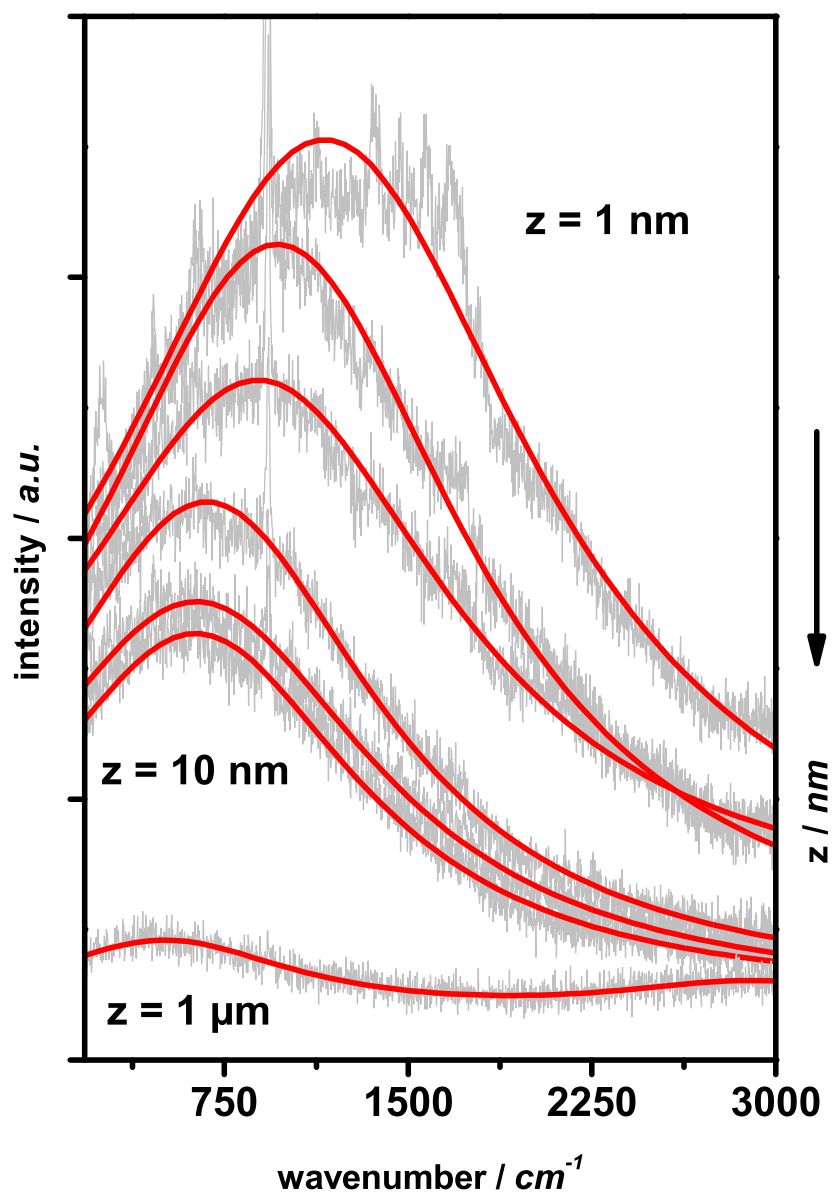


Figure 4.7: The Lorentzian-shaped background of the spectra (the original spectra from Fig. 4.5 are plotted in grey) exhibits a shift of the energy maximum towards lower wavenumbers (higher energies) with increasing tip-sample distance.

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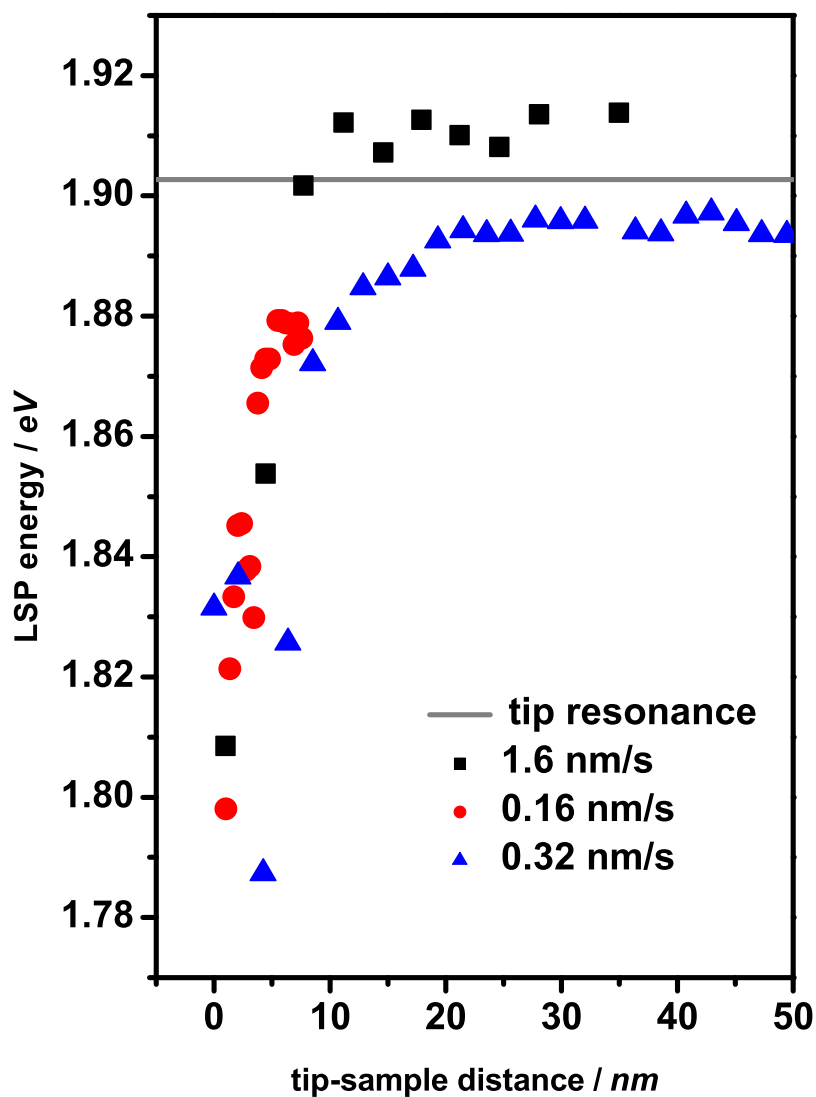


Figure 4.8: The energy of the surface plasmon resonance is plotted vs the tip-sample distance. A clear blue shift of the gap mode with increasing tip-sample distance is seen, as predicted by several theory groups. At $z > 10$, the gap mode energy approaches the resonance energy of an isolated Au tip (solid grey line at 1.906 eV).

tip apex. It should be noted at this point that considerable TER scattering was still observed at distances up to about 25 nm, far beyond the range of appreciable influence of the substrate surface on the LSP frequency.

The spectral blue-shift must be ascribed to changes in the LSP resonance with increasing gap length. The concept of LSP was introduced by Rendell *et al.*, who calculated the LSP modes for a sphere-substrate system dependent on the sphere diameter and the sphere-surface distance.[56] Indeed, a blue shift of the LSP was predicted for increasing sphere-substrate distances. Similar blue shifts were reported in more recent theoretical papers.[61, 64, 90, 101–103]

In particular, Porto *et al.* report LSP energies for a gold sphere of 40 nm radius above a gold substrate of 1.83 eV, 1.95 eV and 2.07 eV at sphere-sample distances of 1 nm, 2 nm and 5 nm respectively.[61] Given the differences in radius and shape of our tip ($r_{tip} = 20$ nm), the absolute values obtained by theory are remarkably close to the experimentally observed ones. Similar blue-shifts (at different energies) of around 0.3 eV for $z = 8$ nm were also reported by Demming *et al.*[104] and Downes *et al.*[54]

Related experimental work was published by Chumanov *et al.* and Jain *et al.*, who investigated the extinction spectra of different nanoparticle concentrations, i.e. different statistical interparticle distances. However, their results are contradictory: Chumanov *et al.* report a red shift for lower particle concentrations,[105] whereas Jain *et al.* observe the predicted blue shift for increased particle-particle separations.[106] Well-defined experimental conditions, like polarization of the incident light and particle distribution, are crucial for a precise determination of the plasmon shift.[107] The tip-sample configuration in the TERS experiment allows for a much more precise investigation of the plasmon resonance with varying distance.

Our findings can be directly transferred to the case of SERS: In general, SERS also exhibits a pronounced background maximum, often located at around 1000 cm^{-1} . Provided that SER scattering mainly arises from surface structures or particles which are closely approaching each other, the low energy of the background maximum points to a very close distance between these structures, a strong confinement of the EM field and, thus, to a large EM enhancement.

In general, the background represents fluorescence-like inelastic light scattering from the adsorbate-substrate system, as discussed in section 4.3, which in NRS usually

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exhibits flat spectral characteristics with extremely weak intensities. In the presence of substantial field enhancement, however, a measurable background with a pronounced intensity maximum visualizing the LSP resonance is observed. The intensity profile of the background directly reflects the underlying enhancement mechanism, i.e. the excitation of LSPs. In other words, the background maximum is correlated with the mode structure and energy profiles of LSPs in the tip-substrate cavity, or gap modes, in the course of inelastic scattering processes. Hence, the background becomes Lorentzian-shaped, like the LSP resonance, exhibiting a rather pronounced maximum. The observed spectral blue shift of the background must be ascribed to changes of the LSP resonances with increasing tip-sample distance.

4.5 Conclusions, difficulties & outlook

The behaviour of TER guanine band and spectral background with respect to varying tip-sample distance was investigated. The TER band intensities follow an z^{-10} behaviour, dropping to nearly zero after approximately 10 nm tip-retraction (for $r_{tip} = 20$ nm). The background shows a similarly steep decrease up to 5 nm gap length. Approximately 10% of the enhanced background intensity is still present at large tip-sample distances > 15 nm. We observe a blue-shift of the background-maximum energy with increasing tip-sample-distance that directly visualizes the underlying effect of plasmon excitation. The resonance energy of the gap modes shifts to higher energies with larger gap distances, approaching the value of an isolated tip from around 15 nm distance.

Originally, we wanted to study the guanine bands, and perchlorate was added to the adsorption solution to increase the solubility. However, the guanine Raman bands are much weaker in intensity and therefore not as easy to monitor as the ClO_4^- stretch band at 930 cm^{-1} , and in addition, they show a decrease with the time (bleaching effect). For strong perchlorate-metal interactions, we would expect a change in the vibration frequency.[108] As the position of the perchlorate symmetric stretch band in our spectra is not shifted with respect to the band in solution Raman spectra, we conclude that the adsorption behaviour of perchlorate on gold is mainly governed by electrostatic forces (nonspecific adsorption). For the present case, it is likely that

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adsorbate-adsorbate interactions with guanine play some role, but we have not investigated this problem any further.

With regard to the tip-sample distances that we calculate from opening times of the spectrometer shutter, there are two points that need to be considered: First, the measurement start is synchronized manually, i.e. the recording of the Raman spectra and the gating of the feed-back loop. This results in some error for the first data points (where the most rapid decay occurs) when calculating the real tip-sample distance from the shutter time recorded by the Raman spectrometer. In addition, we do not know how stable the tip is held with respect to the surface when controlled by the external ramp generator. Recorded test spectra without feed-back control show stable TER signals over at least 10 - 15 s. It is unclear, however, how the movement of the tip will influence the stability. At fast retraction speeds, such internal vibrations might be negligible, whereas the system might not be as stable at slow retraction over a larger time period.

In order to gain more insight into the influence of the gold sample on the gap mode excitation, one could perform similar experiments with a different metal or also an insulator substrate and analyze the tip-sample distance behaviour as well as the LSP resonance energies. It may also be of interest to employ a different excitation energy to tune the latter.

