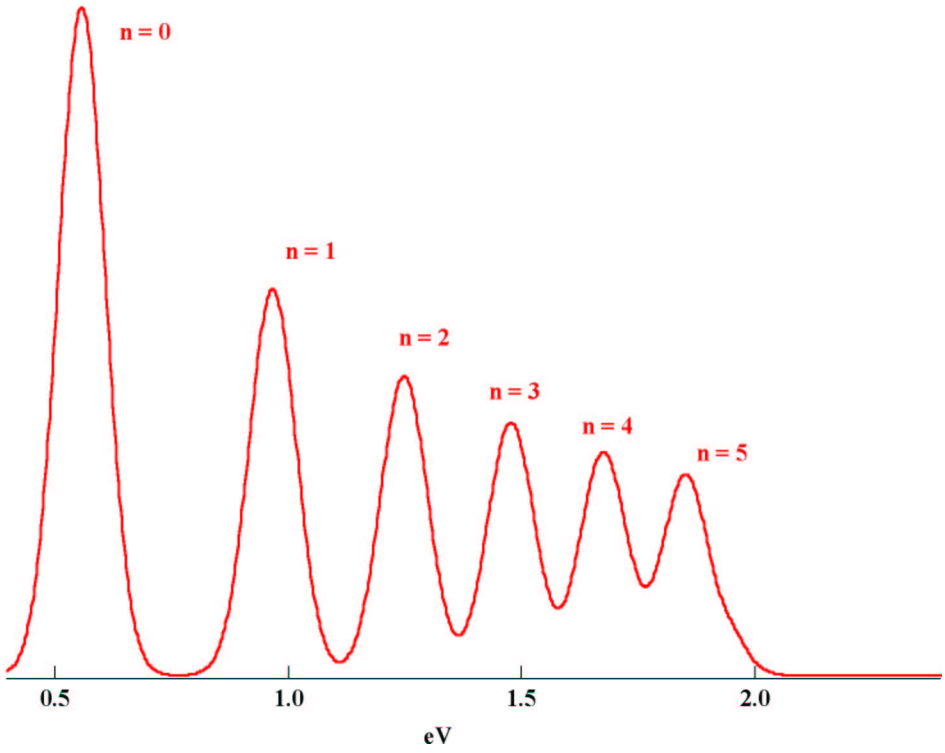
5. STM LIGHT EMISSION



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5.1 Gold-gold junctions

Surface plasmon modes localized within the cavity formed by the tunneling tip and a conductive surface can be excited in two ways: *(i)* by illumination and *(ii)* by electron tunneling. The previous chapter illustrated the former case where the excited mode are exploited to enhance locally (in the near field region) the electromagnetic field, and thus the Raman scattering of an adsorbate.
This chapter deals with the emission of light from a metal-insulator-metal tunneling junction. Photons are created as a consequence of the radiative decay of the electron gas oscillations excited by the inelastically tunneling electrons. The frequency of the emitted light is directly related *via* eq. (22) and (26) to the kinetic energy lost by the electron(s), thus to the energies of the LSP modes. Then, a minimal kinetic energy of the tunneling electrons is required for the photoemission process, *i.e.,* the junction bias voltage has to be kept above a certain threshold value. The upper limit for surface plasmon excitation at a gold surface is given by the onset of the interband transition from the d band to the Fermi level, located at 2.45 eV. Moreover, it has been observed [74,76,77] that scanning at voltages higher than 2.1 V causes surface modifications: rearrangement of atoms can take place in the high field, for example, or even removal of gold atoms from the first layer, or depending on the bias polarity, deposition of atoms from the tip, leading to both quenching and regeneration of the luminescence. In general, at high voltages an unstable light emission regime is observed. For these reasons, in the experiments performed with gold surfaces, the bias voltage was mainly kept below this value. This is still sufficient for a good yield of emitted light.
The value for the tunneling current has to be chosen considering the overall photon

detection efficiency of the experimental set-up. It is expected that the higher the tunneling current, the more light is generated. The inelastic process has a certain probability: the quantum yield is roughly 10^{-5} in vacuum. By increasing the number of electrons travelling through the gap, an improved signal to noise ratio is also obtained. On the other side, tunneling in air with a high current (> 10 nA) certainly has drawbacks such as an instability of the tunneling process. Due to the air humidity, a water meniscus is often formed between tip and surface. This lowers the value for the apparent tunneling barrier [132–134]. In order to maintain the fixed value for the current, (in the constant current mode of the STM) the tip is moved away from the surface. Then, the meniscus may collapse and a smaller gap is needed since the tunneling barrier is higher. Once again, as the tip approaches closer to the surface, the meniscus is formed. The alternate forming and breaking of the water meniscus leads to an oscillation of the tip relative to the surface, with an increasing probability of finally ramming it. This behavior is more and more pronounced as the tunneling distance is made shorter, that is, as the current is set to higher values. A compromise must be found between the quality of the signal and a stable tunneling condition.

In Fig. 5.1, STM-light emission spectra from a gold-gold junction are reported. Before (and after) the high voltage is applied to the junction, a spectrum is recorded to test that no external light is detected. An additional frame, supporting light proof black texture, is mounted on the optical table; easy access to the STM head and the positioning elements is provided by a sliding curtain. The microscope objective used for the light collection is placed at an angle of 60° to the surface normal. As for the TERS, the optical alignment is obtained by, first, bringing the body of the tip into the field of view of the objective and then by directing the laser light into the gap (see Fig. 4.15). Finally, the laser is switched off; a minute or two may be needed before the tip "cools down".
It is seen that the emission maximum moves to higher wavelength, that is, to lower energies, as the tunneling voltage, V_t is decreased. When the STM is operated in the constant current mode, by lowering V_t, the tunneling distance, d

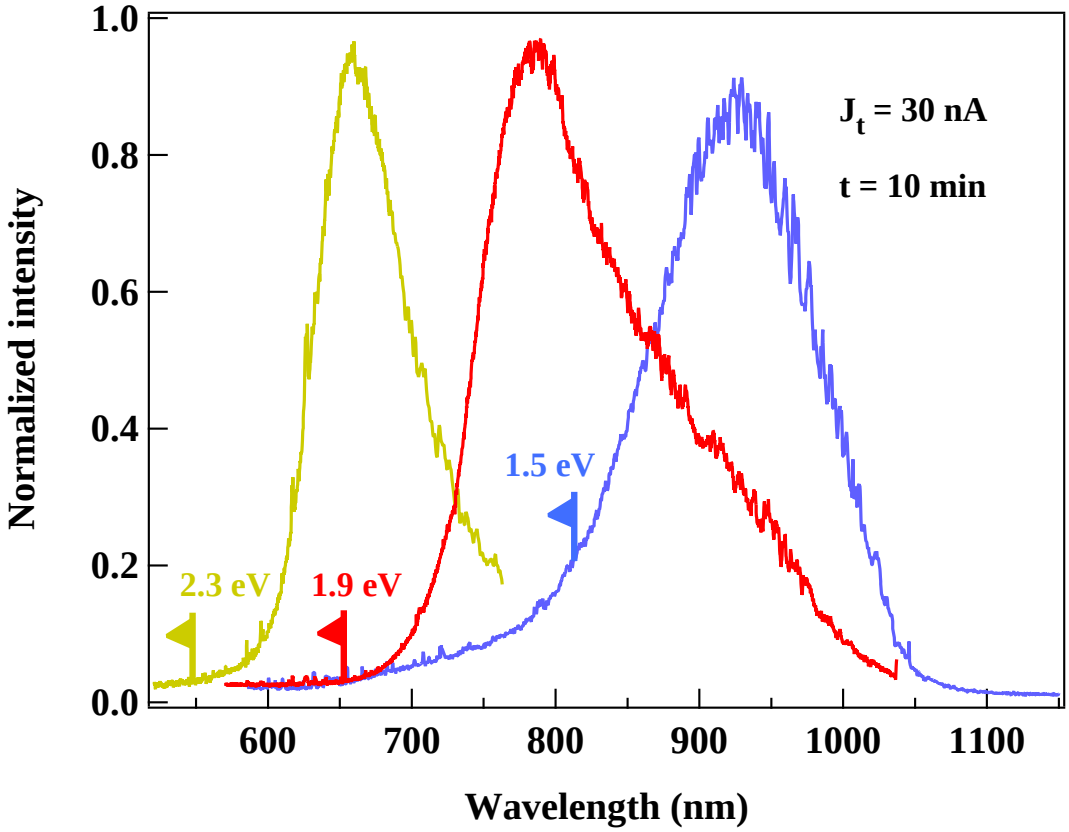

Figure 5.1: Normalized light emission spectra from a gold gold tip-gold surface junction kept at different bias voltages.

actually changes. To maintain the same current the gap has to be closer. Eq. (26) predicts qualitatively what is observed: $\omega_{LSP} \propto \left(\frac{2d}{R}\right)^{1/2}$. Concomitantly, the emission threshold shifts, so that the energy conservation, eq. (23), is satisfied. In the graph the small flags mark the wavelength equivalent to the energy eV_t, *i.e.,* the kinetic energy of the electrons. For a single electron process, no emission should be observed at energies higher than this limit. Still, it is possible to observe, especially when tunneling with very high currents, some tailing of the peaks at higher energies. A two electron mechanism must be invoked to explain the recorded signal [135, 136]. Then, we may suppose that the excess energy is provided by a second electron. This indicates that an electron may lose all or a

fraction of its energy during tunneling to the other side of the junction, but it may also be multiply (inelastically) scattered. As for two photon processes, the probability of these events is fairly small.

A long integration time and a high current value were used to record the spectra. The peaks are very broad and very often shoulders are clearly seen, see also Fig. 5.3. Similar spectra have been recorded, under similar experimental conditions, for example by Bischoff *et al.* [75]. As noted by these authors, a cavity size effect may be not the only explanation for the observed shift. Due to the broadening of the emission peak "a larger part of the spectrum will be excited when increasing the bias voltage", that defines the high energy cut-off of the process. A small graph, shown below, may be useful to illustrate this point. The entire peak shape (broadening) is observed only if all the possible energies for excitation are allowed; an artificial shift results by normalizing the partial emissions to the total.

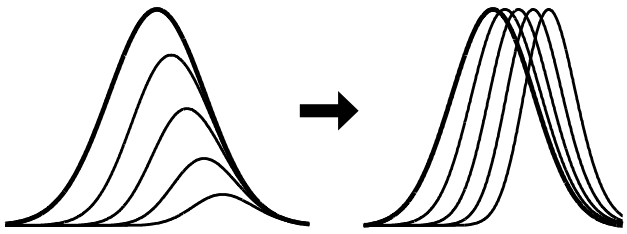

Figure 5.2: A shift of the emission maximum, not to be related with any cavity size effect, is also observed when changing the tunneling bias voltage, since this defines the energy cut-off for the light emission process. On the right the intensities are normalized to the highest, as done in Fig. 5.1.

Both effects have to be considered. Other spectra are reported in Fig. 5.3: it is seen that the component at higher energy is progressively "cut out", resulting in a reduction of the emission intensity, but the main peak at roughly 775 nm truly shifts to higher wavelength, before completely desappearing. In Fig. 5.4 the emission peak(s) lie(s) much below the energy of the exciting electrons and,

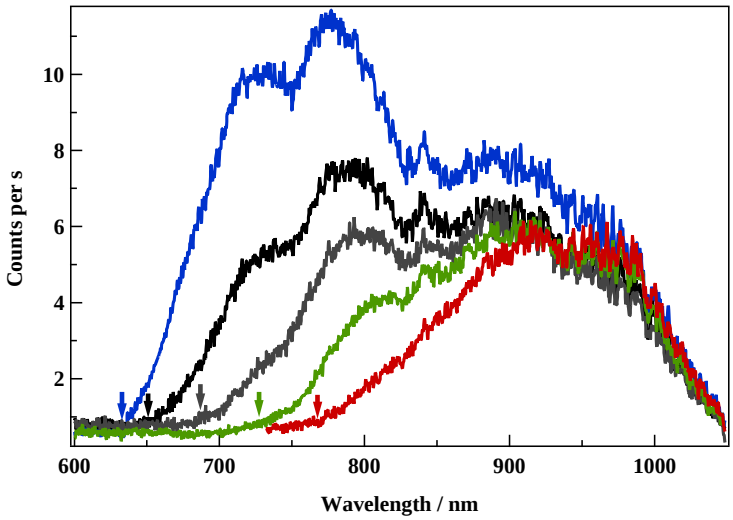

Figure 5.3: Light emission spectra from an etched gold tip tunneling over a smooth gold film. The tunneling voltage was lowered while keeping the tunneling current at the constant value of 2.5 nA. The arrows mark the high energy cut-off corresponding to the kinetic energy of the tunneling electrons, from left to right V_t = 1.95 V, 1.90 V, 1.80 V, 1.70 V, 1.60 V. The exposure time for each spectrum was 30 s.

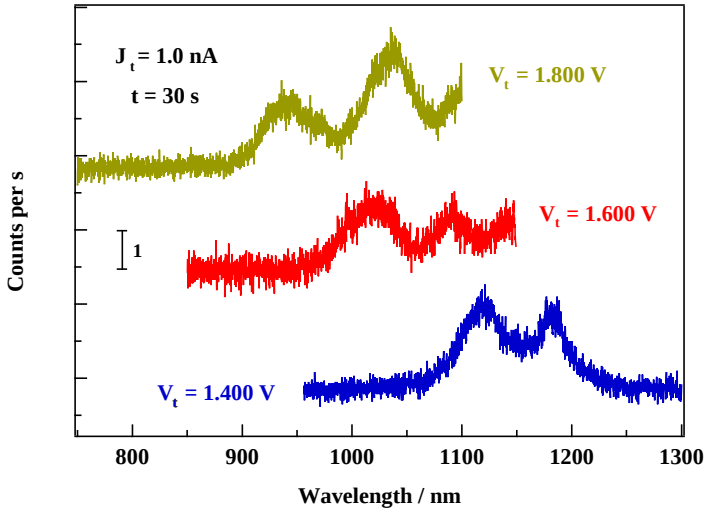

Figure 5.4: As above, but with a different gold tip.

in this case, the shift must be attributed only to the size change of the junction. Differences in the relative peak intensities have to be attributed to the frequency dependent CCD camera sensitivity, which is quite poor for frequencies above 1000 nm and finally collapses at around 1200 nm.

Intuitively, it can be already understood that more than just one LSP resonance is excited by the tunneling electrons, hence, the presence of multiple peaks and shoulders. A spectral analysis is difficult due to the width and partial overlap of different features. An improvement in the quality of the spectra was obtained by drastically reducing the integration time and the tunneling current. The lateral drift of the tip and the high sensitivity of the light emission process to the surface topography have been already mentioned. A number of different resonant cavities are then the source of the light signal if the integration time is long and the tip drifts over surface irregularities. For a better correlation of the experimental data and the theory, which usually describes the metal surface as a smooth interface, the gold films were repeatedly flame annealed in a hydrogen flame prior to the experiment. This treatment cleans the surface and provides enough energy for the rearrangement of surface atoms into low indexed flat terraces with dimensions ranging between 20 nm up to 100 nm. Before applying the high voltage, a brief scan is performed to search for a flat area over which the tip is then located for the light emission expirement. [17] The still existing drifting along a terrace is then, in a sense, acceptable and the integration time was kept to the minimum. Also, low values for the tunneling current are instrumental for measuring light from a stable tip/surface configuration. Despite the flatness of the surface,[18] the short integration time and the reduced flow of electrons (actually the opposite way in which most of STM light emission experiments are performed for photon mapping), the quality of the signal was still very good and reproducible.

[17]The topography of the scanned surface could not be recorded since the additional electronics (Digital-Analog-Converters) and the software for the treatment of the images were available only at the latest stage of this experimental work.

[18]Rough sample may emit more light since surface plasmon localization is expected to be very effective at irregular structures.

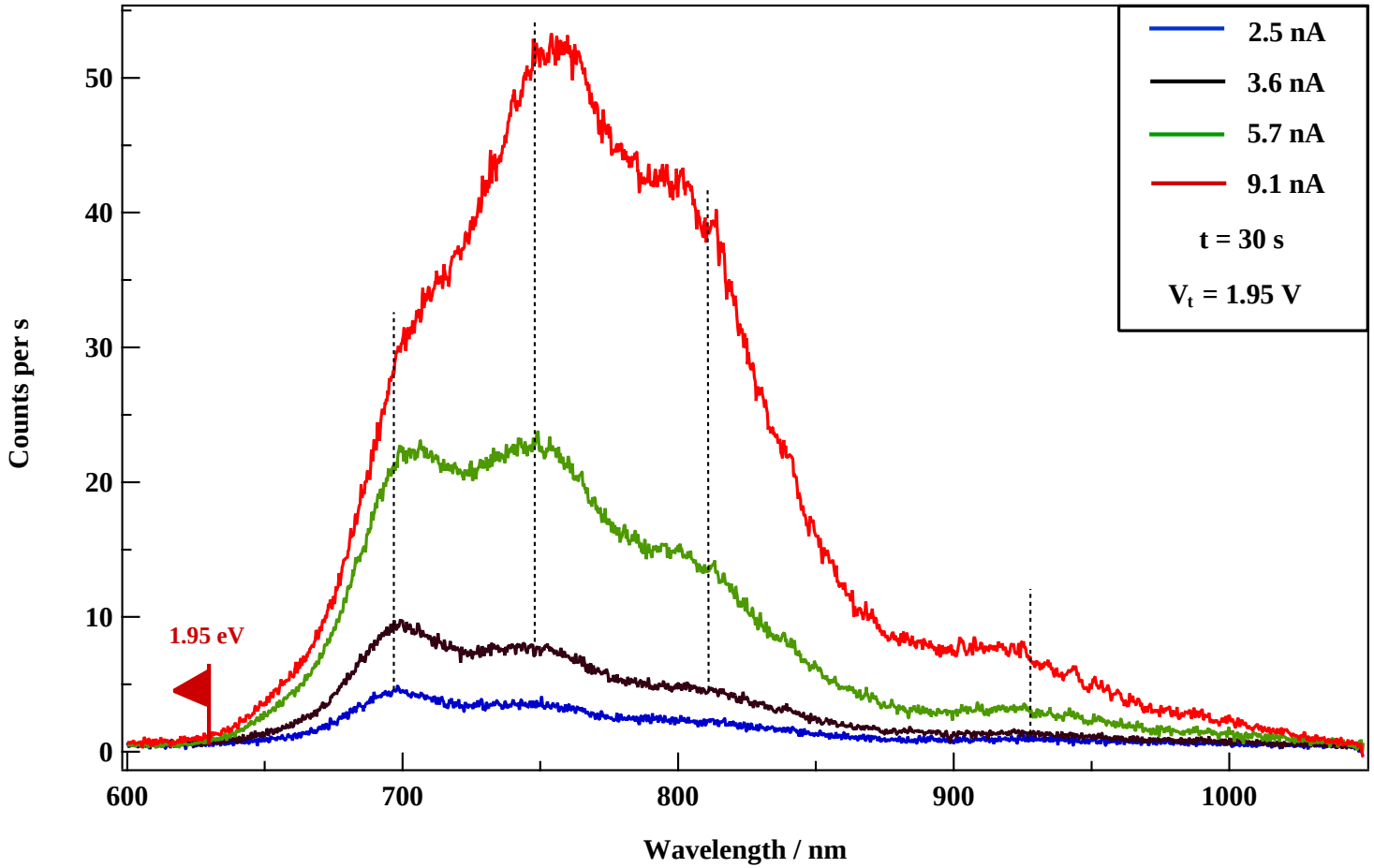

Figure 5.5: Light emission spectra from an etched silver tip tunneling over a smooth gold film. The tunneling current was increased while keeping the tunneling voltage constant. The exposure time for each spectrum was 30 s.

In general the reproducibility was checked by taking consecutively for each value of V_t and J_t more than one spectrum. Moreover, since the grating does not cover all the whole range from 600 nm to 1200 nm, a full spectrum is actually taken by recording subsequent spectral sections at different grating positions; the excellent overlap of the different wavelength intervals demonstrates also the stability of the system. Under these conditions it is possible to focus on the geometry of the tip, *i.e.,* to exclude the surface contribution (local roughness) in defining the LSP resonances. The spectra in Fig. 5.5 were taken with the same bias voltage, $V_t = 1.95$ eV but increasing current. The spectral features are stable and the peak intensities scale almost linearly with the current, at least for values $J_t < 10$ nA. Because of the flatness of the surface, the intensity maxima are attributed to the LSP resonances supported by a single cavity and not to multiple contributions from different sites on the surface. The dashed lines in the graph have been drawn to show that, actually, there is a small shift of the peaks to higher wavelength with increasing tunneling current. Once again, as for the value V_t, also J_t defines the size of the cavity, *i.e.,* the distance of the tip apex to the metal surface. Indeed, to have a higher current established through the gap, a closer approach of the tip to the surface must occur (according to the well known exponential relationship between the tunneling probability and the tunneling distance). The LSP resonances move to lower energies as the gap size, d, reduces. The observed shift of the emission peaks upon modification of the tunneling parameters, either V_t or J_t, may be more or less evident. One more parameter defines the energies for the LSP resonances: the curvature radius of the tip, considered in the model as the radius of a sphere. In principle, the energy shift of any (or all) of the peaks may be used to evaluate a value for R. Such an analysis is lengthy and also redundant; a more straightforward way is to rely on the spacing between consecutive peaks, which also reflects the cavity geometry.

Equation (22) from the Rendell and Scalapino theory was used to fit light emission spectra from gold surface-gold tip junctions that showed a reproducible and rich pattern of peaks all over the available recording window, that is from 600 nm

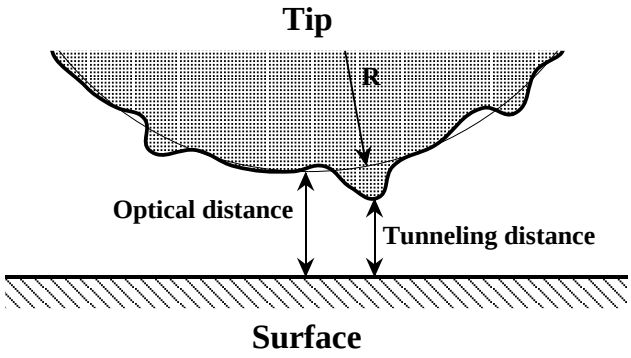

Figure 5.6: The actual tunneling gap and the optical gap used in the fit.

to roughly 1000 nm. The theory describes the energies of a ladder of localized plasmon modes. The broadening of the modes was simulated by Gaussian energy distributions having the same width ($\sim$ 100 meV) .[19] Regarding the intensity with which each mode emits (*i.e.*, it is excited by the tunneling electrons), a calculation of the radiated power per unit photon energy is far beyond the scope of these preliminary fits [87,88]. A simple reasoning was applied to account for the possibility of (quantized) kinetic energy losses by the tunneling electrons. Considering equal *a priori* probabilities to excite any one of the modes with different energies, each mode was multiplied by a factor inversely proportional to its energy to account for an higher excitation/emission rate of low energy modes. The wavelength dependent sensitivity of the light recording system must also be taken in account. An experimental sensitivity curve was obtained by numerically dividing the spectrum recorded from a tungsten halogen lamp by the semi-empirical emission curve of a

[19]The narrow halfwidth (FWHW) of the experimentally observed LSP modes is substantially lower than the FWHW of surface plasmon absorption for spherical gold nano-particles with radii around 60-100 nm. Similar FWHW ($\sim$ 100 meV) are found for extended gold nanorods with diameters $\sim$ 20 nm and explained by reduced radiative damping and/or a reduced rate of $e^- - h^+$ pair excitation [138]. The reduced damping of the excited modes permits the build up of highly enhanced fields. According to Sönnichsen *et al.* the electromagnetic field enhancement lies between 15-20; thus, SERS (TERS) from these nano-rods should be higher ($10^4 - 10^6$) than our experimental findings.

full radiator (black body) to which the lamp may be approximated. The correlated color temperature[20] of the emitter was set at 3300 K. The applied tunneling voltage defines the energy cut-off of the emission process. To mimic this, a step function (Fermi-Dirac) entered in the global fit as a multiplying factor. The distance d from the surface to the lower point of the sphere cannot be taken directly as the actual tunneling distance. Fig. 5.6 may be helpful to explain this point. Realistically, the bottom of the tip is not (only) a section of a sphere. It presents most likely a corrugated surface, at least on the nanometer scale. In the limit one may think of a single smaller feature (even a single atom) establishing the tunneling contact. Two gap distances have then to be defined: a tunneling distance d_{tun}, the smallest separation between the two metals, and an optical distance, d_{opt}[21], the real distance defining the optical behaviour of the system in the framework of classical electrodynamics, *i.e.*: the localization of the surface plasmon polaritons underneath the tip apex. In the normal tunneling regime the tunneling gap is between 0.4-0.7 nm, while the optical distance is unknown. In Rendells equation, only the ratio d/R determines the optical response; therefore, for the fits this ratio is estimated.

The following figures show a few emission spectra and the best fits that could be obtained by employing eq. (22). An exact match of the fit curve maxima with the emission maxima is not always possible. It is sufficient that the shape of the tip apex departs slightly from the spherical symmetry to have the resonances shifted to different values that are not possible to reproduce completely. Despite that, the indexing of the peaks is realistic, in the sense that reasonable quantum numbers n are needed to follow the energy sequence of the emission maxima. As a general trend the smaller R (*i.e.,* the larger the ratio d/R), the more separated are the resonances, a feature that simplifies considerably the fitting procedure. A final remark on how to properly interpret the results of these simulations must be made: even when a satisfying matching of calculated and experimental LSP

[20]The temperature at which the black body emits light of similar chromacity as the lamp. Data are available from the Oriel Instruments web site.

[21]Ushioda prefers to speak of an electromagnetic distance [137].

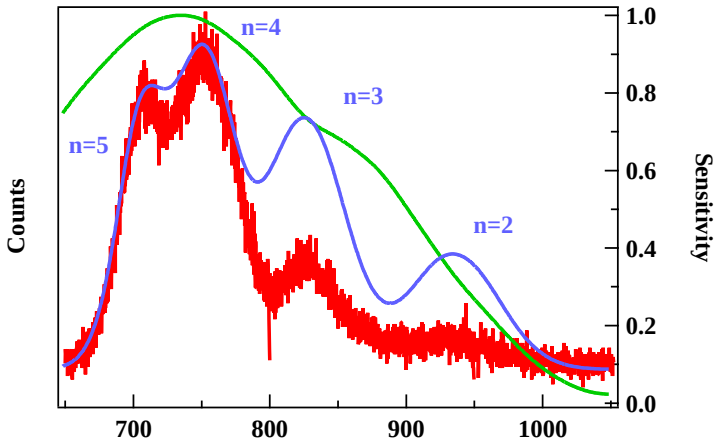

Figure 5.7: Light emission spectrum from a gold tip - gold surface junction taken at $V_t = 1.8$ V and $J_t = 2.5$ nA. Parameters for the fit curve were: $\omega_{sp} = 2.45$ eV; $KT = 0.0025693$; $\sigma = 0.05$; $d = 1$ nm; $R_{Fit} = 450$ nm. The (smoothed) sensitivity curve of the light detection system is also reported.

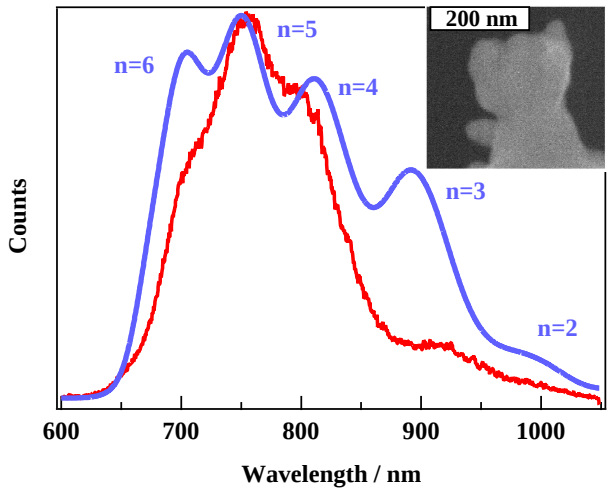

Figure 5.8: Light emission spectrum from a gold tip - gold surface junction taken at $V_t = 1.95$ V and $J_t = 9.1$ nA. Parameters for the fit curve were: $\omega_{sp} = 2.45$ eV; $KT = 0.0025693$; $\sigma = 0.05$; $d = 1$ nm; $R_{Fit} = 459$ nm. An SEM image of the tip is reported in the inset, $R_{SEM} \simeq 110$ nm.

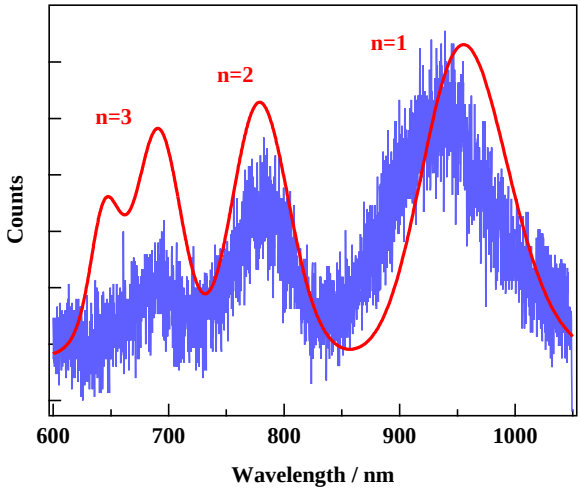

Figure 5.9: Light emission spectrum from a gold tip - gold surface junction taken at $V_t = 2.0$ V and $J_t = 7$ nA. Parameters for the fit curve were: $\omega_{sp} = 2.45$ eV; $KT = 0.0025693$; $\sigma = 0.05$; $d = 1$ nm; $R_{Fit} = 164$ nm. An SEM image of the tip is reported on page 52, Fig. 3.7c, , $R_{SEM} \simeq 70$ nm. The fit curve was not multiplied by the experimental sensitivity curve.

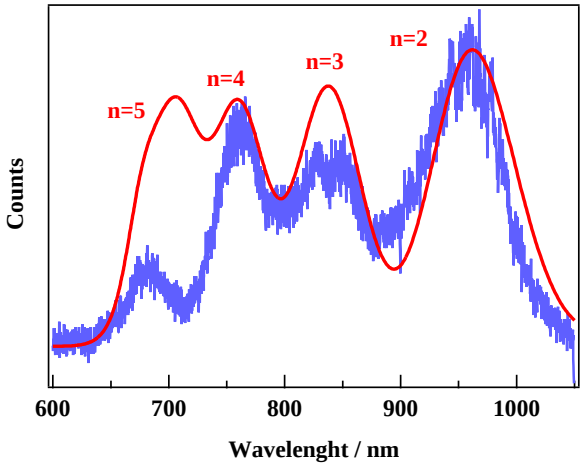

Figure 5.10: Light emission spectrum from a gold tip - gold surface junction taken at $V_t = 1.85$ V and $J_t = 5.7$ nA. Parameters for the fit curve were: $\omega_{sp} = 2.45$ eV; $KT = 0.0025693$; $\sigma = 0.0483$; $d = 1$ nm; $R_{Fit} = 473$ nm. The fit curve was not multiplied by the experimental sensitivity curve.

resonances is obtained, it can not be realistically concluded that the STM tip *is* a sphere, rather it emits *like* a sphere of radius R. The spherical tip model may indeed reproduce some of the observed features. A major difficulty was to reproduce correctly the emission intensities for different modes. It can be seen that in certain cases an higher intensity was recorded for the lower modes than for the higher ones.

This is theoretically correct, but considering the sensitivity curve, the observed sequence should be the opposite: modes at higher energy, in the near visible, where the camera sensitivity is fairly good, should be more intense than modes in the near IR. It is surprising that also in regions where the sensitivity is down to a few percent, very strong signals can be recorded. A tentative explanation is given. A regular decrease of the peak intensities, from $n = 0$ to $n = \infty$, is expected for an isotropic emission and, in the case of a spherical tip, the direction for the light detection is irrelevant. In the real experiments, the tip apex is not axially symmetric.This may already cause departures from the modeled intensities because only a certain solid angle of emission is inspected. Certain modes, supported by an asymmetric cavity, may radiate photons with different propagating directions[22].

Recently, a paper from Ushioda's group, possibly one of the most active in the field of light emission from STM junctions, appeared reporting on the "Origin of multiple peaks in the light emission spectra of a Au(111) surface induced by the scanning tunneling microscope" [137]. There, it is pointed out that very broad tips may yield several peaks extending into the visible region and corresponding to LSP resonances of higher order ($n \geq 2$). In their case, very broad, blunt tips (apex size $\approx$ 1000 nm) are used and a single confinement length L of the plasmon modes cannot account for all the observed emissions. Two values for L are needed (L_a and L_b), in the range between 50 nm and 500 nm. Some of the resonances are associated with L_a and the remaining may be reproduced by L_b. Two confinement

[22]Possibly, the best experimental set up to couple with this limitation is the one adopted by Yamamoto [93]. The tunneling tip, considered as a light point source, and the detecting unit are placed at the foci of (a section of) an ellipsoidal mirror. Another interesting experiment would be to change the angle of detection during the emission.

lengths are necessary for a cavity formed by the flat surface and the opposing flat tip apex, having an elliptical form. Thus the two lengths define the long and short axes. A relevant conclusion is that the calculated values are by one order of magnitude smaller than the width of the tip apex as observed from the SEM images. To reduce the mismatch, wider optical distances (up to 5 nm) were used in the simulations and/or the possibility of more rounded apices is taken in account, since this effectively leads to an higher localization of the modes (smaller values of L).
In our experiments, the tip apex were much smaller ($\ll$ 1000 nm). In a number of experiments, the apex radii were determined by SEM images, R_{SEM}. From the analysis of LE data low values of the ratio d/R were obtained. For an (assumed) optical distance of 1 nm, the R values become significantly larger than the R_{SEM} (or *vice versa*, for $R_{SEM} = R_{fit}$, $d_{opt} < d_{tun}$). For a better understanding of this result, one has to consider the following: for the real emission process it is more correct to discuss in terms of the *local* curvature of the tip, actually the real curvature felt by the highly confined electromagnetic modes. For a flattened apex, the radius of curvature at the bottom of the tip apex may be larger than the apex width. Returning for one moment to the spherical model, this results if one side of the sphere (the bottom side, the one facing the surface) gets flattened. In a sense, our conclusions are complementary to those from Ushioda: the real cavity geometry, defining the light emission process, lies between the two (theoretical) limits of a perfectly spherical and a perfectly flat apex.

Gold-gold junctions are the best system to study in detail the emission behavior from a tunneling tip and to test the validity of the proposed theoretical models[23]. These studies may be extended to silver-gold junctions. Silver has the bulk plasma resonance at higher energy than gold, this should move the localized resonances slightly more into the visible range, by eq. (24). Moreover, a stronger light emission is expected, since silver is, in a sense, a more free electron metal. Light emission spectra from a silver tip have been recorded as well, but the tunneling

[23]Simulated emission spectra from an hyperbolic tip may be found in another recent paper by Aizpurua [89], see also Fig. 2.23.

current at high voltages becomes more unstable, actually hindering a comparison with the simulations, for which the reproducibility of the experimental spectra and the stability of the tunneling junction are crucial.

With the results provided by STM-light emission, an important conclusion connected to TERS may be reached. It was shown that the resonances appearing in the visible range are only of higher order. The fundamental mode ($n = 0$) and the first resonance could not be observed experimentally. According to the theory, plasma excitations are expected even above 1 μm, the low energy modes radiating more than the high energy modes. Thus, a very high light emission intensity could be recorded in the infrared region. The energy gap between lower modes is wider (the ladder of LSP resonances resemble the set of levels given by an unharmonic oscillator, with the limiting surface plasma frequency as dissociation limit) and the fitting procedure might be carried out with less ambiguity if the emission peaks were well separated.

Furthermore, it is possible to foresee a strong(er) coupling of an incident electromagnetic wave with the localized plasma oscillations at wavelengths beyond the visible range. Already the calculations by Demming *et al.* hinted at the possibility of having much higher field (and tip) enhancement factors by using a laser source in the near-infrared.