A Study of Plasmon Coupled Emission from Molecules Confined in Plasmonic Nano-Cavity

A Thesis

submitted to
Indian Institute of Science Education and Research Pune
in partial fulfillment of the requirements for the
BS-MS Dual Degree Programme

by

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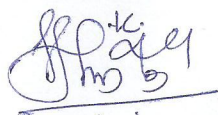Dr. Homi Bhabha Road,
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May, 2018

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Certificate

This is to certify that this dissertation entitled A Study Of Plasmon Coupled Emission from Molecules Confined in Plasmonic Nano-Cavity submitted towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents work carried out by Jesil Jose at Indian Institute of Science Education and Research under the supervision of Dr. G.V Pavan Kumar, Associate Professor, Department of Physics, during the academic year 2017-2018.

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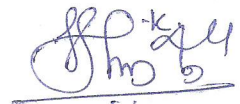Dr. Shouvik Datta

Dedicated to My Parents

Declaration

I hereby declare that the matter embodied in the report entitled A Study Of Plasmon Coupled Emission from Molecules Confined in Plasmonic Nano-Cavity are the results of the work carried out by me at the Department of Physics, Indian Institute of Science Education and Research, Pune, under the supervision of Dr. G.V Pavan Kumar and the same has not been submitted elsewhere for any other degree.

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Acknowledgments

This thesis, and all the research I have done in the past year alongside it has been with the help of several people whom I would like to thank here.

Firstly, I would like to thank Dr. G.V.Pavan Kumar, who has been my guide for the past two and half years, and has given me his valuable advice and directions as to where I should proceed. He has always supported me when I did something correctly, and corrected me whenever it was required. Discussions with him have always given me new insights. I am grateful to him for believing in me and encouraging me to move forward, overlooking my faults.

I would like to thank Mr. Sunny Tiwari with whom I have performed the experimental measurements mentioned in this thesis. Discussions with him helped me in understanding the experimental system better. Working with him has been fun and helped me a lot in my skills on optical allignment.

I would like to thank Mr. Adarsh Vasista whose advice I have always sought regarding my research. His knowledge in plasmonics and optics has helped me a number of times. The fruitful discussions I had with him, be it regarding Physics, history or politics, has been a great experience and helped me in shaping my views.I would also want to thank Mr. Deepak Sharma, for introducing me to the concepts in optics and with whom I have worked in a research project for the first time.

I would like to thank Mr. Shailendra Chaubey for the deposition of gold films and Mr. Diptabrata Paul, who synthesized the wires that were used for the project.

I would like to thank former post doctoral fellow in our lab Dr. Debrina Jana who have given me valuable lessons in synthesis of nano-structures in my initial days in the lab.

My time in the lab was made really interesting by my present and past labmates: Dr. Vijay Kumar, Vandana Sharma, Chetna Taneja, Rajath Sawant, Harshvardhan Jog and Dr. Ravi Tripathi, who made the daily chai time into a discussion forum for everything from research to politics to IISER gossip. Of course, Special mention goes to all my friends, who have made this journey enjoyable through all the lunch and dinner table conversations, as well as the random hangout sessions and parties.

Finally, I want to express my deep gratitude towards my father and mother, who have always supported me and believed in me, whatever choices I make in life. Their constant concern for me has helped me be focused and given me inspiration to work towards my chosen goal.

Abstract

The hot-spots or the region of highly enhanced electric fields between a nanostructures possesses interesting properties. These cavity structures have electric fields that are highly confined and enhanced. Thus placing a fluorophore in this cavity will results in highly enhanced molecular emission. Depending on the nature of cavity the signals can be enhanced and the molecular emissions can be re-directed due to the antenna effects of the nanostructures. This thesis addresses plasmon coupled emission from molecules confined in an one dimensional plasmonic cavity and the resultant enhancement in fluorescence and directionality of emission.

The first chapter introduces the various concepts that are necessary to understand the problems addressed in this thesis. This includes an introduction to plasmonics, different types of plasmons, molecular emission processes and the basic theory of surface plasmon coupled emission.

The second chapter deals with the materials and methods used to address the problems. This involves the synthesis of silver nanowires, deposition of gold films and a section on the concepts of Fourier plane imaging.

The third chapter deals with the experiments performed on the cavity systems formed by the coupling of silver nanowires and plasmonic films. The molecular emission from a system of silver nanowire placed on a thick mirror is considered. Here the thick film acts as a mirror. The enhancement and polarization dependence of fluorescence and the effects of plasmonic film and the silver nanowire has on the intensity has been studied. This chapter also addresses the surface plasmon coupled emission from molecules confined in the cavity between silver nanowire and a semi-transparent gold film. Highly directional emission from such kind of system is observed.

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Chapter 1

Introduction

Antennas are one of the most revolutionary inventions of the past century. The origin of the word antenna relative to wireless apparatus attributed to Italian inventor and Nobel Laureate Guglielmo Marconi. It was Marconi who used the power of antenna effects in radio frequency regime to make the first radio in 1895.[1] However, the credit for the invention of the first ever antenna goes not to Marconi but to Heinrich Rudolf Hertz, who using his invention successfully demonstrated Maxwells theory of Electromagnetism for the first time in 1887.[2] This set of Experiments by Hertz conclusively proved the existence of the electromagnetic waves theorized by James Clerk Maxwell in 1873. The invention by Marconi and its perfection in the subsequent decades revolutionized human lives. From the simple set of dipolar antennas built by Hertz to the cutting edge wireless device like WLAN, Television antennas and Mobile phones, the technology of antennas has advanced probably even beyond the expectations of the inventor himself. Over the past century, the technology of antennas has perfected and modified to include radio and microwave frequencies successfully.[3] The integration of electronics has provided high specificity, high fidelity, and ultrafast communication speeds between the transmitter and receiver antennas.

Advances in modern scientific instrumentation enable us to study nature in many ways. Among these methods, optical instrumentations are a first and foremost method to study nature. Since the energy of light lies in the energy range of vibrational and electronic transitions in the matter, we can gain unique information regarding the structural and dynamical properties using visible light.[4] Even though the use antennas in the high-wavelength regime was a grand success and led to revolutionary inventions, it was not that easy to extrapolate this technology to visible frequency regime. This, mainly because the visible wavelength lies in the nanometer regime, and for the antenna to work effectively, its dimensions should be of the order of the wavelength under consideration.[5]

The fabrication and the manipulation at Nano-level was one of the difficult and cumbersome tasks in the scientific history. However, the advent of Nanotechnology overcame this barrier and with this started a new era in the technology of antennas.[4, 6]

Richard Feynman in one of his famous talk titled "There is plenty of room at the bottom" delivered in 1959 seeded the basic concepts of Nanotechnology.[7] These ideas and concepts were taken forward and popularized by the American engineer Eric Drexler.[8] The 1980s witnessed another breakthrough in Nanotechnology with the invention of Scanning Tunneling Microscopy and Atomic force Microscopy which provided unprecedented visualization of single atoms and bonds as well as enabled manipulation at Nano-regime.[8, 9, 10, 11] This, with the advancement in synthesis procedures for Nano-materials and inventions of highly sophisticated instrumentations for fabrications such as Field Emission Scanning Emission Microscope and Electron Beam Lithography it has now become possible and less cumbersome to design, synthesize and fabricate nanostructure with accuracies as precise as tens of nanometers. The optical antenna effects have been successfully demonstrated using nanostructures fabricated using Photolithography[6], Electron beam lithography,[13, 18, 19] Focused ion beam lithography[6, 12] and also using 0-D and 1-D structures synthesized using wet phase methods.[20, 21]

For an efficient optical antenna, it should be able to convert propagating EM radiation from far-field to enhanced and localized near-field radiation. Plasmonic structures are one such good candidates for this purpose since they provide high field enhancements near sharp features and can be used to confine fields to sub-wavelength regimes in gap structures.[13, 14, 15, 16, 17, 18, 19, 20, 21, 22] Also, the physical properties of plasmonic materials such as negative real permittivity[23] and low reactivity (Au) made them ideal choices. The research related to enhancement and directionality of antenna effects in plasmonic nanostructures is of foremost importance. And there are still major challenges remains on optimizing the optical antennas for high field enhancement and unidirectional. Plasmon Coupled Emission is one of the most promising phenomena in which isotropic emission such as molecular fluorescence is converted to a highly unidirectional one due to the proximity and interaction with plasmonic nanostructures. The sections following this will introduce the basic principles and theoretical background for the plasmonic nano-antennas and molecular emissions followed by a section on Plasmon-Coupled Emission, and the motivation and definition of the thesis problem.

1.1 Plasmonics

The 21st century has seen an unprecedented revolution in communication technology. We have ultrafast communications and everything is digitized and connected. Even day to day processes have become digitalized and we have communication speeds improving

every year all thanks to the semi-conductor based technology.[24] Using the technology based on semi-conductors we have made circuitries that are of the dimensions of tens of nanometers with the help of nano fabrication techniques.[26] This miniaturization of electronic circuits have helped us achieve greater performance, speed and high density data packaging.[25] However as we are pushing and pushing the size limits of these semi-conductor based circuits the fundamental limitation of these systems are also closing in. It wont be long before we reach a dead end in terms of the speed and data packaging density.[27] One of the alternate solutions that has been suggested in the past and now being explored extensively is to use light as carrier of information rather than electrons like in semi-conductor based circuits. Eventhough highly promising, using light for such kind of applications had its own short comings mainly due to the unavailability of miniaturized circuit elements that can allow the transmission of the light and the integration of these circuit elements on a circuit. There were other fundamental constrains as well, the existence of diffraction limit of light, meaning that it is not possible to focus a light beam of particular wavelength such that the beam waist is lesser than half the wavelength of the light beam.[3, 25] Hence an entirely different approach had to be taken to overcome this fundamental constraints.

Plasmonics is promising field of science that studies the interaction of electromagnetic fields with free electrons in metals usually, silver and gold. Plasmonics tries to solve the fundamental constraint of diffraction light in visible region and hence help us focus light in to dimensions lesser than $\lambda/2$. Plamsonics exploits the unique properties of plasmonic (metallic) nanostructures in optical regime to sustain and manipulate optical electromagnetic fields at sub-wavelength scale. The plasmonic nanostructures which can sustain coupled oscillations of electrons and optical field at the metal-dielectric interface, known as surface plasmons leads to confinement of fields to the surface of metallic structures which have sub-wavelength dimensions hence breaking the diffraction limit of light.[3, 4, 25, 26] In addition to confinement, extended nanostructures can be used to propagate electromagnetic field hence acts as a waveguide through propagating surface plasmon polaritons (SPPs).[15, 16, 17] However since we are using metal structures losses are inevitable due to ohmic loss and electron-core interactions in plasmon oscillations. Despite the presence of losses, plasmonics presents various advantages. These are as previously mentioned the confinement of optical fields to sub wavelength volumes (thereby breaking of diffraction limit of light) and producing highly localized intensity. Also the mode volume (ν_m) supported by a plasmonic resonator can be lower than the $(\lambda/2)^3$ limit in case of dielectric resonators.[25, 28] These properties have been harnessed to build applications based on enhanced light matter interaction such as enhanced molecular spectroscopy techniques,[29, 30] highly sensitive bio and molecular detection,[31, 32] sub-diffraction limit resolution microscopy techniques,[33, 34] miniaturized plasmonic nanolasers.[35, 36]

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etc

Apart from focusing light to sub wavelength dimensions the optical properties of an emitter such as a quantum dot or a Fluorescent molecule can be altered by placing it in close proximity to a plasmonic structure. This is due to interaction and coupling between the light emitted from the emitter and the plasmonic modes of the nanostructure. This interaction between the nanostructure and the emitter can result in an altered fluorescence cross-section and lifetimes also it may result in reshaping the emission spectra and most importantly spatial redirection of the emission (antenna effect).[37] These properties of plasmonic nanostructures has been utillized to enhance the detection efficiencies in molecular spectroscopy,[38] building communication devices and photodetectors.[39]

1.1.1   Localized Surface Plasmons

Localized surface plasmons are the resonant oscillations of conduction electrons in a metal nanoparticle due to its interaction with an oscillating electric field. These kind of resonant oscillations occurs in metal particles with very small volume and hence as the name suggests are non-propagating in nature.[3, 40] A simplest nanostructure that can sustain a localized surface plasmon is a metallic nano-sphere. Figure 1.1 shows a schematic of localized surface plasmons (LSPs) on a nanosphere. For a nanoparticle of diameter much less than that of an incident electromagnetic radiation$(d << \lambda)$, the conduction electrons in the particles are driven to oscillations in phase with the field. This oscillations of conduction electrons leads upto accumulation of opposite charges o either sides of the sphere. The coulomb interaction between these opposite charges builds up a restoring force inside the particle, leading to a natural frequency of oscillation. When the frequency of the incident electromagnetic radiation matches the natural frequency of oscillations of conduction electrons the energy is coupled into LSP modes.[41] This energy coupling leads to resonantly enhanced homogenous field inside the sphere which leads to highly enhanced dipolar field in the immediate vicinity outside the particle. This leads to increased absorption and scattering cross section for the electromagnetic field known as the localized surface plasmon resonances (LSPR).[3, 4, 42] The LSPRs can be studied by examining the farfield spectra from dark field microscopy or by using near field optical microscopy. In dark field spectroscopy we shine whitelight on to the particle under study at an angle such that only the light scattered by the nanoparticles enter the objective lens. This can be done using special dark field apertures (Condensors), Oblique angle incidence[43] or total internal reflection based imaging.[44] The spectra collected using the above means is called a dark field spectra of the nanoparticle and the LSPRs are visible as spectral peaks on the spectra. Additionally there may be various different LSPR modes present in an anisotropic metal nanoparticles which can be probed by coupling
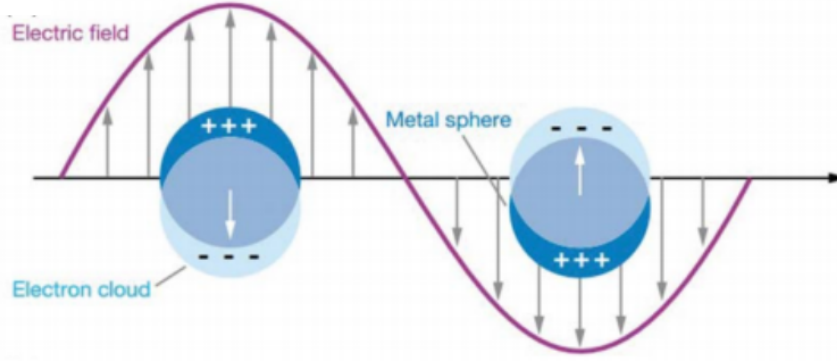
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Figure 1.1: Schematic diagram Localized Surface Plasmons on a metallic nano-sphere. Ref.[75]

the polarization dependent studies to the above mentioned technique.[45] The huge field enhancement in LSPR can be utilized effectively for Surface enhanced Fluorescence spectroscopy (SEF),[38] Surface Enhanced Raman Spectroscopy,[46, 47] since the enhanced electric field in the vicinity of the particle leads to an enhanced molecular emission from the molecules.

1.1.2 Surface Plasmon Polaritons

The coherent oscillations of electrons and the resultant generation of an enhanced near field is not a phenomenon unique to metallic nanoparticles. It is possible for surface plasmon to couple with incident electric field to generate propagating oscillations of conduction electrons. These are surface plasmon modes that can propagate along a metal-dielectric interface and are termed as Surface Plasmon Polaritons (SPPs).[3, 4, 48] Unlike in a nanoparticle where the the propagation is not possible due to the small volume, an extended nanostructure can sustain propagating SPs (hence acting like a waveguide) confined in 2 dimensions. The important thing to note about this interaction is that the momentum of the surface plasmon polaritons is higher than the free space photon of same frequency ($\hbar k_{sp} > \hbar k_0$), where k_{sp} and k_0 are the wavevectors of surface plasmon and the free space photon respectively . This extra momentum of SPP is due to the binding of the charges to the surface. This mismatch in momentum is clear from the dispersion curve of SPP shown in Figure 1.2 (c) where the SPP dispersion relation is given by the equation;

$$k_{sp} = k_0 \times \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \tag{1.1}$$

where the ϵ_m & ϵ_d are the frequency dependent permittivity of metal and the dielectric respectively. Due to this bound and non-radiative nature of SPPs, the field in per-
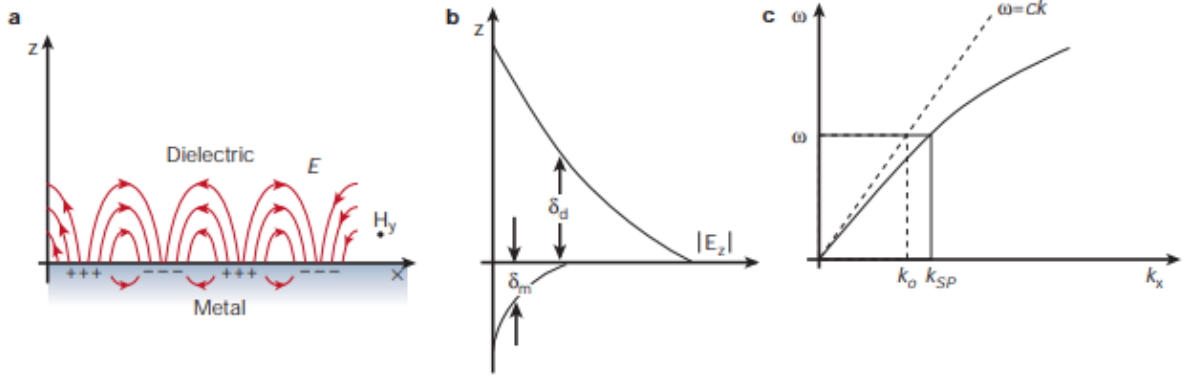
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Figure 1.2: (a) Propagating SPPs in a metal dielectric interface created by an incident normal electric field. (b) The evanescent nature of the SPP field in both the dielectric and metal with decay lengths (δ_d) and (δ_m) respectively. (c) The dispersion curve of SPP modes showing the momentum mismatch. Ref.[76]

pendicular direction to the metal dielectric interface decays exponentially in both the mediums[49, 76] [Fig. 1.2 (a) & (b)].

Since the SPP momentum is always greater than the free space momentum of photon with same frequency, it is not possible to generate SPP by direct illumination of light. Therefore this momentum mismatch between SPP and free space photon has to be bridged in order to generate SPP modes using light.[3, 4, 40, 48] There are several ways to bridge this momentum mismatch; such as grating coupling, prism coupling and shining the light on a defect in the structure where the local symmetry breaking provides the extra momentum required to generate SPP.[3, 4, 48, 49]

1.1.3 Gap/Cavity Plasmons

Gap/cavity plasmons are another category of plasmons, which is prevalently reported in Hybrid configurations such as Metal Insulator- Metal. It has been proven theoretically that to achieve the highest possible enhancement in electric field, the spatial gap between the adjacent plasmonic nanostructures should be of the order of sub-nanometers. This kind of gap structures can concentrate the light to sub-nanometer sizes and hence results in field enhancements of up to 3-4 fold.[50, 51] Hence these plasmonic gap structures have immense importance in plasmonics. These cavities can have various morphology like a hotspot between a metal nanosphere dimers, metal grooves, etc. And depending on the size morphology, the gap structures can support various gap plasmon modes such as gap surface plasmons and channeled plasmon polaritons which may be propagating or localized in nature. The small nanoparticle dimers made of nanospheres and bowtie structures due to their small sizes results in a hot-spot in which the field is confined and highly enhanced.[18] It is possible to create extended cavities as well in which we can

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have propagating gap plasmon modes.[52] The experimental system considered in this thesis, which is a silver wire upon gold film system forms an extended cavity. Thus the gap nanostructures have importance in spectroscopy techniques like surface enhanced fluorescence Spectroscopy(SEF),[38] Surface-Enhanced Raman Spectroscopy (SERS)[46, 47] and also in telecommunication devices.

1.2 Molecular Emissions and Scattering

The absorption and the subsequent re-emission of light by the molecules in the form of molecular emissions and scattering processes forms an important regime of light-matter interaction studies. Fluorescence and Phosphorescence are molecular emission processes and Rayleigh and Raman effect forms the scattering parts of light-matter interaction studies. The Fluorescence and Raman effect which are relevant to the studies part of this thesis are explained in detail in this section.

1.2.1 Flourescence

Fluorescence in simple words is the emission of light by molecules that has absorbed electromagnetic radiation. In Fluorescence an electron relaxes back to its ground state from an excited state releasing a photon that has energy lesser than that of the absorbing radiation which has excited the electron. The compounds/molecules which has excitation wavelength and the subsequent emission of fluorescence lies in visible range are called dyes. The dyes are generally organic in nature. Being multi atomic systems there are a number of vibrational and rotational levels that are embedded in the electronic transition levels of the molecules.

The Fluorescence in a molecule is induced by the pumping of resonant radiation which has an energy corresponding to electronic transition in the molecule. This takes the electrons in the molecule from Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). Once in the excited state the electrons can relax back to the ground state through multiple pathways. The non-radiative transition involves phonons where the electrons relax to the ground state via many ro-vibrational levels that are superimposed on the electronic transition levels of the molecule. The other pathway, radiative in nature, is mediated through the emission of photons and is termed as Fluorescence. The strength of electronic transition between a HOMO and LUMO is determined by the trasition moment matrix between these levels. The dyes or Fluorophores have very less number of ro-vibrational levels which decreases the probability for the non-radiative transitions. Hence strong fluorescence is observed in these type of
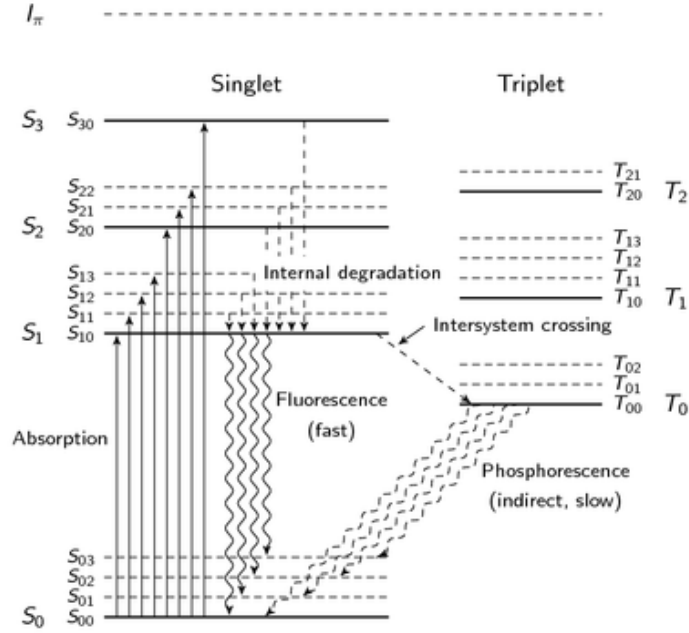
Figure 1.3: Energy level diagram of a Fluorescent molecule. S_0, S_1 & S_2 are different singlet electronic states with multiple vibrational and rotational energy level associated with them. The excited electron have two possible pathways to return to the ground state either radiatively (via photon) or non-radiatively (phonon). Phosphorescence is a much slower molecular emission process in which intersystem crossing of electron occurs.Ref.[53]

molecular systems.

The Fluorescence from dye molecules can be enhanced greatly by placing them in close vicinity to a plasmonic nanoparticle. This enhancement is due to the change in surrounding environment of the molecules.[54] This phenomenon is termed as Purcell effect. For a molecule arreseted in a plasmonic nano cavity the enhancement is given as;[73]

$$P = \frac{3}{4\pi^2} \times (\frac{\lambda}{n})^3 \times (\frac{Q}{V}) \tag{1.2}$$

where the Q is the quality factor of the cavity and V is the modal volume. In the vicinity of a plasmonic nanoparticle or in a plasmonic cavity, the Local Density of States (LDoS) is changed in accordance with the Q & V of the cavity. And since an increase in LDoS pushes the molecules to decay radiatively than non-radiatively, the Fluorescence is enhanced.[73]

1.2.2 Raman Scattering

Raman scattering is another way of light-matter interaction. This is a very important process since the raman scattering spectra produces peaks that are unique to a molecule. Hence the Raman scattered spectra of a molecule can be considered as a fingerprint of

the molecule.[56] Unlike the fluorescence where a resonant radiation is required for the emission, Raman scattering can occur with resonant and non-resonant radiation. In a non-resonant Raman excitation of the molecule, the electron in the molecule is taken to a high energy virtual state. Unlike the electronic and vibrational states these virtual states are not eigen functions of the system and hence very short-lived. The ultrafast relaxation of the electron back to the ground state can be proceeded in two ways; either it can relax back to the initial ground state by releasing a photon that has energy equivalent to that of incident radiation (Rayleigh Scattering). Or the electron can interact with the ro-vibrational states of the molecule's ground state to give rise to Raman Scattering. If the electrons relaxes to a higher vibrational level in the ground state the photon emitted is red-shifted and is termed as Stokes-Raman scattering. And if the electron relaxes to a lower vibrational level comapared to the initial ground state the photon in blue shifted and the process is known as anti-stokes Raman scttering.
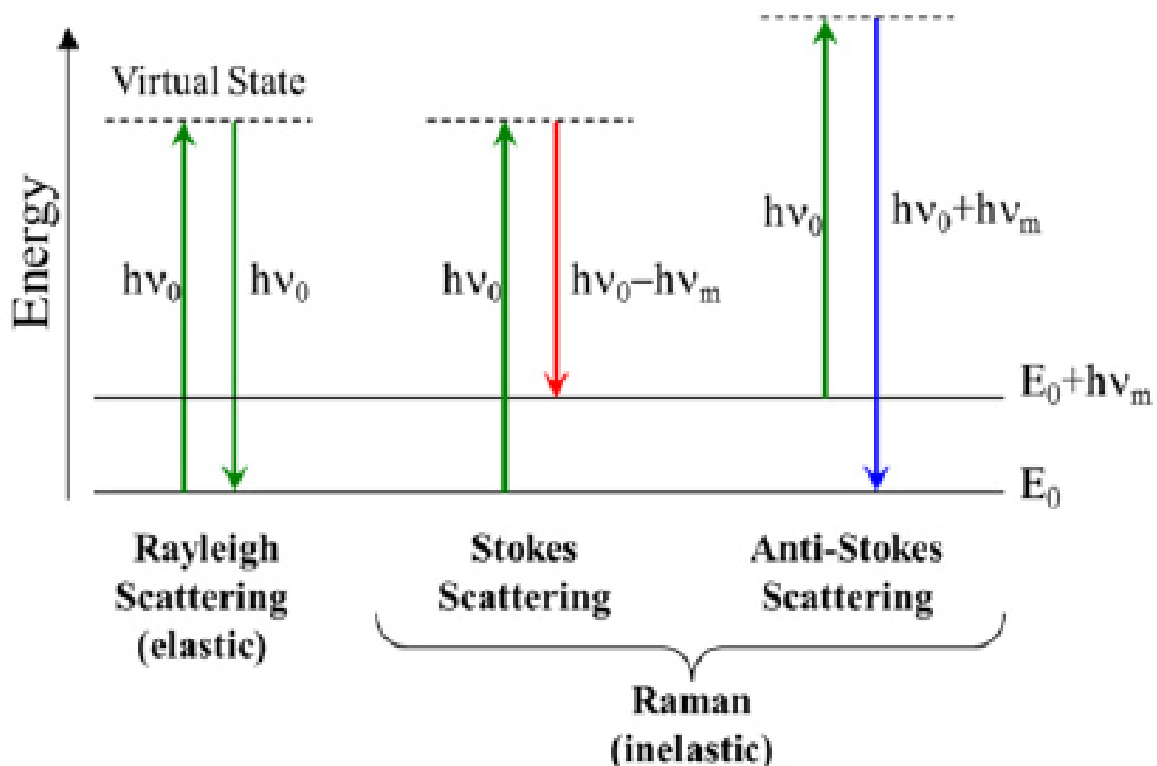
Figure 1.4: Scattering in a molecule. The incoming radiation takes the electron to a virtual energy state from which the electron can relax to initial state (Rayleigh) or absorb a quantum of energy to relax to an excited vibrational level of ground state (Stokes Raman) or emit a quantum of energy to relax to a vibrational level lower than that of initial state (Anti-Stokes Raman).Ref.[57]

In case of resonant Raman scattering the electrons are excited with an incoming

radiation resonant in frequency to one of the electronic transitions of the molecule. Since this is a resonant excitation process the excited electrons can relax back to the ground state via Raman scattering or Fluorescence. Hence in resonant excitation, the Raman and Fluorescence compete each other. However under normal circumstances the absorption cross section of Raman scattering is much much lesser ($\sigma_{fluorescence} \approx 10^{14} \times \sigma_{raman}$) than that of Fluorescence.[3, 4] This difficulty of low Raman intensities compared to that of Fluorescence is overcame in Surface Enhanced Raman Spectroscopy (SERS).[3, 4]

Surface Enhanced Raman Spectroscopy

Surface Enhanced Raman Spectroscopy utilizes the plasmonic effects of tailored metal structures to enhance the raman signals from the molecules. Intensity enhancements up to the order of 10^{14} are observed by taking the molecules to the close vicinity of the plasmonic surfaces.[58] There are two different kinds of interactions that taking place which enhances the Raman signals unprecedentedly.[59, 61] The first kind is the enhancement due to electromagnetic mechanism in which highly enhanced electric fields are present on the surfaces of plasmonic nanostructures and films. This highly enhanced fields at the surfaces of nanostructure is due to the generation of plasmon by the incident electric field.

The enhancement of Raman scattring via electromagnetc mechanism goes as E^4. Where the two powers of E is due to the enhancement of incident electric field as felt by the molecule in the close proximity of plasmonic nanostructure, due to the generation of plasmons. Whereas the other two powers of E is due to the enhancement in raman intensity due to the antenna effects of the nanostructure.[59, 60, 61] Additional factors can be present depending in the case of structure specific antenna effects.

In the second mechanism which is the chemical enhancement, chemisorption of the molecule onto the substrate leads to new electronic states which act as intermediates to the Raman scattering. In case of molecules whose HOMO-LUMO gap energy is in the UV range but very close to to the visible regime, charge transfer processes between the molecules and the film leads to the shifting of HOMO-LUMO gap energy to lower values, i.e, to the visible range. This results in the enhancement of Raman signals, since now the excitation can be resonant with the incoming radiation.[59, 61] The enhancement effect of chemical mechanism is weak compared to that of the electromagnetic mechanism.

SERS is a phenomenon that has been studied extensively in the past 3-4 decades but, not everything is known about this fascinating effect. SERS has various different applications across the disciplines of science and technology such as medical diagnosis, single molecule detection and in explosive detectors.

1.3 Surface Plasmon Coupled Emission

Fluorescence based detections are one of the basic and most important technique in medical diagnosis and biology. Eventhough a highly sensitive detection method, there is always room for improvement in sensitivity to detect smaller and smaller number of molecules. Most of the Fluorescence based detection techniques relies on the free space emission of fluorophores. However the fluorescence emission is a highly isotropic emission due to which the collection efficiency of fluorescence is signal is very low with the normal optical components. This results in a very low detection sensitivity of Fluorescence signal, which is a serious problem when working with a very low concentration of molecules. Surface Plasmon Coupled Emission was proposed in recent past as a potential technique to make the Fluorescence emit in a more directional way, which will increase the collection efficiency and hence the sensitivity of detection of Fluorescence signal.[38, 62, 63] SPCE is a technique which integrates the concepts Fluorescence and plasmonics. In SPCE the Fluorophores are placed very close to the plasmonic thin films coated on a glass substrate typically at a distance of 10-200 nm away from the plasmonic substrate. At this distance the emission from the molecules couples to the surface plasmon polariton modes on the plasmonic film and subsequently re-radiates in to the glass substrate at surface plasmon resonance (SPR) angles.[64, 66, 65] SPCE with very high collection efficiency and very low background noise have applications ranging from DNA Sensing, detection of chemically and biologically important molecules and single molecule spectroscopy.[38, 67, 64]

Theory

The concepts on SPCE can be understood with the knowledge on the physics of surface plasmons and the Surface plasmon resonance (SPR). The SPR is a phenomenon in which the light shined on a metallic film at an angle generates the surface plasmons on the film.[38] For all purposes the SPCE can be considered as a reverse process of SPR. In SPCE the light is emitted by the gold film via surface plasmons which are generated due to the nearfield excitation by the fluorophores.

The SPR occurs when the wave vector of incident light (k_0) matches the surface plasmon wave vector (k_{sp}) on the film. Due to the momentum mismatch describes in the first section, direct illumination of light onto the film will not generate the SPPs. Hence a different approach is taken in which the light is made to travel through a high refractive index medium with dielectric constant ϵ_0 which will result in lowering of light line in dispersion curve by factor of $\sqrt{\epsilon_0}$. This is possible by using a TIR configuration. The

wave vector of the incident light in prism is given by;

$$k_p = n_p k_0 \qquad (1.3)$$

where the n_p is the refractive index of the prism. The wave vector of the surface plasmon modes is given by equation 1.1. The incident light will interact with the surface plasmons on the film when the x component of the wave vector of incident light is equal to the wave vector of the surface plasmon on film.
ie,

$$k_x = k_0 n_p \sin(\theta_i) = k_0 \times \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \qquad (1.4)$$

This equation 1.3 is an important one since it implies that the electric field vector of incident light has to be modified by a factor of $\sin(\theta_i)$ at the metal plane. This condition can only be satisfied when the incident electric field vector is parallel to the plane of incidence. Hence only the component of light that is polarized parallel to the plane of incidence (p-polarized) can result in SPR.
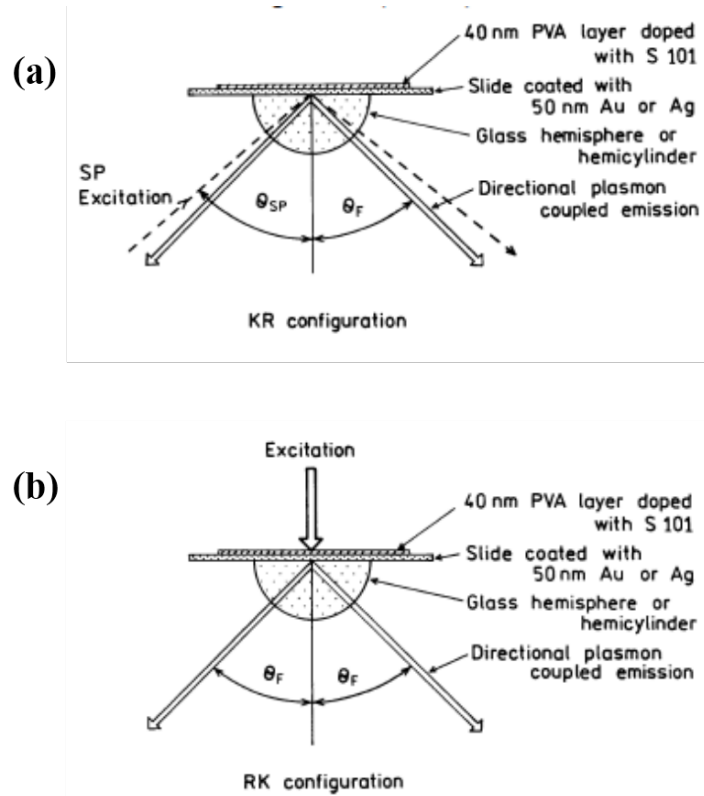

Figure 1.5: Different configurations with which we can achieve SPCE (a) Kretschmann configuration (b) Reverse Kretschmann configuration. Ref.[38]

The phenomenon of SPCE can be described in relation with SPR. The excited surface

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plasmons on the metal film propagates along the metal-dielectric interface with an intensity that is exponentially decaying in perpendicular and parallel to the surface due to damped oscillations. Similar to this, In SPCE all the out-coupled photons are p-polarized irrespective of the polarization of the incident light. This evanescent field extends about 200 nm into the media. The fluorophores that are present in the near field will experience an enhanced electric field and these excited dipoles will couple strongly to these oscillations and results in radiation towards the prism side. This de-coupling of surface plasmons into photons is also a momentum matched process and hence the p-polarized emission is emitted in directions where the prism and surface wave-vectors matches exactly.

We can achieve SPCE mainly in two different configurations; Fluorophores are excited either through the prism side or through sample side. In the first mode, the light is incident on the metal film through the prism generating surface plasmons which excites the fluorophores in near field. This configuration is similar to that in SPR and is known as Kretschmann (KR) configuration. (Fig. 1.5 a) In the second configuration the incident light excites the Fluorophores directly, these excited dipoles then couples to the surface plasmons in near field to generate a directional emission. This configuration is known as Reverse Kretschmann (RK) configuration (Fig. 1.5 b). For our studies on surface plasmon coupled emission from Ag NW-Au mirror system we will be using the RK configuration.

Important properties of SPCE

(1) Directional emission : Nearly all the signal that is generated in SPCE is emitted in one particular direction which increases the collection efficiency and the sensitivity drastically. Due to the combined effect of enhanced directionality and enhanced electric field in the excitation configuration, very low concentrations of molecules can be detected easily.

(2) Background Suppression : Since the SPCE arises due to the interaction between the Fluorophores and gold film, only the emitters that are really close to the film will be coupling to the surface plasmon modes in the film.. This way the contribution from the background is rejected.

(3) p-polarized emission: The SPCE signal is p-polarized, which is a result of coupling with plasmons. Hence one can reject any background scattering components by using an analyzer.[38]

1.4 Motivation for the Thesis Problem

Antenna effects of metal nanostructures and modification in molecular emission due to these structures are an important area of research which has wide range applications in nano-optics and telecommunication technology. So its imperative to study these nanostructures with which we can tailor light matter interaction at nano-scale.

Various hybrid nanostructures were reported previously which can confine and enhance electric field in its vicinity. Such kind of systems can enhance the molecular emissions from molecules placed in their vicinity. This phenomenon is known as Surface enhanced Fluorescence. The emission from these kind of structures not only modifies the intensity but can also affect the re-direct the radiation in certain directions.

The system discussed in this thesis deals with an anisotropic metallic nanowire placed on a plasmonic film made up of gold. Eventhough there has been a number of studies on the molecular emission from hot-spots created due to coupled nanostructures, the effect of an extended cavity/hot-spot on molecular emission is seldom discussed. We can address several questions concerning this system. How a fluorophore's emission is modified when placed in a 1-D extended cavity ? What will be the effects of plasmonic film and silver nanowire on the emission intensity? How the isotropic emission of molecular fluorescence is re-directed when the molecules are placed in an extended cavity? what might be the polarization dependence of the output signal in remote excitation? Another interesting study is the SPCE of molecular emission with an extended cavity system. As mentioned in the previous section the SPCE provides a very high directional emission compared to that free space molecular emission. So it will be worth to look at this system, and how the directionality of the emission is modified? chapter 3 deals with this Ag nanowire-gold film system and tries to address the questions mentioned above.

Chapter 2

Methods and Materials

The optical antenna effects in the visible frequency regime require antenna dimensions of the order of nanometers.[5] Hence the fabrication/synthesis of nanometer-sized structures has become an integral part of the research in Plasmonics and Photonics. As mentioned in the first chapter there are several tops to bottom and bottom-up ways for the fabrication of nanostructures, Electron Beam Lithography, Chemical Vapor Deposition techniques and Wet-phase synthesis to name a few. Each of this techniques has its own advantages as well as disadvantages.

The lithographic methods are highly precise and gave us accurate control over the size and geometry of the nanostructures. Hence for experiments where we need precise control over the size, shape, and gap between the nanostructures lithographic methods are required. However, the lithographic techniques are tedious, time-consuming and can only be done with highly sophisticated machinery. Another major drawback is that the lithographically prepared structures are always in polycrystalline in nature and will results in defects which will result in damping of propagating plasmons. In contrast to lithographic techniques, CVD provides highly single crystalline structures which are ideal for Plasmonics. But the major drawback of this method is that this also requires highly sophisticated machinery, Ultra-high vacuum, and ultra-clean environments.

However, the chemically prepared nanostructures via Wet-phase synthesis presents us many unique advantages over other fabrication methods such as EBL and CVD etc. This is mainly due to the fact that it is highly cost-effective, have high yields as well as this will result in structures that are highly single crystalline. The chemical synthesis techniques dont need any sophisticated types of machinery and can be done in normal lab environments at standard temperature and pressure. This method also presents high versatility in the size and shape of the resultant structures and can be used to make a wide variety of nanostructures with various different materials.

Silver NWs are one of the most extensively studied metal nanostructures. They sup-

port propagating Surface Plasmon Polaritons and hence a leading contender for integrated plasmon Optics and has applications in Nanoelectronics, NanoOptics, and devices as well. They are quite interesting due to their inherent anisotropy in the geometry, various novel optical and physical properties such as strong SERS and SEF activity, dual plasmon resonance bands, photoluminescence, electrical and thermal conductivity and antenna effects which modifies the emission properties of molecules placed in their vicinity. In a recent publication, it has shown that counter propagating plasmons could generate Second Harmonic Generation in Ag NW-Molybdenum DiSulphide hybrid system.[69] The chemically prepared Ag NWs possess a thin layer of PVP coating (which prevents the aggregation of NWs in solution) which will result in a Huge enhancement in SERS if a Raman active molecule is brought to its vicinity. Such kind of SERS enhancements has a crucial role in cancer diagnosis and Analytical chemistry .

2.1 Synthesis of Silver Nano-Wires

Penta-twinned Ag NWs were prepared using Ascorbic Acid (AA) reduction method. There are several existing polyol based techniques for the synthesis of Ag NW. but most of them requiring seed particles at one stage of the reaction. This AA reduction synthesis of Ag NW does not involve any heterogeneous or homogeneous seed particles or any other ionic impurities. In most of the polyol synthesis techniques of metal nanostructures, Poly Vinyl Pyrrolidone (PVP) acts as the capping agent and gets adsorbed on the specific crystal facets of the precursor structures and direct the growth of anisotropic structure in one particular direction. However, in the AA reduction scheme, the rapid growth of the microrods are controlled by the kinetic activation of Ascorbic Acid, which results in 1-D structures which remain perfectly straight unlike in the other polyol synthesis pathways.[68] A typical AA reduction synthesis protocol of Ag NW is as follows;

Firstly, all the different solutions that have to be added to the reaction mixture are prepared:

(a) 0.2 M AgNO3 in 3 ml Ethylene Glycol.

(b) 0.35 M Poly Vinyl Pyrrolidone (Mol. wt. 25 kDa) in 3 ml Ethylene glycol.

(c) 0.1 M Ascorbic Acid in 1 ml of Ethylene glycol

After the preparation of all solutions, 5 ml ethylene glycol was heated at 160 °C for 1 hour with continuous stirring in a small glass vial using magnetic stirrer cum heater. After 1 hour heating of ethylene glycol, 60 μl of solution (a) was added, immediately followed by the addition of 60 μl of solution (b) and then 20 μl of solution (c). In this manner, all reactants were added within 7 min after the one-hour heating. The Pictorial scheme of reaction is given in fig. 2.1
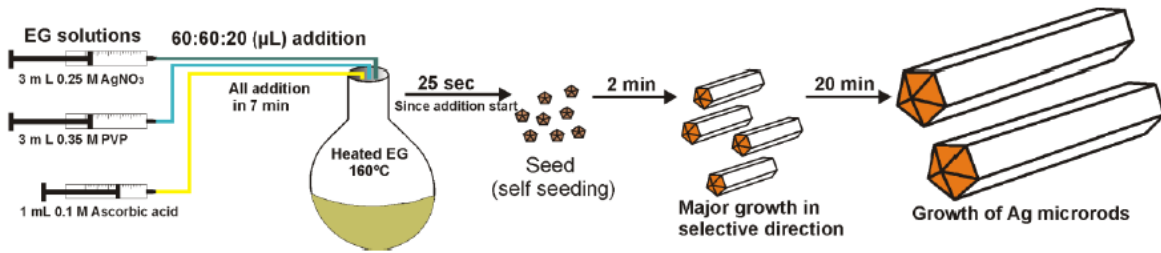
Figure 2.1: Schematic diagram of Ag NW synthesis using Ascorbic Acid reduction method.Ref.[68]

Ascorbic acid is the driving force to form Ag micro-rods. Increasing/decreasing the concentration of Ascorbic Acid from the ideal value will result in significant and unwanted changes in the structures formed. An increased concentration of AA will result in bigger structure since the extra amount of AA added will increase the nucleation rate of Ag atoms. Whereas a decreased amount of AA will stunt the formation of elongated structure and hence will result in Ag colloidal particle solution. In the absence of AA, the Ethylene glycol will reduce the Ag ions at high temperature. But, Ethylene glycol is a weak reducing agent in nature compared to AA and hence the resultant nucleation and growth process is very slow as opposed to faster rate when AA is used. The FESEM images of Ag NW prepared through AA reduction scheme is given in Fig. 2.2

2.2 Au Thin Film Deposition

Metal thin film structures have a variety of important applications in plasmonics, organic transistors, 2D metal devices and as a substrate for 2D material growth etc. The metal thin films are deposited by physical vapor deposition. The surface onto which the films are deposited is termed as substrates and usually can be dielectric or semiconducting in nature. Thin film deposition has an important role to play in Solar cell physics and manufacture of optical components as well. The films deposited can have a thickness of the order of Angstroms to micrometers depending upon the problem at hand.

One of the most common and popular methods of PVD is Thermal Evaporation. We can use Thermal evaporation technique to make thin films of various different materials including both metals and non-metals or can be molecules such as silicon oxides and nitrides. Thermal Evaporation or Thermal Vapor Deposition (TVD) involves heating a solid material inside a high vacuum chamber in which pressure as low as 3×10^{-7} mbar (Torr) is attained using a combination of normal pump and a Turbopump.

The material to be coated is placed in boats which are normally made up of high-temperature resistant metals such as Tungsten. These boats have troughs into which the material is placed. High current is applied to the boats which will heat up and vaporize
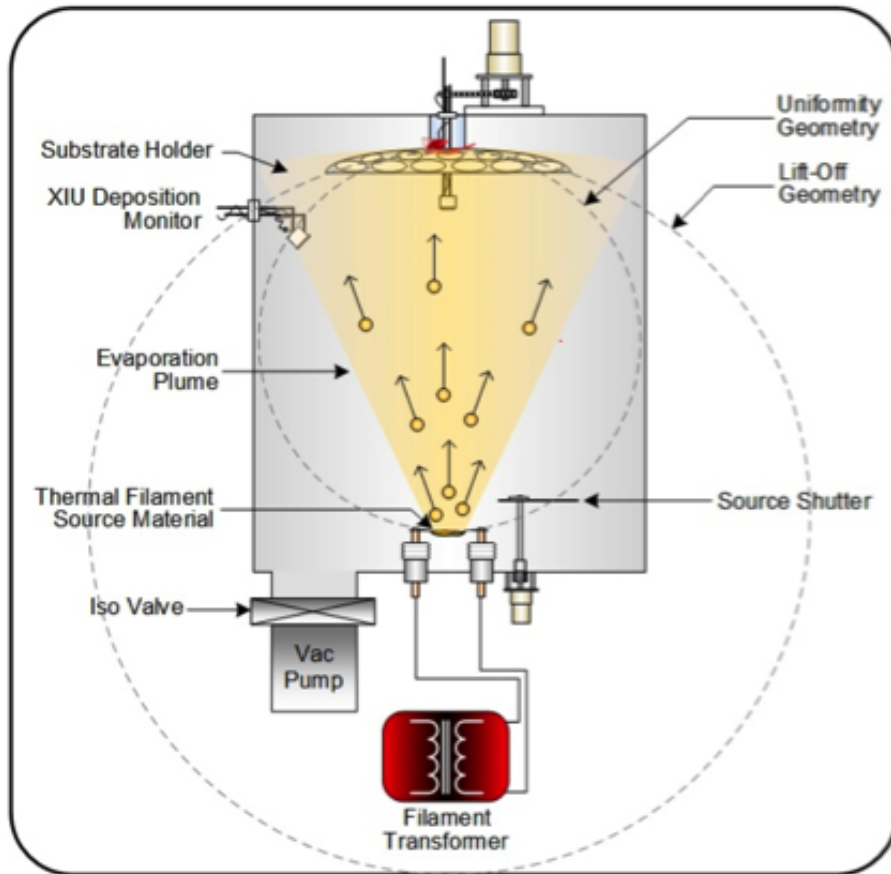
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Figure 2.2: Schematic diagram of Thermal Vapor Deposition. Ref.[70]

the material placed inside. At Ultrahigh Vacuum chamber, even a low vapor pressure is sufficient enough to raise a vapor cloud. The vapor stream then traverses and hits the substrate, sticking to form a film. Since the material to be coated is heated to melting point and forms a liquid, the boats are usually placed at the bottom of the chamber. The surfaces that are intended to be coated (Glass coverslip) are fixed on the top side of the chamber facing downwards toward the heated source material to receive the vapor cloud

Au films of thicknesses 50 nm and 170 nm have been deposited by Thermal Evaporation using an Inficon SQC 310 deposition machine ( ). The films have been deposited with a deposition rate of 0.1 Å /s, a chamber pressure of 3×10^{-7} mbar, and a substrate temperature between 17 and 20 °C. The system is left for an entire night to build up the ultra-high vacuum necessary for the deposition. The thin-film thickness has been monitored by the use of a quartz crystal thickness monitor (QCM). Further Atomic force Microscopy measurements have been done to confirm the film thickness.

2.3 Fourier Microscopy

The Ultimate aim of Plasmonics and Photonics is to build functional optoelectronic components and devices from single and coupled plasmonic and metamaterial scatterers. So, it is crucial to quantify and understand how the individual components scatter light into the far-field. Such a quantification requires information not only on the magnitude and cross sections of scattering but also on the angular distribution of light in the far field. The technique with which we measure this far-field angular distribution of light is called Fourier plane imaging or Back Focal Plane Imaging (BFP).[71, 73]

Back Focal plane imaging microscopy works on the very basic concept that the image formed at the back focal plane of a lens is the Fourier transform of the actual image.[73] Figure 2.3 shows the schematic diagram of image formation at the back focal plane of the objective lens. BFP imaging is a crucial tool in quantifying the scattering properties of single and arrays of plasmonic scatterers, which are in future expected to be the main building blocks of solar cells and nanoantennas etc. Over the years there have been multiple reports on the use of BFP in imaging of the angular distribution of light from various single and coupled nanostructures as well as a single molecule. In one of the earliest reports on BFP imaging, it has shown that it is possible to reconstruct the molecules emission dipole moment from its emission pattern.[72]

Objective lens

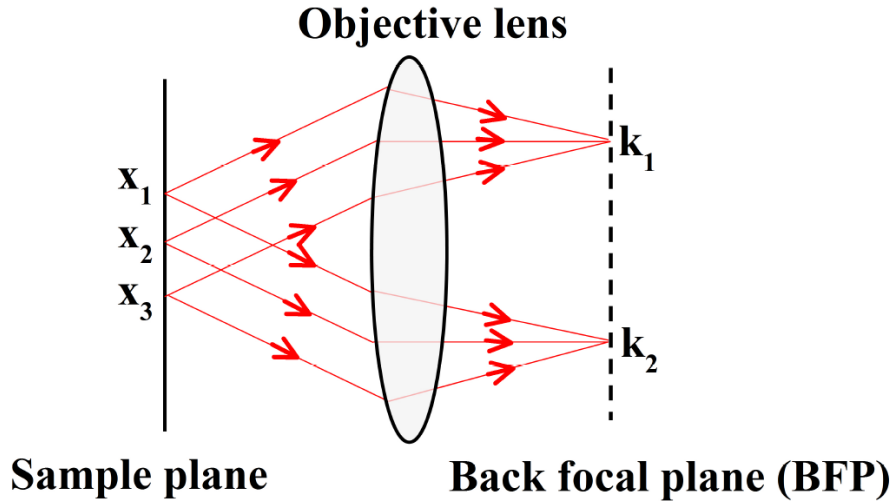**Sample plane**   **Back focal plane (BFP)**

Figure 2.3: Schematic showing image formation at the back focal plane of a lens. Ref[41]

In BFP imaging, we collect the emitted photons from the sample using an objective lens to image the intensity distribution at the back focal plane of the objective lens. ie, the light emitted from the sample plane is decomposed into individual plane waves by the objective lens and all the plane waves with same wave vector (same direction) is focused to a unique point in the BFP of the lens (or the back-aperture plane for an infinity-corrected system). The difference between the image plane and the back focal

plane lies in the way the image points are resolved. At the back focal plane the imaged points are resolved by the direction of emission (k-vectors) and at the real image plane, the image points are resolved spatially. Since the rays having the same direction meets at a unique point in the back focal plane (Fig.2.3), each point in the BFP image represents a k-vector or emission direction. For a simple lens definition and imaging of BFP is easy, however, not so for a complex lens system such as an objective lens. The BFP of an objective lens is formed at a very short distance from the lens itself. Since it is an infinity corrected system, the Fourier image is formed at the back aperture plane of the lens and hence not possible to image using a detector. Therefore a relay of lenses has to be used to image the BFP by forming a conjugate back focal plane at the imaging CCD. Figure 2.4 is a schematic of the formation of conjugate BFP using a combination of tube lens and a Bertrand lens.
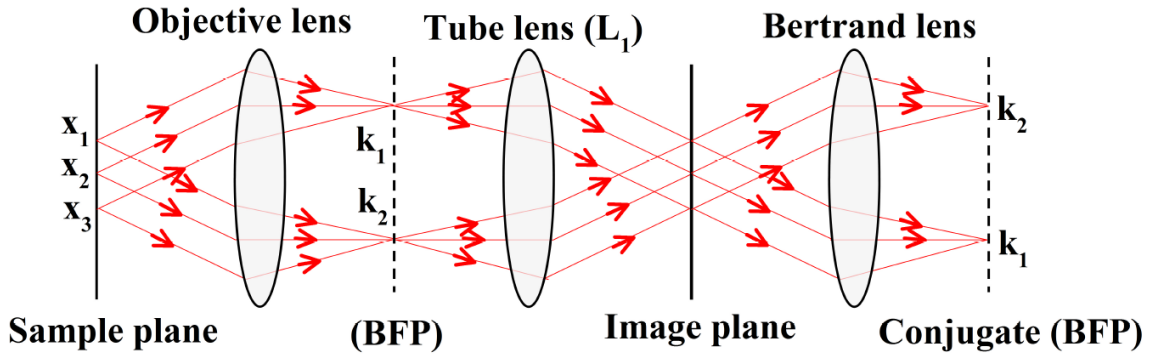

Figure 2.4: Schematic showing formation of conjugate BFP using a combination of tube lens and a Bertrand lens. Ref[41]

As mentioned in the previous chapters, silver nanowires are known to act as nanoantennas for the visible regime. Our motive is to probe whether this characteristic property of nanowire affects or alter the nature of emission from the molecules confined in the plasmonic cavity. BFP imaging and further E-k spectroscopy are helpful in separating out the various molecular emission processes which might be having different wave vector distribution in the Fourier space.
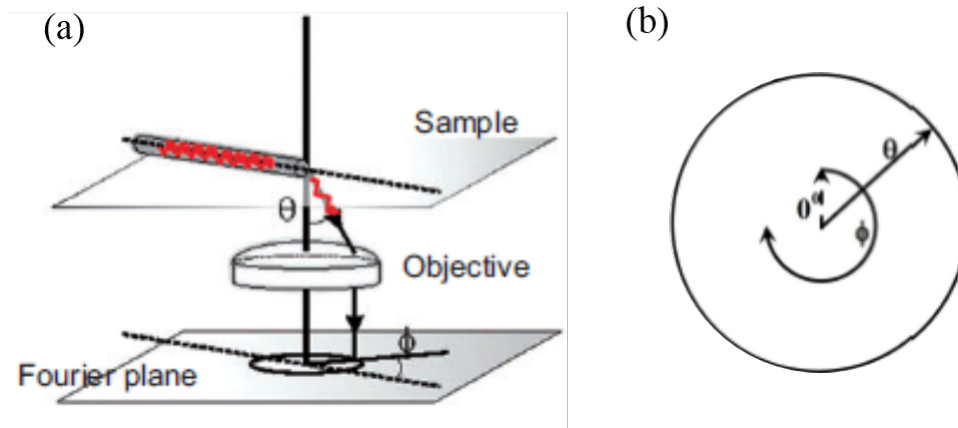
2.3.1 Cordinate system in back focal plane

Figure 2.5: (a)The projection of angular emission emission from the distal end of a nanowire on to the Fourier space. (b) Cordinates in the fourier space image. The radial direction is the polar angle θ and the tangential direction is the azimuthal angle ϕ.Ref[72]

Figure 2.5 depicts how the angular emission from a nano-structure is projected onto the back focal plane of a lens. In a back focal plane image the polar angle θ is the radial direction and azimuthal angle ϕ is given the azimuthal direction. For the experiments we have used a 100X, 0.95 NA air immersion lens and a 100X, 1.49 NA oil immersion lens which has a maximum collection angle of 71.8° and 78.6° respectively.

Chapter 3

Plasmon Coupled Emission from Silver NW - gold Film System

As mentioned in the chapter 1, the Emission from the molecules that are placed on the dielectric substrates exhibits an isotropic nature of emission. Ie, the molecules doesnt have any preferential direction of emission. The directionality and enhancement of molecular emission is crucial in shaping efficient nanoantennas. The emission from the molecules can be altered by changing the dielectric environment in which they are placed. Coupling the molecules with plasmonic nanostructures is a potential method by which we can achieve this modification of molecular emission. As mentioned in previous chapters, silver NW exbibits antenna properties and the emission from molecules that are placed in the vicinity of the NWs can get affected by the propagating surface plasmons that are generated on the wire. This propagating plasmons that are generated on the NWs can not only affect the emission direction but also can enhance the intensity of the emission from the molecules since the plasmon oscillations generated in subwavelength nanostructures causes near field enhancement in the vicinity of the molecules. Due to the synthesis procedure followed, there is a coating of PVP around the Ag NW which acts as a capping agent and prevents aggregation of NWs in solution. Due to the presence of the coating of PVP which has refractive index value similar to that of glass (approx. 1.5) the molecules are not in direct contact with silver. A slight modification of the aforementioned system of molecules in vicinity of Ag NW can further modify the molecular emission. By adding a bare metallic film of gold on to which the molecules and the Ag NW are drop casted results in a plasmonic cavity structure (due to the presence of thin coating of PVP) in which the molecules are confined. This cavity structure with an average gap size of 5-10 nm can sustain gap plasmon modes and hence the emission from the molecules confined in the cavity will be enhanced greatly due to the extremely high enhancement in local electric field. This extended cavity that formed which essentially is a hot-spot is of high

interest since this structure forms image dipoles on the film, which will enhance the local electric field. The image effect and the resultant enhancement in electric field is only true for the vertical dipoles since the horizontal dipole will be cancelled out due to the film.
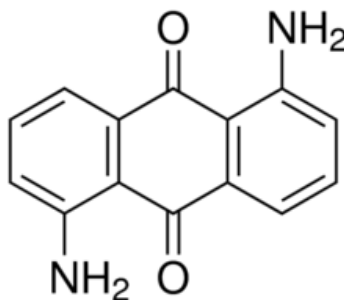
Figure 3.1: Molecular structure of 1,5-Diamino Anthraquinone (DAAQ) molecule

Changing the thickness of the gold film can also affect the plasmon coupled emission from the molecules greatly as the surface plasmons will not be generated efficiently in plasmonic films of thickness greater than 60 nm. So for our purposes a gold film of thickness greater than 150 nm will act as a mirror and the plasmons that are coupling to the molecular emission are solely due to the propagating surface plasmons from the silver NW. Using a gold film of thickness 50 nm will enable the formation of surface plasmon on the film. In this particular configuration the highly enhanced electric field will result in an enhanced emission from the molecules confined in the cavity which will in turn couple to the surface plasmons on the thin gold film. Using a thin film will enable us to perform leakage radiation microscopy of this particular configuration and since the emission that leaking towards the substrate is due to SPCE, it is expected that this emission will be highly directional in nature compared to the emission from an Ag NW-gold mirror system. For the study of enhancement and directionality of molecular emission (Fluorescence) from Ag NW-gold mirror system, 1,5-Diamino Anthraquinone (DAAQ) a dye resonant at 532 nm is chosen.

3.1 Plasmon Coupled emission form Ag Nanowires on a thick gold film

This set of experiments deals with a system of silver Nanowires coupled to a Thick gold film of thickness close to 170 nm. The gold film is thermally evaporated onto a glass coverslip. Since the thickness of the gold film is greater than 100 nm, surface plasmons will not be generated on it. The silver NWs are synthesized using a well-known procedure. These NWs have pentatwinned structures and have a length of 10-12 μm and width of 350-400 nm. Figure 3.2 (a) shows an optical image of typical silver NW as seen through a

100X, 0.95 NA objective lens. The wires have a coating of Polyvinyl Pyrrolidone (PVP) of thickness up to 5 nm on all sides. PVP is a dielectric material and has a refractive index close to 1.5 which is pretty close to the refractive index of the glass. The presence of this coating will prevent the molecules from coming in contact with the metal and resultant quenching of fluorescence. Since we are drop-casting the dye molecules onto a gold film, the proximity of the molecules to the film can also result in quenching of Fluorescence. To prevent this unwanted quenching of fluorescence, the gold film is coated with a very thin layer of SiO2 which has a thickness of 2-5 nm using the sputtering technique. The presence of the PVP coating on the silver NW and the additional SiO2 coating on the gold film ensures the formation of an extended cavity of width 5-10 nm in between the wire and film. The molecules confined in the 1-D elongated system is highly interesting Since opposed to a 0-D particle (in which only localized plasmons can be excited) the Ag NW sustains propagating surface plasmons. This system will enable us, to study about the enhancement and directionality of molecular emission due to the interaction between the molecules and the propagating surface plasmons. Since the molecules are confined in a plasmonic nanocavity between the silver nanowire and gold film, the local electric fields will be highly enhanced due to the confinement effects of the cavity. The presence of the silver nanowire can also affect the directionality of emission from the molecule due to its antenna properties. In a typical experiment, the DAAQ molecules with a concentration of 10^{-7} M in Ethanol is drop-casted onto the gold film and kept for drying. The Ag NWs are drop-casted on top of the molecules.Figure 3.3 shows the schematic of the system under study.
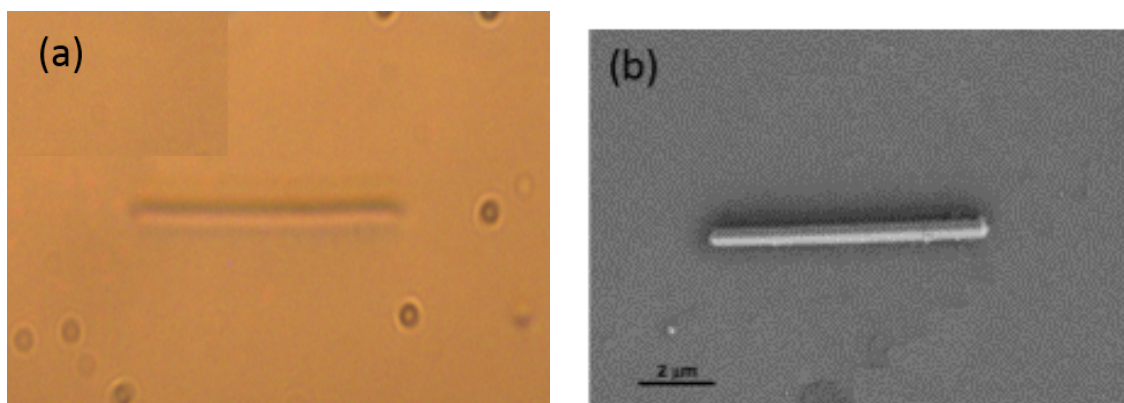

Figure 3.2: (a) Optical image of an Ag NW resting on a gold film. Illuminated using a white light source. as seen using a 100X, 0.95NA objective lens. (b) FESEM image of Ag NW. The petatwinned facets of NW are visible.
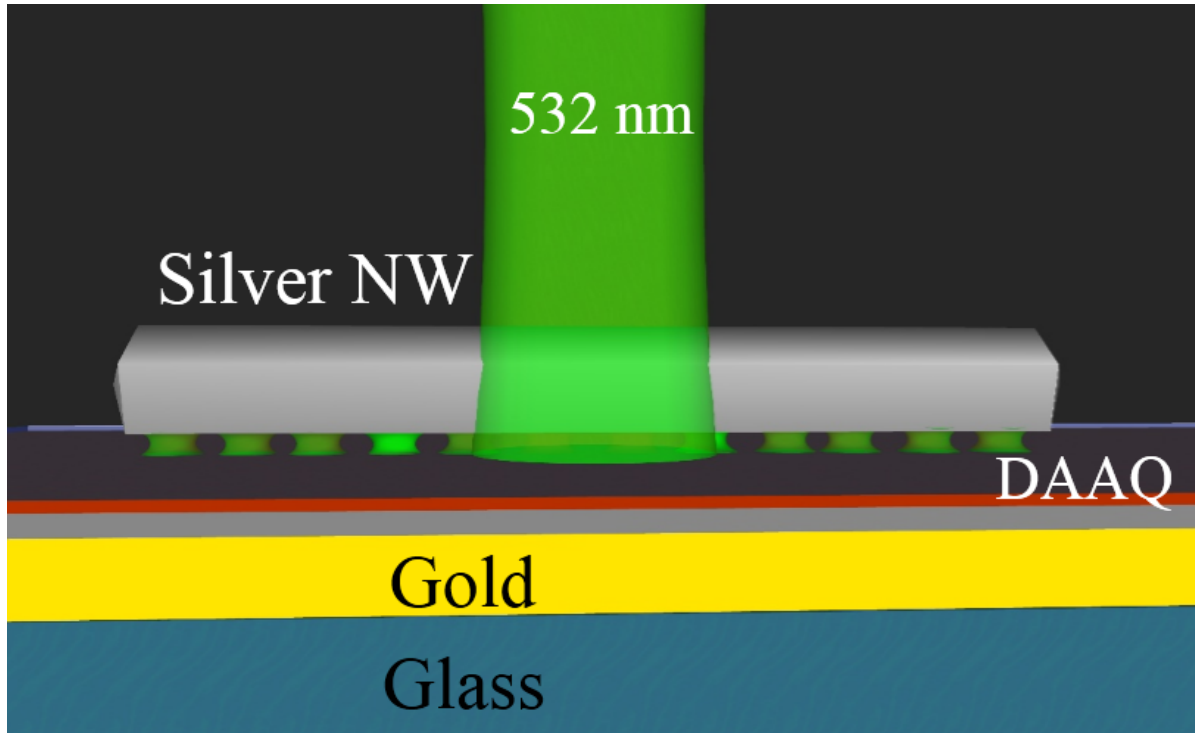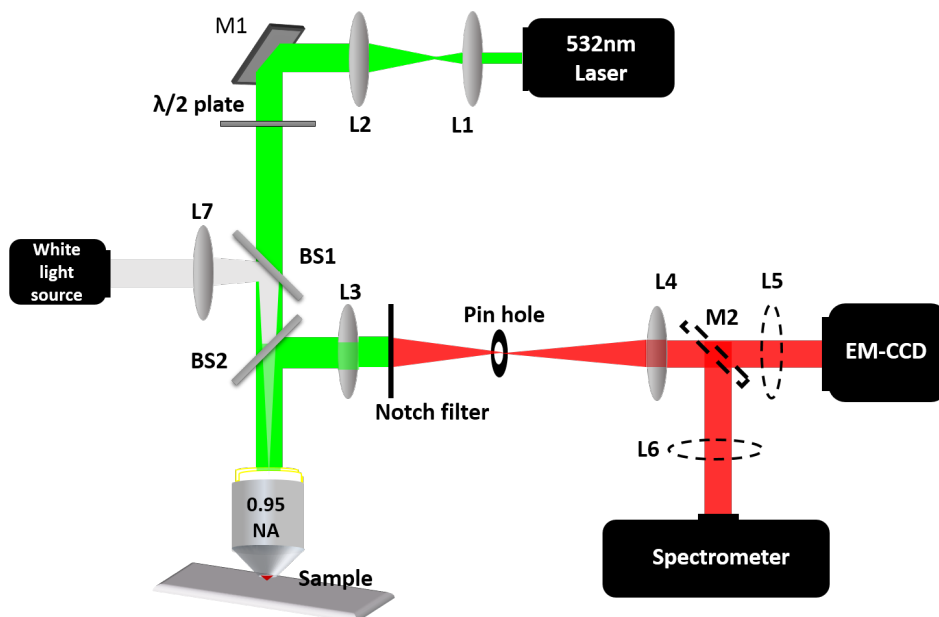
Figure 3.3: The schematic of the system used for enhancement of molecular emission studies. The Ag NW is excited at the center using 532 nm gaussian beam and the collection is also from the same point done using a 100X, 0.95 NA objective lens.

3.1.1 Experimental setup

For the studies on the silver nanowire-gold mirror coupled system, a home built microscopy setup (Figure 3.4) is used. This setup is coupled to a Horiba IHR320 spectrometer. The experimental system is excited using a 532 nm gaussian laser beam. A combination of lenses L1 and L2 is used to expand the beam to fill the back aperture of the objective lens. a $\lambda/2$ plate is used to control the polarization of the input beam. The Ag NW is illuminated using a white light source. The wires are easily visible in the white light illumination. A 100X, 0.95 NA objective lens is used to focus the laser on to the sample. The emission from the system is collected using the same lens. A 532 nm edge/notch filter is used to filter out the Rayleigh emission from the collected signal. A pin hole placed at the conjugate plane is used to spatially filter the radiation from desired areas of the structure under study. A flip mirror is used to to channel the collected signal to CCD and spectrometer. An EM-CCD is used to image the angular emission pattern of the nano-structures. This set up is built by Mr. Adarsh B. Vasista. This is a highly versatile setup and we can insert multiple optical components like analyzers, wave plates etc in both input and output path depending on the experimental scenario.

Figure 3.4: Schematic of the experimental setup used for the studies on Ag NW-gold mirror system. A 532 nm laser is used for the excitation of experimental system. A 100X, 0.95 NA objective lens is used for focusing the laser. A $\lambda/2$ plate is used to control the input polarization of the incident laser. L3: Tube lens, L4: Bertrand lens, M2: Flip mirror, L5 and L6: Focusing flip lens, BS: Beam splitters.

3.1.2 Enhancement in Fluorescence

The spectroscopy of the aforementioned system given in figure 3.3 is done on the experimental set up described in figure 3.4. The sample preparation for the experiments is briefly explained below;

(i) A small piece of glass coverslip coated with gold film of thickness 150-170 nm is washed with acetone to remove any impurities glued to the surface.

(ii) 6-10 μl of 10^{-4} M DAAQ molecule solution in ethanol is drop-casted on to the gold film.

(iii) After the molecules are dried, Ag NW solution is drop-casted and kept for drying.

Since the wires are of micron size it is easy to visualize them in white light illumination. We have used a 100X, 0.95 NA objective lens to focus the lase on to the system and to collect the generated signal. The excitation and collection of signal is from the same point on the wire. Acquisition time for all the measurements are kept at 5 seconds. Figure 3.5 (a) shows the effect of presence of gold film. The enhancement in fluorescence emission from molecules confined in silver NW-gold mirror cavity is huge compared to that of the emission from molecules that are resting between Silver NW-Glass. This huge enhancement is due to the formation of plasmonic cavity by silver NW and gold film. To make

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sure that this enhancement is in fact due to the formation of the cavity, experiments have been done where the signal has been collected from the substrate (off cavity) and from NW (On cavity). Figure 3.5 (b) shows the enhancement in fluorescence from molecules in the presence and absence of silver NW on a gold film.

The calculation of purcell enhancement factor is an important part in the study of cavity systems. But, It is not straightforward to calculate the Purcell enhancement factor in this particular case as we dont have strict control over the cavity parameters. The Au film is not of uniform thickness and the PVP coating over the silver nanowire has also variations in thickness over the length. Moreover the thickness of the molecule layers is case to case dependent. Since we are drop casting the molecules on to the film it is very difficult to obtain a single or a definite number of layers with a uniform thickness. All these experimental constraints explained above makes the calculation of Purcell factor for this open cavity cumbersome. However we can calculate an approximate value by taking the area under the curve for the Fluorescence from the NW on film and NW on glass substrate. This ballpark figure of Purcell enhancement factor is close to 4.

The Purcell effect describes the enhancement in spontaneous emission rate due to the change in LDoS. It does not have any effect on the directionality of emission from the molecules. The directionality of the emission arises due to the antenna effects of the nanostructure, in this particular case the silver nanowire. The directional emission from these cavity structures are presented in Figure 3.10 & 3.15.
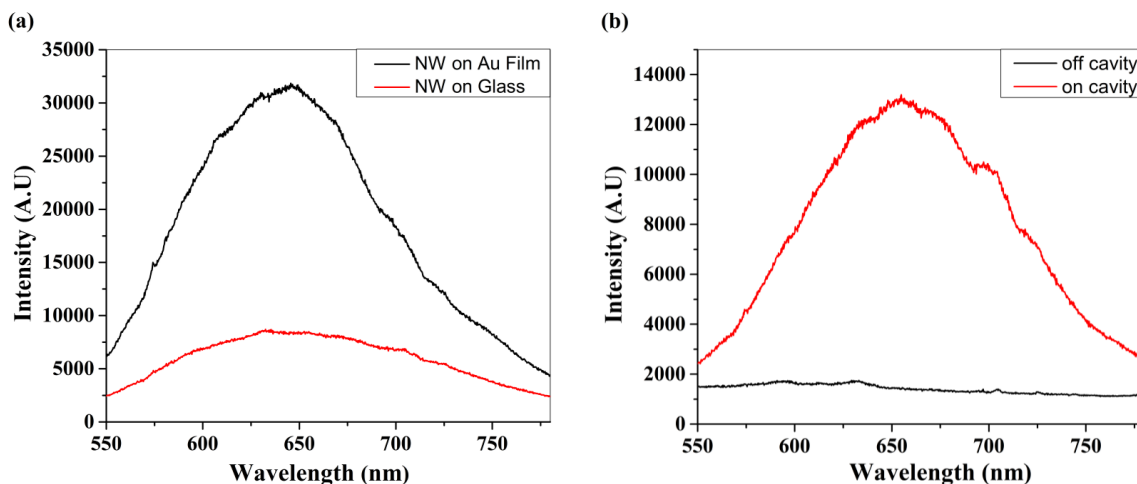
Figure 3.5: (a) The enhancement effect of gold film. As expected the enhancement in fluorescence is huge in case of Ag NW-Au mirror system compared to that of Ag NW-Glass system. A 4-fold enhancement in fluorescence is observed. The reason for this observation can be attributed to the formation of cavity and the resultant local field enhancement in the presence of Au film. (b) Fluorescence from the molecule in presence and absence of Ag NW. Signal is collected from the molecules on Au film (off cavity) and molecules confined in cavity formed by Ag NW and Au mirror.

3.2 Remote Excitation Fluorescence

To probe the antenna effects of the Ag NW-Au mirror system further, remote excitation fluorescence experiments has to be done. Ag NW on glass are shown to have propagation with 532 nm laser. So the remote excitation experiments on this altered system of Ag NW-Au mirror can reveal a lot about the antenna properties of the system. Since the remote excitation experiments involves excitation at one distal end and the collection from the other. ie, information is transmitted from one point to another using a nanoscale waveguide. Due to this reason this set of experiments has crucial importance in nano-communication devices. This coupled system of NW-Film have interesting directional emission properties, which will be addressed shortly.

For the remote excitation studies experimental setup shown in figure 3.4 is used. The 532 nm laser is focused on to one distal end of the wire using a 100X, 0.95 NA objective lens. Acquisition time of 2 Seconds is used while taking spectra. Higher exposure times resulted in signal saturation. The signal that is transmitted to the other end of the NW has been spatially filtered using a pin hole and spectrally filtered using a 532 nm edge/notch filter to filter out rayleigh component. Figure 3.6 depicts the experimental system in remote excitation measurements.
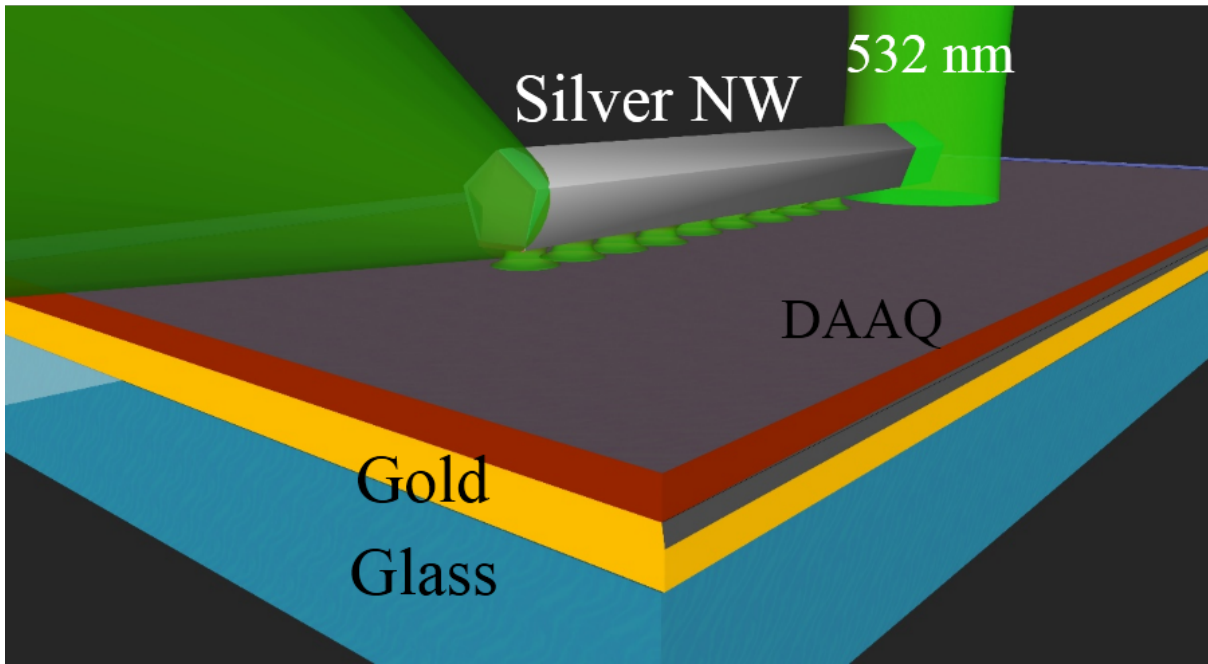
Figure 3.6: The schematic of the system used for remote excitation fluorescence studies. The Ag NW is excited at one distal end using 532 nm gaussian beam and the transmitted signal from the other end is filteres spatially and spectrally using a pin hole and 532 nm edge filter respectively. Excitation and collection of the system is using a 100X, 0.95 NA objective lens. All the experiments described in section 3.1 and 3.2 are performed using this set up.
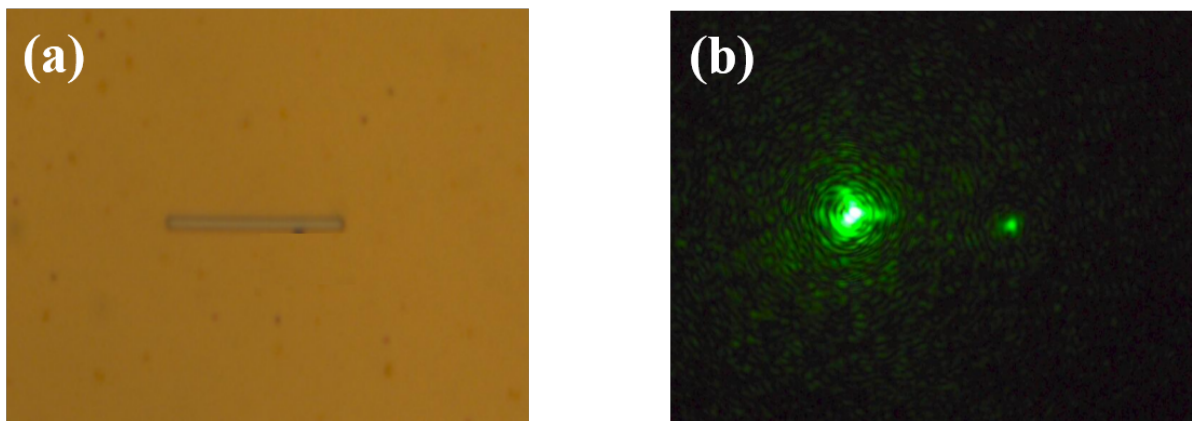
Figure 3.7: The optical image of Ag NW resting on gold film. (a) under white light illumination, and (b) when excited at a distal end using 532 nm laser. The green light emitting from the other end indicates that there is propagation in the waveguide.

Figure 3.7 (a) shows the optical image of our experimental system under white light illumination. 3.7 (b) shows the propagation of 532 nm green laser from one distal end to the other. The Outcoupling light from the distal end has multiple components including the 532 rayleigh component. It is expected that the propagating surface plasmons in the silver NW and confined gap plasmons will excite the molecules along the extended

cavity. The photons from the de-excited molecules can possibly couple to the propagating plasmons to get outcoupled back to photon at the distal end. Additionally there is a huge amount of 532 nm Rayleigh component that is propagating to the distal end as propagating surface plasmons and outcoupling as photons. This Outcoupled emission also can excite the dye molecules at the distal end.

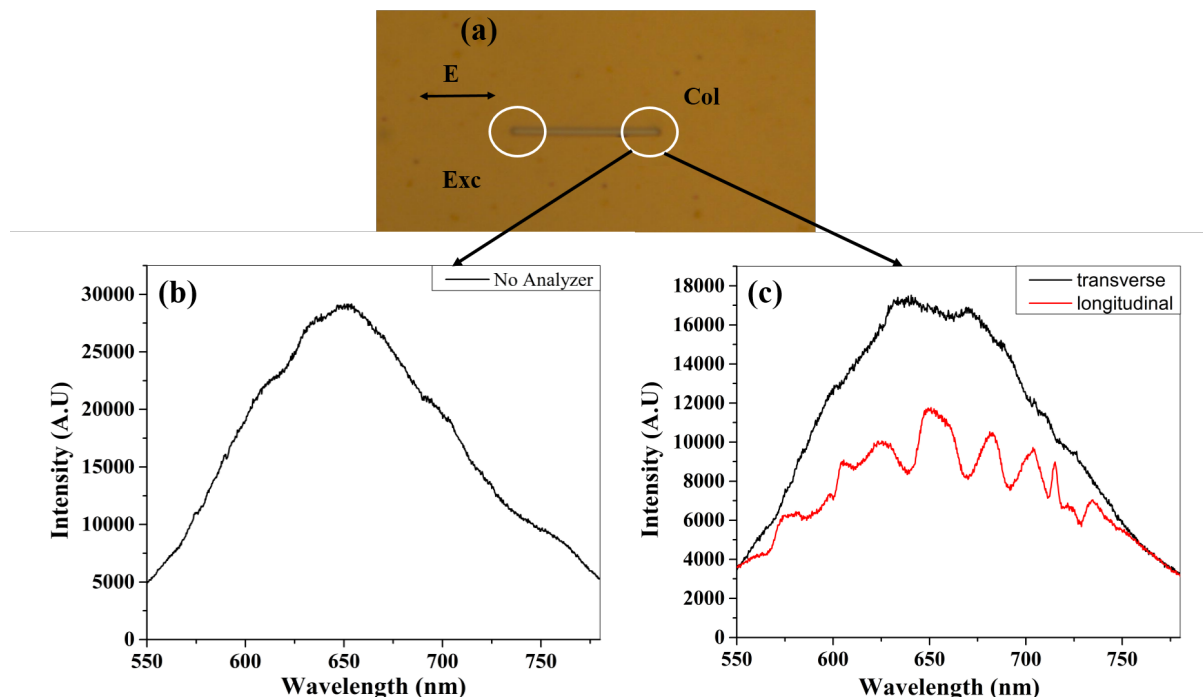**Polarization resolved Fluorescence from the distal end**

Figure 3.8: Polarization resolved fluorescence emission from the distal end of the Ag NW on gold film. (a) Optical image of silver NW under white light illumination, input polarization is along the axis of the nanowire. (b) Fluorescence emission from the distal end in the absence of analyzer. (c) Polarization resolved Fluorescence emission from the distal end of the nanowire. Even though the input polarization was along the axis of NW, major contribution to fluorescence at the distal end of the NW was found to be polarized transverse to the axis of the nanowire. The longitudinal component has undulations in the spectral peak which corresponds to the Fabry-perot modes of the waveguide.

Polarization dependence data is an important piece of information in the study of antennas. To probe the polarization dependence of the Ag NW- Au mirror system the distal end of the wire is excited with 532 nm laser with a polarization along the axis of the wire. As mentioned earlier, there are different modes that can be sustained in a penta-twinned silver nanowire. When the input polarization is perpendicular to the wire the propagating mode of the wire is not excited. However when the input polarization is along the axis of the nanowire the propagating $m = 0$ mode will be excited.

In case of a silver nanowire resting on a glass substrate, when excited at one distal end with an input polarization longitudinal (transverse) to the wire the outcoupled light from the other distal end will be along (perpendicular) to the wire. However, the Ag NW-Au mirror system is a hybridized system with a cavity in between. The interaction between the gap plasmons in the cavity and the propagating surface plasmon polaritons on the silver nanowire can lead to hybridized modes and hence may lead to modifications in the output polarization.

To check the the output polarization dependence of this hybridized system, An analyzer is placed in the output path to resolve the output polarization with respect to the long axis of the wire. Figure 3.8 (b) shows the output intensity in the absence of the analyzer. For all the measurements the input polarization was kept along the axis of the wire to maximize the output intensity. The output polarization resolved data is shown in Figure 3.8 (c). As opposed to an Ag NW on glass substrate, (where $m = 0$ SPP mode results in large component of along the wire polarized light at the output) this hybridized system has a counter intuitive output polarization dependence. Here, for input polarization along the wire ($m = 0$) majority of the out-coupled photons are polarized transverse to the axis of the wire. This is a strange observation since the SPP on the silver nanowire was polarized along the axis of the wire. This effect is attributed to the hybridization of the propagating SPP on the wire and the gap plasmons inside the cavity. However, further studies has to be conducted to fully understand the mechanism by which this phenomena occurs.

Field Distribution Inside the Cavity

The fig.3.9 shows the near field electric field map inside the extended plasmonic cavity for (a) Ez (b) Ex (c) Ey. The orientation of the nanowire is along y-axis. The cavity is excited by a polarization along the y axis. As seen from the near field intensity map the maximum intensity of electric field is along Z axis followed by X axis (transverse) and Y axis (longitudinal) respectively. This relatively high intensity of Ex in the cavity is attributed to the hybridization of SPP modes on the wire and the confined gap plasmons in the cavity. This rich polarisation structure of the cavity affects the molecules inside the cavity. The emission from the distal end is a collective signature of all the molecules inside the cavity. The molecules inside the cavity will experience strong Ez and Ex components, while molecules near the distal end will experience strong Ey component. Since the Ex component excites a larger number of molecules than Ey all along the cavity, most out-coupled photons are polarized transverse to the long axis of the wire.
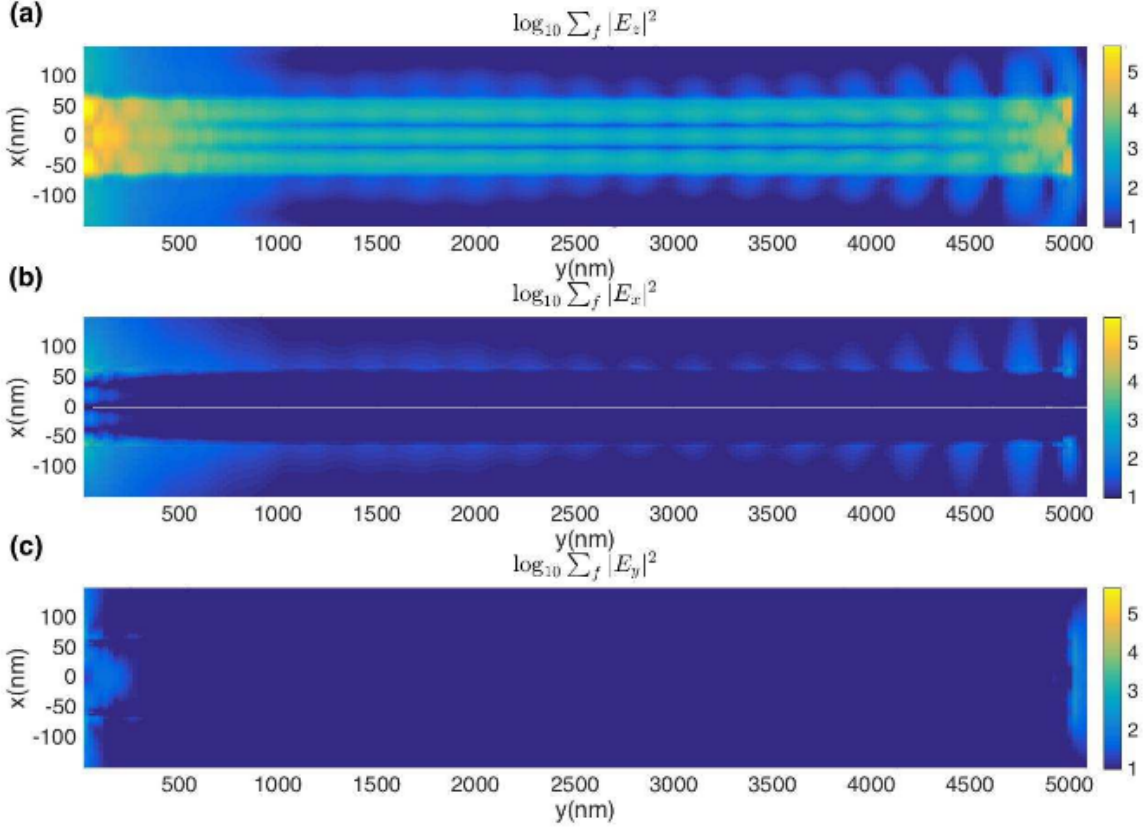
Figure 3.9: Calculated component-wise near field electric field map inside the cavity (x-y cross section) for (a)Ez, (b) Ex and (c) Ey. Intensity is plotted in log scale. (Reproduced with permission from [52])

Directional Emission of Fluorescence

The Ag NW-Au mirror system is also a great model for directional emission studies in fourier space. This is because the silver NWs are known to have directional emission properties and now that the molecules are in close proximity to the NWs the their emission can get modified. Molecular fluorescence in general is an isotropic emission process. ie, there are no preferential direction of emission. The numerical aperture and collection angle of a lens is related as;

$$NA = n_{eff} \times Sin(\theta) \tag{3.1}$$

Where n_{ref} and θ corresponds to the refractive index of the medium and the collection angle respectively. So the collection angle of the lens can be calculated from the equation;

$$\theta = Sin^-1(NA/n_{ref}) \tag{3.2}$$

Since the collection is done in the free space n_{ref} becomes unity and numerical aperture

of the objective lens we have used is 0.95. So from Eqn. 4.2 the collection angle of the objective lens we have used is 71.8°
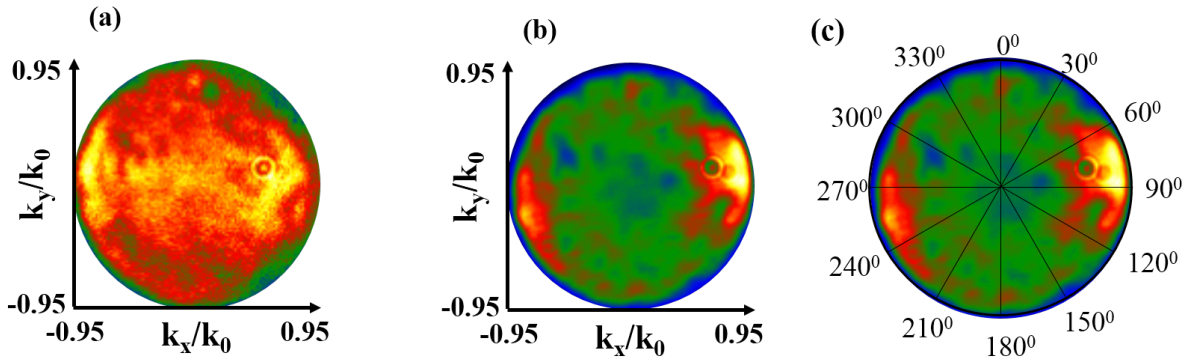

Figure 3.10: The angular emission pattern of molecular emission in the fourier plane (back focal plane. (a) from the bare substrate (gold film) note that the emission is isotropic. ie, no preferential wave vector direction. (b) from the distal end of Ag NW. The emission is not isotropic but directional. (c) azimuthal angle ϕ distribution of angular emission from nanowires.

Figure 3.10 shows the back focal plane images of molecular emission from DAAQ molecules on (a) a bare gold film (b) confined between Ag NW and Au film. The fluorescence from the molecules on bare film does not have a preferential emission direction all the k vectors are present in the back focal plane. However in case of molecules confined in the cavity, the emission is directional. The emission is confined only to the higher values of k vectors and have a very narrow ϕ distribution which comes around between 37° to 120° and higher polar θ values as opposed to isotropic emission from bare gold substrate. So the proximity of the dye molecules to the silver NW has a profound effect on the directionality of emission from the molecules.

3.3 Surface Plasmon Coupled emission form Ag Nanowires on a thin gold film

There have been various interesting studies on the Surface Plasmon Coupled Emission of molecules placed in proximity to plasmonic films. These studies were mostly focused on the improved collection efficiency and directionality of the emission, mainly Fluorescence. But not that many information exists on the other molecular emission process which is Raman scattering. An interesting area of study is the SPCE from hybridized structures. In the past, there have been studies on SPCE from hybridized plasmonic structures such as nanoparticle-thin film. These studies were again mostly focused on Fluorescence. Since Raman scattering signal can be used as a unique ID for a molecule, SPCE studies on a

Raman active molecule has huge importance. The SPCE will result in improved collection efficiency of Raman scattered signal and hence can be utilized for single molecule studies. A very recent study on molecular emission from dye molecules confined in an elongated cavity revealed a very interesting phenomenon of differential wave-vector scattering of molecular emissions in Fourier space.[52] Motivated by this set of experiments, we have chosen to study SPCE of Raman signal from an elongated cavity structure on which not much known as of now.

In SPCE an emitter placed close to a 50 nm thin film of gold when excited in reflection geometry () with a laser will emit isotropically, i.e., without any preferential direction of emission. However, when the collection of the signal is from the glass side (transmission) where the emitter excited in reverse Kretschmann/transmission configuration, there is a drastic change in the directionality of the emission. This is because of the near-field coupling of the surface plasmons in the film with the emitter. SPCE for all purposes can be considered as the reverse process of the surface plasmon resonance. SPR is a process in which the plasmons in a metal film is excited by laser incident on the substrate at an angle. In SPCE, however, the emission is due to the out-coupling of plasmons (generated due to the near-field excitation by the emission from the molecules) to photons at the metal-dielectric interface.

This set of experiments on SPCE deals with emission from molecules confined in a cavity between silver Nanowires and a Thin gold film of thickness close to 50 nm. The gold film is thermally evaporated onto a glass coverslip. Since the thickness of the gold film is close to 50 nm, surface plasmons will be generated on it when excited using a laser. The silver NWs are synthesized using a well-known procedure. These NWs have pentatwinned structures and have a length of 10-12 μm and width of 350-400 nm. Ref. Figure 4.1. The wires have a coating of Polyvinyl Pyrrolidone (PVP) of thickness up to 5 nm on all sides. PVP is a dielectric material and has a refractive index close to 1.5 which is almost same as the refractive index of the glass. The presence of this coating will prevent the molecules from coming in contact with the metal and resultant quenching of fluorescence. We have chosen to work with the dye Nile blue which is resonant at 632.8 nm. Because this is a resonant excitation the Raman and Fluorescence processes compete to dominate each other. Since we are interested in the Raman signal rather than the fluorescence, drop-casting the molecules onto the gold film will quench the molecular fluorescence, and were left with a majority of Raman signal. The molecules confined in the 1-D elongated system is highly interesting Since opposed to a 0-D particle (in which only localized plasmons can be excited) the Ag NW sustains propagating surface plasmons. This system will enable us, to study about the enhancement and directionality of molecular emission due to the interaction between the molecules and the propagating surface plasmons. Since the molecules are confined in a plasmonic nanocavity between

the silver nanowire and gold film, the local electric fields will be highly enhanced due to the confinement effects of the cavity. The presence of the silver nanowire can also affect the directionality of emission from the molecule due to its antenna properties. In a typical experiment, the NB molecules with a concentration of 10^{-6} M in Ethanol is drop-casted onto the gold film and kept for drying. The Ag NWs are drop-casted on top of the molecules. Figure 3.11 shows the schematic of the system under study.
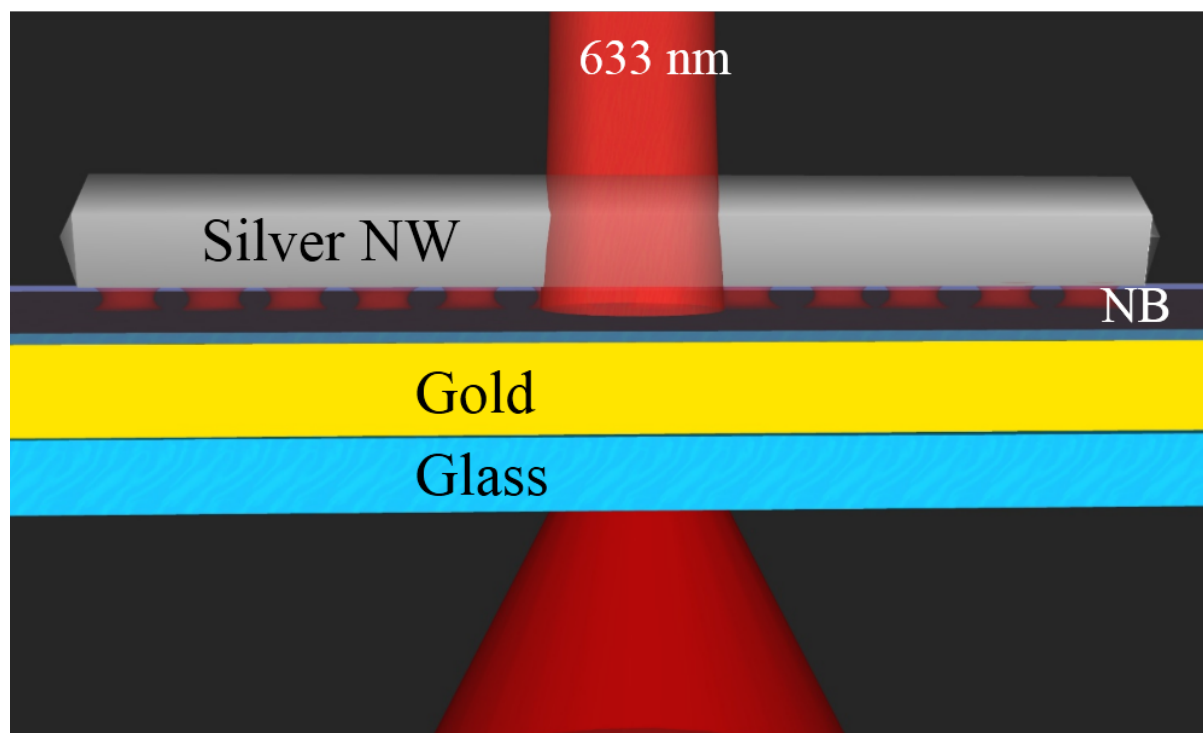

Figure 3.11: The schematic of the system used for Surface Plasmon Coupled Emission studies. The system is excited through the upper channel 100X, 0.95 NA objective lens with a 632.8 nm He-Ne laser. And the generated SPCE is collected through lower channel using 100X, 1.49 NA.

3.3.1 Experimental setup

For the studies on the SPCE from the Ag NW-Au thin film system a home-built dual channel fourier microscopy system is used. The schematic of the experimental setup is given in Figure 3.12. This setup is coupled to an Andor SR500i spectrometer and an Andor EM-CCD which is sensitive enough to image even the very faintest of emissions. This setup is highly versatile and can be used to
image and conduct experiments in various excitation geometries. It is possible to visualize and probe the experimental system through the upper channel 100X, 0.95 NA objective lens and the lower channel 100X, 1.49 NA oil immersion objective lens. The Flip mirror (FM1) is used to switch between upper and lower channel excitation. It is possible to
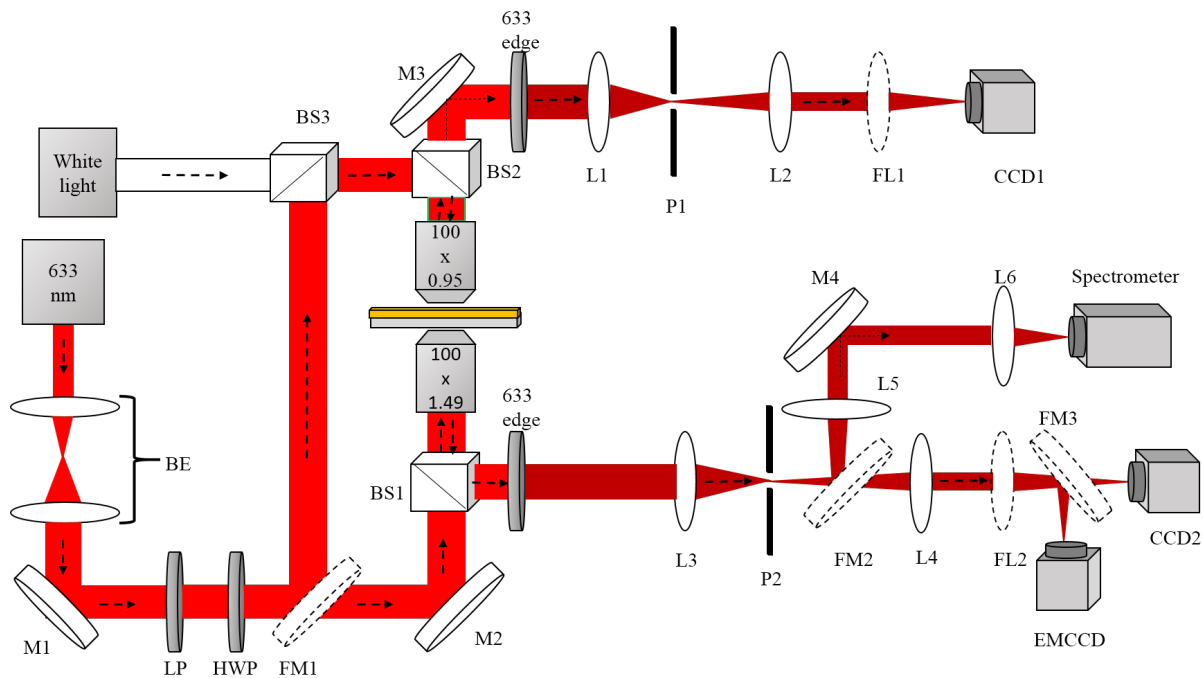
Figure 3.12: Schematic of the experimental setup used for the SPCE studies on Ag NW-gold thin film system. A 632.8 nm He-Ne laser is used for the excitation of the experimental system. The system is excited by the upper channel 100X, 0.95 NA objective. The leakage radiation is collected through the lower channel 100X, 1.49 NA objective lens. A $\lambda/2$ plate is used to control the input polarization of the incident laser. 633 nm edge/notch filter is used to filter out the Rayleigh component from the generated signal.

study the experimental system in reflection as well as transmission geometry (For all our experiments the excitation of the system is through upper channel and the generated signal is collected through the lower channel). The Ag NW is illuminated using a white light source through upper channel. A 632.8 nm He-Ne gaussian laser beam through upper channel (100X, 0.95 NA) is used to excite the experimental system. A combination of linear polarizer and a $\lambda/2$ plate is used to control the input polarization of the incident beam. The generated signal is collected through lower channel (100X, 1.49 NA). A 633 notch/edge filter is used in the collection path to filter out the Rayleigh component. A pin hole placed at the conjugate plane filter out the radiation spatially. Flip mirror (FM2) is used to channel the collected signal between the spectrometer and the EM-CCD.

3.3.2 Surface Plasmon Coupled Raman Scattering

Spectroscopy of the surface plasmon coupled raman scattering from molecules confined in a cavity formed by a silver nanowire and semi-transparent gold film is studied. The sample preparation is same as the procedure explained in section 3.1.2, except that a $10^{-5}M$ solution of Nile blue molecules are used. The Molecules are excited using a 632.8

nm He-Ne laser in reverse kretchmann configuration using the experimental setup given in Figure 3.12. The laser is focused on to the substrate using 100X, 0.95 NA air immersion objective lens and the surface plasmon coupled emission is collected using the 100X, 1.49 NA oil immersion objective lens in the lower channel. The signal is collected using an Andor SR-500i spectrometer. The acquisition time is kept at 2 seconds.

The Nile blue molecules were dropcasted on a glass substrate and excited in RK configuration. Since this is a resonant excitation, the Raman scattering and Molecular Fluorescence compete each other. The signal consists entirely of Fluorescence (Figure 3.12). This is because under the normal circumstances the absorption cross section of Raman scattering is much much lesser than that of Fluorescence.
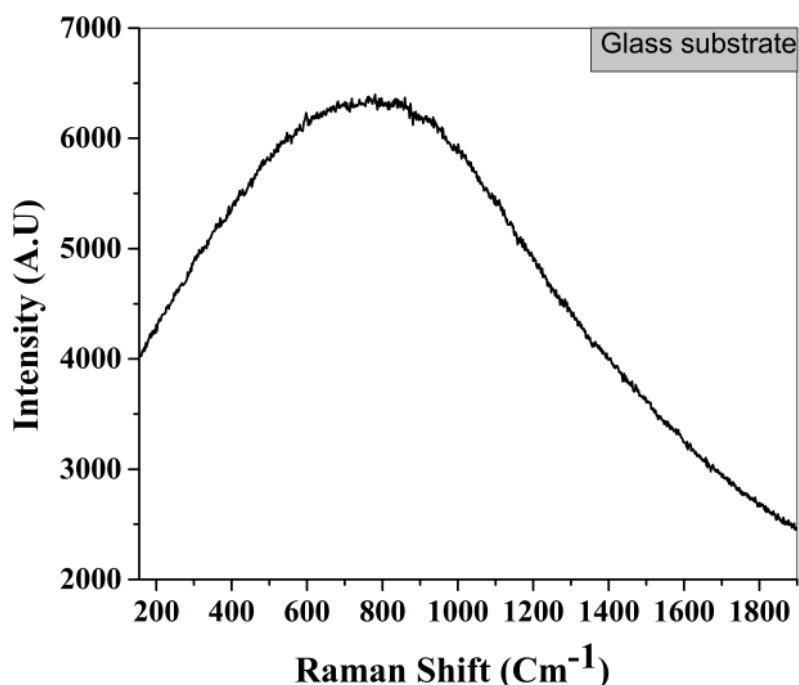

Figure 3.13: Spectra from the Nile Blue molecules on glass substrate collected in Reverse Kretchmann configuration using setup in Figure 3.12. Only fluorescence is observed, as there is no gold film to quench the fluorescence or no cavity to enhance the emission.

The proximity of the plasmonic film to the molecules results in quenching of molecular Fluorescence since it will change the local density of states which results in an increased number of non-radiative channels through which the electrons can relax to the ground state. Figure 3.14 depicts the initial results from the Surface Plasmon Coupled Raman scattering (SPCR) from Nile blue molecules confined in an extended cavity. In case of SPCR from dye molecules on bare gold film (Figure 3.14 (a)), the intensity of Raman signal is comparatively less. This can be explained with the fact that SPCR occurs

through the near field excitation of surface plasmons on the gold film by the molecules. To excite the surface plasmons effectively the molecules has to be in close proximity to the plasmonic film. Since the molecules are in close proximity to the film the fluorescence is quenched and there is an increase in the Raman scattered photons due to the field enhancement near the film. The dropcasting of molecules may result in multiple layer of dye molecules on the film. The molecules that are farther away from the film generates fluorescence but, since it is not closer to the film it will couple very weakly to the surface plasmons. This will hence results in an increased amount of Raman scattered photons in the detected signal. The $590 cm^{-1}$1 Raman mode involves all atoms of the molecule, and cannot be attributed to a single bond.
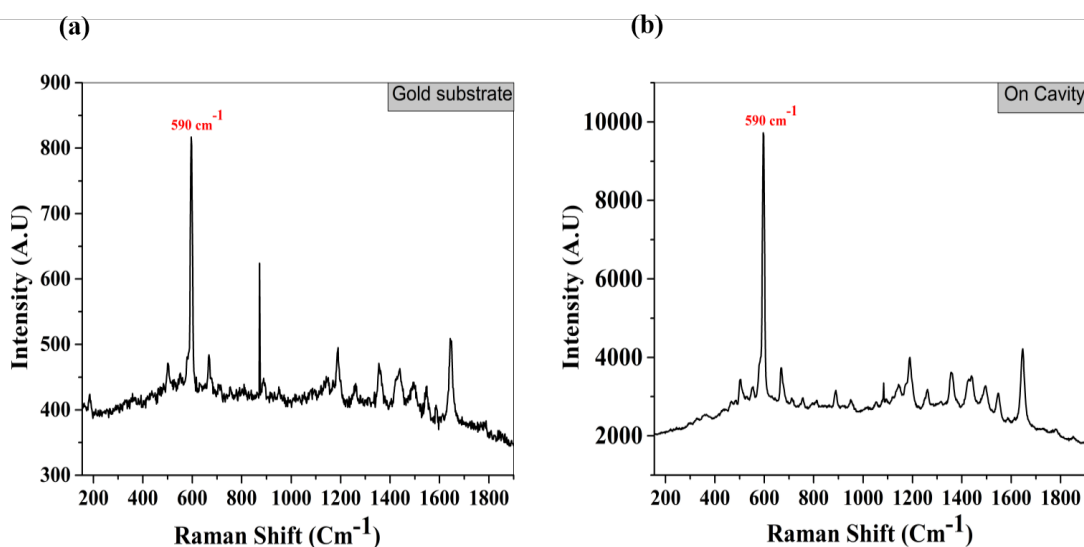

Figure 3.14: (a) Spectra from the Nile Blue molecules on gold substrate (off-cavity) collected in Reverse Kretchmann configuration using setup in Figure 3.12. Fluorescence is quenched due to the presence of the film and the Raman signals are clearly visible ridingover the very minimal fluorescence. (b) Spectra from the Nile blue molecules confined in the cavity between the gold film and the silver wire. There is a huge enhancement in the surface plasmon coupled raman signals compared to that of off-cavity (on bare gold). This enhancement is due to the existence of gap plasmons exciting the molecule.

Figure 3.14 (b) depicts the enhancement of SPCR emission from the nile blue molecules due to the confinement within the cavity formed by the silver nanowire and semi-transparent gold film. The formation of cavity results in an enhanced electric field which leads to a strong excitation of molecules in the gap.

3.3.3 Directional Emission in SPCE

The increase in directionality of the molecular emission due to the proximity of the emitters to a thin plasmonic film is studied. The Nile blue dye molecules dropcasted

on a substrate is excited with 632.8 nm laser in Reverse-Kretchmann configuration. ie, Excitation through the upper channel (100X, 0.95 NA) and collection through the lower channel (100X, 1.49 NA) using the experimental setup in Figure 3.12. The effect of the substrate on the emission pattern in the back focal plane is observed. Figure 3.14 shows the Nile Blue molecular emission pattern in the fourier space. (a) in the absence of a plasmonic thin film.ie, the molecules are placed directly on the glass substrate. and (b) when the molecules are placed on a plasmonic thin film. and (c) the SPCE emission collected from the distal ends of a nanowire. As clearly evident from the figure proximity of the molecules to a plasmonic thin film results in highly directional emission. The emission from the molecules placed on glass substrate has wide distribution in polar angle θ. Whereas in case of emitters on the gold substrate, the nearfield excitation of surface plasmons on the film by the molecular emission from the molecule and the subsequent conversion of these SPPs to photons at the metal dielectric interface at SPR angle leads to a much narrower distribution in polar angle θ. in case of SPCE from distal ends of nanowire it has an azimuthal angle (ϕ) distribution ranging from 60° and 100°.By comparing figure 3.10 (a) and (b) with figure 3.15 (b) and (c) we can see that there is difference in directionality of emission when collected in reflection (Fig. 3.10 (a) and (b)) and transmission (Fig. 3.15 (b) and (c)). The high directionality of emission in SPCE (transmission) is due to the near field coupling of molecular emission with the SPPs on the Au film.
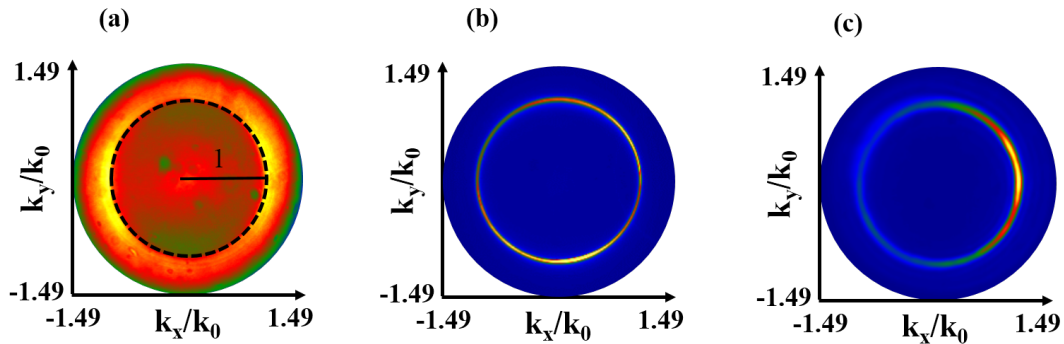
Figure 3.15: The angular emission pattern of molecular emission in the fourier plane (back focal plane). (a) through the glass substrate note that the emission has a wide radial (θ) distribution. The dotted circle inside marks the critical angle at the air-glass interface. (b) through the gold coated substrate. note that the polar angle θ distribution has become narrower compared to that of (a). (c) SPCE from the distal end of a nanowire. The maximum intensity of emission come at ϕ values ranging between 60° and 100°.

3.4 Conclusions

This chapter has addressed two different systems: (i) Ag nanowires on Au mirror with DAAQ, and (ii) Ag nanowires on thin Au film with Nile Blue. For the Ag nanowires-on-mirror system, enhancement of the DAAQ molecular fluorescence signal has been observed for various nanowires. The effects of the substrate and of nanowires on the enhancement of the signal has been observed. The nano-antenna effects on the molecular emission from DAAQ molecules due to the proximity of Ag nanowires has been observed and is found that the molecular emission from the distal ends of Ag nanowires are directional in nature. As opposed to an isotropic emission in the absence of Ag Nanowire. The remote excitation studies on the nanowire-mirror has been conducted and the enhancement in outcoupled fluorescence signal is observed. The output polarization resolved studies on nanowire-mirror system has yielded some counter-intuitive effects. The major component of outcoupled photons at the distal end was found to be polarized perpendicular to the nanowire. This was unexpected since the SPPs in the nanowire and were polarized along the axis of the nanowire. The exact reason for this phenomena is not completely understood but has been attributed as a result of the hybridization of propagating SPPs on the nanowire and the gap plasmons in the cavity. Surface plasmon coupled emission from a hybridized Ag nanowires on thin gold film structure has been addressed. As expected, the directionality of the emission from the nanostructure has been improved due to the generation of surface plasmon polaritons on the plasmonic thin film. The enhancement of SPCR due to the formation of cavity is observed. Further studies has to be done on this system regarding the the spectral features of the Raman signal and its polarization dependence.

Chapter 4

Conclusions and Future Directions

Anisotropic nano-structures, as previously mentioned have crucial importance in nano optics. The optical antenna properties and the ability of these structures to confine light to sub wavelength volumes makes them an important system to be studied for vast range of applications in technology.

The interactions of Ag nanowires with gold films of varying thicknesses has been studied in this thesis. The silver nanowires are synthesized using a standard protocol of wet-phase synthesis and the gold films are prepared using Thermal Vapor Deposition technique.

The enhancement in Fluorescence from DAAQ dye molecules which are resonant at 532 nm is studied. These molecules are confined in a plasmonic cavity made up of a thick plasmonic gold film of thickness 150-170 nm and silver wire (length:10 microns & diameter: 300-400 nm). The enhancement in Fluorescence emission due to highly confined electric field in the cavity is studied. Additionally the effect of the silver nanowire and the gold film on the enhancement of molecular emission is probed. Since the cavity formed is an extended one the remote excitation studies were conducted. The remote excitation of Fluorescence resulted in high intensity of signals from the distal ends. The polarization resolved spectra from the distal ends have been measured. This polarization resolved data revealed some counter-intuitive results. The majority the of out-coupled photons from the distal ends were found to be polarized perpendicular to the wire even though the SPPs on the silver nanowire which excited this flurophores were polarized along the axis of the wire. This observation is attributed to the hybridization of surface plasmon modes on the wire and the confined gap plasmons in the cavity.

The directional emission of fluorescence from the nanowire-mirror system is observed using Fourier plane imaging and it has been found that proximity of the molecules to the nanostructure has resulted in redirection of fluorescence as a result of antenna effect of the silver nanowire.

Surface plasmon coupled emission of the molecules confined in a plasmonic cavity made up of silver nanowire and a thin plasmonic film of thickness 50 nm is probed. The directionality of emission that is collected in Reverse Kretschmann configuration has been found to be highly directional in nature, having a narrower $\theta \& \phi$ distributions in fourier space. For the studies on SPCE a dye resonant at 632.8 nm named Nile blue is used. Further studies related to the spectral intensities of the Surface plasmon coupled emission from nile blue has to be done. We couldn't do it earlier due to the unavailablity of plasmonic film with a uniform thickness of 50 nm due to technical problems in the TVD set up.

The SPCE configuration we have considered is that of an extended cavity. Most of the previous studies in SPCE were focused on the fluorescence emission bar a very few addressing Raman signal.[74] There were reports on SPCE from a hybrid cavity structure as well, probing the enhancement in fluorescence and showing the possibility of single molecule detection.[67] There were no studies as of now on the SPCE of molecular emission from an extended cavity like one we have considered here. SM detection using SPCE from an extended cavity is one of the future direction we have in mind. Since the coupling of emission with plasmons in the film results in defined emission angles the sensitivity and the collection effieciency in SPCE is much higher and hence suitable for SM detection.

The large field enhancements in these cavity structures also lead to enhanced metal PL and possibly Two Photon Luminescence signals (if one used extremely high input powers). These signals can also be studied in great detail, including polarization dependent studies as well as Fourier space studies, which will show what momentum states are occupied by the PL or the TPL signals, and what directionality is observed for these signals.

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