
Metal Film based Micro- and Nano-cavities: Optical Polarization and Wavevector Studies

A thesis

*submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy*

by

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PUNE

CERTIFICATE

Certified that the work incorporated in the thesis entitled ("Metal Film based Micro- and Nano-cavities: Optical Polarization and Wavevector Studies") submitted by **Adarsh B. Vasista** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.

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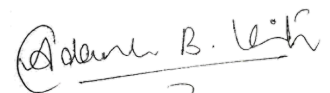
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Declaration

I declare that this written submission represents my research work in my own words and where others' ideas or works have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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Abstract

Probing light-matter interaction is at the heart of nanophotonics. Studying the interaction of light with molecular emitters have wide implications including applications like developing molecular probes for sensing, molecular antennas etc. To achieve control over the molecular emission and harness it, one has to modulate emission parameters like intensity, wavevectors, and polarization of the molecular emitter. In this context, various cavity architectures have been studied to manipulate molecular emission. Design of cavity architectures play a very critical role in tailoring the emission properties from the cavity. Architectures based on metallic nanostructures, dielectric resonators, hybrid metal-dielectric cavities can be used to tailor specific parameters of light-matter interaction effectively. Metal film based cavities have emerged as an important design architecture in the recent times. This design facilitates flexibility to create both metal and metal-hybrid based cavities. In the past, intensity enhancement of molecular emission in cavities has been studied extensively. But the effect of cavity on wavevector distribution and polarization of molecular emission signatures have not been studied in great detail. Understanding them, potentially, can give rich information about the coupling strength of the interaction, modes of the cavity and much more. It can also be used to efficiently design cavities focusing on antenna aspect of the cavity design.

Herein, we discuss the effect of different metal film based cavities on the wavevector and polarization states of the molecular emission coupled to them. We probe various metal-dielectric hybrid cavities using Fourier plane imaging and spectroscopy. First, we discuss the effect of an elongated cavity created using plasmonic nanowire placed on gold film on the wavevector signatures of molecules sandwiched between the wire and the film. We discuss the effect of such extremely small cavities on different relaxation process like Raman scattering and molecular fluorescence. Next we present the effect of vertical molecular nanowire cavity coupled to thin plasmonic film on its emission pattern as a function of operational wavelength. Finally, we will discuss the effect of microsphere cavity placed on metal film on wavevector and polarization states of molecular emission.

List of Publications

Included in thesis:

- **Adarsh B.Vasista**, G. V. Pavan Kumar, Quantum emitter coupled to plasmonic nanotriangle: Spatially dependent emission and thermal mapping, *Opt. Commun.*, 381, 227-233 (2016).
- **Adarsh B Vasista**, G V Pavan Kumar, k-space analysis of nanotriangle antenna, *International Conference on Fibre Optics and Photonics*, W4D. 3 (2016).
- **Adarsh B. Vasista**, Harshvardhan Jog, Tal Heilpern, M.E. Sykes, Sunny Tiwari, Deepak K. Sharma, Shailendra K. Chaubey, G.P. Wiederrecht, S.K. Gray, G.V.Pavan Kumar, Differential wavevector distribution of surface-enhanced Raman scattering and fluorescence in a film-coupled plasmonic nanowire cavity, *Nano Lett.*, 18, 650-655 (2018).
- **Adarsh B. Vasista**, Ravi Tripathi, Shailendra K. Chaubey, Sunny Tiwari, G.V.Pavan Kumar, Doughnut shaped emission from vertical organic nanowire coupled to thin plasmonic film, *Opt. Lett.*, 43, 923-926 (2018).
- **Adarsh B. Vasista**, Sunny Tiwari, Deepak K. Sharma, G V Pavan Kumar, Vectorial fluorescence emission from metallo-dielectric photonic molecule, *Adv. Opt. Mater.*, 1801025 (2018).

Not included in thesis:

- Ravi P.N. Tripathi, Arindam Dasgupta, Rohit Chikkaraddy, Partha. P. Patra, **Adarsh B.Vasista**, G. V. Pavan Kumar, Optics of an individual organic molecular mesowire waveguide : Directional light emission and anomalous refractive index, *J. Opt.*, 18, 065002 (2016).
- Ravi P.N. Tripathi, **Adarsh B. Vasista**, Rohit Chikkaraddy, G. V. Pavan Kumar, Radiative channelling of nanowire Frenkel exciton-polaritons through surface plasmons, *Adv. Opt. Mater.*, 5, 1600873 (2017).

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- **Adarsh B.Vasista**, Deepak K.Sharma, G V Pavan Kumar, Fourier plane optical microscopy and spectroscopy, *Encyclopedia of applied physics*, *In press* (2018).
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- Deepak K. Sharma, Vijay Kumar, **Adarsh B. Vasista**, Diptabrata Paul, Shailendra K. Chaubey, G.V.Pavan Kumar, Optical orbital angular momentum read-out using a self-assembled plasmonic nanowire, *ACS Photonics accepted* (2019).
- Debrina Jana, **Adarsh B.Vasista**, Harshvardhan Jog, Ravi P N Tripathi, Monica Allen, Jeffery Allen and G.V. Pavan Kumar, V-shaped active plasmonic meta-polymers, *Nanoscale*, *manuscript under revision*.
- **Adarsh B.Vasista**, Shailendra K. Chaubey, David Gosztola, Gary P.Wiederrecht, Stephen K.Gray, and G.V.Pavan Kumar, Directional outcoupling of SERS from nanowire-nanoparticle junction, *manuscript under preparation*.

Acknowledgments

The work I did in the past half a decade at IISER and other places would not have been possible without the help of a bunch of people and I would like to thank them here.

Firstly, I would like to thank Prof. G V Pavan Kumar, my supervisor for his constant help and support throughout my stay at IISER. He was very supportive during my lows and stood very strong beside me. Specifically, I am very inspired by his writing and presentation skills which I would definitely like to inculcate. He gave me absolute freedom to work in the laboratory and to chose and design a problem, which makes me indebted to him. His constant advice on career development has definitely honed my skills.

I would like to thank Anshul Kapoor. It is difficult to put words to the kind of friendship we share. It would have been very difficult to spend years at IISER without him. He made me return to the theater, which I will never forget.

I would like to thank Deepak Sharma, my pal, who is a strong support to all my endeavors. I cherish all the great moments that we enjoyed together including long bike rides, tasting different cuisines, and gossips. I thoroughly enjoyed his company to discuss both academic and non-academic issues (of course with arguments and disagreements !).

I would like to thank Chinamyee Mishra, a person with so many facets. She was an ear to all my joys, sorrows, and fear alike. I cherish all those long talks about politics, socio-economic issues, movies, stories, and the brief cooking sessions.

I thank my lab-mates Sunny Tiwari, Shailendra Chaubey, Vandana Sharma, Diptabrata Paul, and Chetna Taneja for all the tea-time talks. Sunny is a person gifted with wit and I have enjoyed working with him in the lab, without whose support most of my research work would not have been possible. Shailendra is my materials-manager, particularly with organic nanowires. I thank him for his support and for the transfer of his urdu knowledge. I had great time with these folks and it is deeply appreciated. I extend my heartfelt thanks to my former lab-mates Dr. Arindam, Dr. Partha, Dr. Danveer and Dr. Ravi. They have been a constant source of enthusiasm. I also acknowledge the efforts of former undergraduates of my lab Harsh Jog, Rajath Sawanth, Dr. Rohit Chikkaraddy, Aswathy V G in making the working environment of the lab enjoyable.

I also thank my batch-mates Deepak Khurana, Dhriti Nagar, Mehak Malhotra, Aditi Dixit, GARSRK Kashyap, Sandeep George, Bharath Tandon, Anish Rao, Ron Sunny, Divya Rao, Amarendranath Soory, Akhila Gungi, Harpreet Singh, Swathi Sharma, Neeladri Sen, Jay Mangaonkar, and Charu Garg. They have made my stay at IISER very comfortable and worthy.

I would like to thank Harsha Hampapura, Chaitra Agrahar, Harsha M B, Vibishan B, and Amogh Kulkarni. They have constantly poked me to write and work in theater. I am indebted to them.

I also thank present and former members of the Art club and the Drama club of IISER Pune. They have rare talents and have never failed to impress me. I am privileged to work with such talented kids.

I would extend my heartfelt thanks to all my collaborators: Dr. Gary Wiederrecht, Dr. Stephen Gray, Dr. Mathew Sykes, Dr. Tal Heilpern, and Dr. David Gosztola. Without their support and help chapter 3 of this thesis would not have existed.

I extend my thanks to my research assessment committee members Dr. Angshuman Nag and Dr. Atikuar Rahman for their important suggestions and insights provided during my seminars. I am indebted to Prof. Sunil Mukhi and Prof. Anil Gangal for their constant support and advice all along my stay at IISER.

I thank IISER Pune for providing me necessary facilities and an enjoyable working environment. I also extend warm thanks to the people of MDP canteen for fueling our tea-time talks.

Last but not the least I would like to thank my parents and grandmother for believing in me and supporting every decision I took. It is difficult to explain the pain they underwent during this time. They are an inexhaustible spring of enthusiasm and courage to me. I would also thank my friends outside IISER: Abhilash T B, Chandramouli N, Sahana Hebbar, Sahana S, Malti Sharma, and Savitri. They have made this period of 6 years colorful. I also like to mention my love towards the monsoon rains of Pune, which have made my stay lively at this place.

Dedicated to my parents...

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Chapter 1

Introduction

Engineering light-matter interaction is an important research area as it affects both scientific and technological advancements. This problem has been probed with various view points and architectures. The relevance of the problem has shot up in recent times as the advancement in nanofabrication has lead to creation of subwavelength structures with ease. Hence the practical applicability of problems under the broad umbrella of light-matter interaction has been increased over the last decade. Molecular emission processes like fluorescence and Raman scattering have been enhanced and directed using structured nanomaterials.[1–8]

On these lines, cavity enhanced light-matter interaction has grown as an important field of research. Specifically, the effect of optical cavities on molecular emission has been investigated since the work of E M Purcell.[9] Due to the change in the local density of optical states (LDOS), the emission of the molecules trapped inside the cavity can be modified.[10] The LDOS offered to an excited molecule inside the cavity is critically dependent on the design of the cavity. Hence the design becomes very crucial for engineering molecular emission from a cavity. This has propelled many studies on designing different cavity architectures to engineer molecular emission.[11–16]

Broadly, one can classify the cavity architectures utilized for engineering molecular emission in recent times into three categories as,

- Whispering gallery mode based cavities
- Fabry-pérot resonance based cavities
- Gap plasmon based cavities.

We will briefly introduce molecular emission processes like fluorescence and Raman scattering first and then explain each of the above mentioned cavity architectures.

1.1 Molecular fluorescence

Molecular fluorescence can be treated as a combination of absorption (to an electronically excited state) and subsequent spontaneous emission (electronic relaxation). [10, 17, 18] The absorption of a photon by the molecule depends on its absorption cross-section σ_{abs} . Usually, the excited electron relaxes to a singlet ground state S_0 resulting in a photon which can be measured in far-field. The absorption cross-section of molecules is usually measured by passing a beam of polychromatic light through molecules and measuring the transmitted power P_{trans} and then calculating the extinguished power $P_{ext} = P_{inc} - P_{trans}$. Thus one can define the extinction cross-section σ_{ext} as sum of absorption and scattering cross-sections:

$$\sigma_{ext} = \sigma_{abs} + \sigma_{scat} \quad (1.1)$$

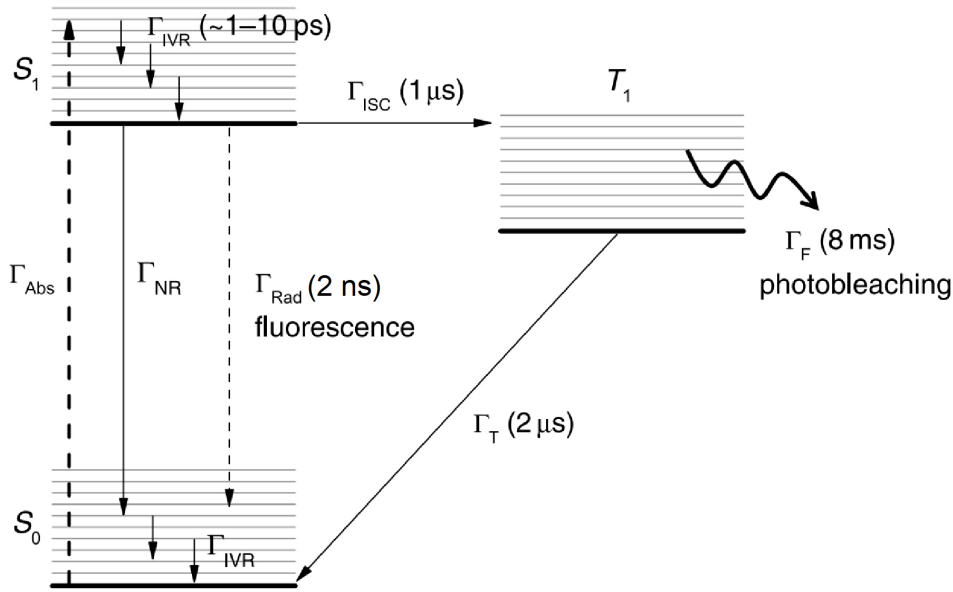


FIGURE 1.1: Schematic describing molecular fluorescence and photobleaching process. The typical approximate transition rates given are that of Nile blue dye molecule. Figure adapted with permission from [17]

For molecules the extinction cross-section will be dominated by absorption as scattering will be minimal. Hence absorption spectroscopy gives information about the optical extinction, in the case of molecules. The excitation of a molecule depends crucially upon the absorption cross-section and so does the fluorescence intensity. This makes the choice of the wavelength of the illuminating light very critical. Once the molecule is pumped to the excited state, there are multiple pathways for the excited state to relax and

are clearly shown in figure 1.1. The fluorescence is characterized by the probability of a transition from the excited level to the ground state resulting in a photon and is termed as *radiative decay rate* (Γ_r). Now the *radiative decay rate* can be easily calculated using Fermi's *golden rule* as,[19]

$$\Gamma_{ij} \propto S_{ij} \rho(f_{ij}) \quad (1.2)$$

where Γ_{ij} is the transition probability of the molecule from excited state i to the lower energy state j , S_{ij} is the transition matrix element that connects the excited and lower energy states and $\rho(f_{ij})$ is the density of optical states available for the molecule at the transition frequency f_{ij} . To manipulate spontaneous emission, one can either modify the transition matrix element (S_{ij}) or modify the density of optical states $\rho(f_{ij})$. Modifying the transition matrix element needs modification at the wavefunction level for an emitter and it is very difficult to achieve using optical means, while the latter can be achieved quite easily. Since the LDOS strongly depends on the local environment of the molecule, one can easily perturb the LDOS and hence the transition probability. This modification using optical cavities will be discussed in the upcoming sections.

The molecule in excited state can also relax using multiple non-radiative ways (processes which do not result in a photon in the far field). They may have various physical origins, but for the discussion here we group them under a macroscopic parameter *non radiative decay rate* (Γ_{nr}). So the total probability of transition can be written as $\Gamma_{total} = \Gamma_r + \Gamma_{nr}$. The inverse of the total decay rate gives an account of the excited state life time. Typical life times of fluorescence ranges between 100 ps - 10 ns. Spectrally, fluorescence occupies broad range as there are multiple closely spaced vibrational levels in the ground state S_0 and multiple allowed transitions from S_1 to any of these levels (see figure 1.1). [17] A detailed discussion on the calculation of decay rates is given in chapter 2.

Photo-bleaching :An important aspect of fluorescence which needs attention is photo-bleaching. This is usually prevalent in resonant excitation of molecules, where the molecules suddenly stop fluorescing and has also been observed in single molecule experiments. [20, 21] The photo-bleaching rate increases linearly with the input power.[17] The reason behind photobleaching is still disputed and the most satisfactory explanation is through the inter-system crossing (see figure 1.1). For an electron in the excited state S_1 , there is a non-zero probability of transition to a triplet state T_1 . This is called inter-system crossing. The triplet state T_1 has large life times (in ms). The electron then can radiatively decay causing *phosphorescence* or non-radiatively decay. Also, the triplet state is characterized by high chemical reactivity and the probability of molecules getting fragmented and destroyed is large. This makes the fluorescence intensity getting

strongly quenched or photobleached.

Blinking :Single molecule fluorescence signals show a typical *ON* and *OFF* pattern in time with continuous laser excitation. This process is termed as *blinking*.[\[22, 23\]](#) The concept of *blinking* is a widely debated phenomenon and is believed to be because of the continuous shift of molecular states from radiative (bright) and non-radiative (dark) regimes. *Blinking* has been seen in various single molecule emission measurements and is considered as a typical single molecule signature.[\[24\]](#)

1.1.1 Enhanced fluorescence

In the previous section, we described the phenomenon of molecular fluorescence in homogeneous environments and in the absence of strong electric field distributions. But when the molecules are subjected to very strong electric fields, the absorption cross-sections and the decay rates will undergo substantial change. The total fluorescence enhancement is a combination of absorption enhancement (M_{abs}) and enhanced fluorescence yield (Q). The absorption enhancement can be described as,[\[17\]](#)

$$M_{abs}(\omega) = 3 \left| \frac{\mathbf{E}_l}{\mathbf{E}_i} \right| (\mathbf{e}_{mol} \cdot \mathbf{e}_l(\omega))^2 \quad (1.3)$$

where $\mathbf{E}_l$, $\mathbf{E}_i$ are local electric field experienced by the molecule and incident electric field respectively. $\mathbf{e}_{mol}$ represents the orientation of the molecular axis, $\mathbf{e}_l(\omega)$ represents polarization of the incident light. Hence the enhancement in absorption is directly dependent on the local electric field enhancement. The second component of enhancement comes from the enhanced quantum yield. This can be understood using a classical dipole placed in a complex environment eg. near a metallic nanostructure. Now the molecular dipole is influenced by the local electric field experienced by the dipole. The driving of the dipolar source is now modified by the reflected electric field from the metallic nanostructure. Dipolar power emitted to the far field can be altered by changing the distance of the dipolar source from the structure and the wavelength of emission. One can encode this effect in a factor M_r , which modifies the radiative decay rate ($\Gamma_r = M_r \Gamma_r^{mol}$). The non-radiative decay rate, power absorbed onto the metallic nanostructure, is also modified by factor M_{nr} ($\Gamma_{nr} = M_{nr} \Gamma_{nr}^{mol}$). Γ_r^{mol} and Γ_{nr}^{mol} are the intrinsic radiative and non-radiative decay rates of the molecule in homogeneous environment respectively. Hence the modified quantum yield can be written as,

$$Q = \frac{M_r(\omega)}{M_{total}(\omega) + (Q^M)^{-1} - 1} \quad (1.4)$$

where M_{total} is the total enhancement factor and Q^M is the intrinsic quantum yield of the molecule. For molecules with large quantum yield ($Q^M \approx 1$), the above equation reduces to $Q = \frac{M_r(\omega)}{M_{total}(\omega)}$. In this picture, the modified quantum yield is completely defined by the electromagnetic interaction with the metal.

1.2 Surface plasmons

As we have seen in the previous discussion, the modified enhancement factor for molecular fluorescence depends very strongly on the local electric field enhancement. Thus the fluorescence from molecules near the metallic nanostructure crucially depends on the extinction cross-section of the structure. Thus fluorescence can be enhanced many folds near the *plasmon* resonance of the structure. *Plasmons* are the collective oscillations of electrons in a metallic structure. Surface to volume ratio increases as the size of the particles reduce and hence the surface electrons play very critical role in the electromagnetics. Thus, the resonance associated with those electrons is called *surface plasmon resonance* and the electric field is concentrated at the metal-dielectric interface. One encounters different types of *surface plasmons* depending on the structure and dimensions of the material used. We discuss two relevant types of *plasmons* here.

- *Localized surface plasmons* : When any quasi zero dimensional nanostructure (nanoparticle) is illuminated by electromagnetic radiation, the electrons tend to oscillate following the illumination. This creates a strong local electric field near the metallic nanostructure. When the illumination frequency is equal to the natural frequency of the structure, there is a large electromagnetic response from the structure. This state is called *localized surface plasmon resonance*, as the electric field is localized near the surface of the structure.
- *Propagating surface plasmons* : Metallic thin films and nanowires have an additional degree of freedom for the surface excitation to propagate. To couple the incident light energy to the *propagating surface plasmons* one has to satisfy the momentum matching criterion, as the momentum of *surface plasmons* are larger than that of light in the free space. For semi infinite thin films, this can be matched by providing additional momentum through different means: coupling through grating, exciting through prism etc.[1, 25, 26] In the case of wires, symmetry breaking at the ends of the wire provide the additional momentum needed and hence one can excite *propagating surface plasmons* in the wire.

In the following chapters we will discuss the importance and applications of the *plasmons*.

1.3 Raman scattering

We briefly discussed the concept of molecular fluorescence in the previous section. Now we discuss another important molecular emission process, Raman scattering. It was discovered by Sir. C V Raman and hence the name Raman effect.[27, 28] When light is scattered from any material, the frequency of the scattered radiation is usually unchanged. This is termed as *Rayleigh scattering*, an example of elastic scattering. But in certain materials, there can be additional discrete frequencies present due to inelastic scattering of light from the material. This effect is called *Raman effect*. The *Raman* signals are fingerprint of the material under investigation, as the frequencies at which one gets the *Raman* signal is intimately related to the material properties like bond length, symmetries etc.[29]

The scattered light from any *Raman* active material contain three important parts,

- **Rayleigh scattering:** It is the dominant part of the three and is a resultant of elastic scattering from the material. Thus, the frequency of the scattered light is same as that of the incident light ($\nu_{ray} = \nu_{inc}$).
- **Stokes scattering:** It is one of the resultants of the inelastic scattering from the material. The frequency of the stokes scattered photon is lesser than the incident photon ($\nu_{stokes} < \nu_{inc}$). The difference between the frequency of incident light and the inelastically scattered light is called the *Raman shift*.
- **Anti-stokes scattering:** Here the frequency of the scattered photon is greater than that of the incident photon ($\nu_{anti-stokes} > \nu_{inc}$).

As Raman scattering cross-sections are extremely small ($\sim 10^{-29} \text{ cm}^2$),[17] detection of *Raman* signals are difficult. This poses a hurdle in performing *sensitive* analysis of molecules. Similar to the concept of *modified fluorescence*, Raman scattering also gets modified when molecules are subjected to non-homogeneous environments with strong electromagnetic fields.

1.3.1 Enhanced Raman scattering

Enhanced Raman scattering was first observed by Fleishmann et.al. using pyridine molecules adsorbed on silver electrode.[30] The concept was later interpreted by Richard van Duyne's and Creighton's group independently.[31–34] In the conventional Raman scattering, the average intensity of any Raman mode is proportional to the input power and the Raman cross-section.[17] But in the case of enhanced Raman scattering the intensity will be modified by an *enhancement factor* which can be as large as

10^{10} .^[35] Traditionally the enhancement factors are separated into two *multiplicative* factors:

- *Electromagnetic enhancement factor*: This is considered, by far, the principal contribution towards the enhancement of *Raman* signal. Molecules in close proximity to a metallic nanostructure experiences a large electric field enhancement, due to *surface plasmons*. Thus the total power of stokes scattered *Raman* signal can be written as,

$$P_{stokes} = N\sigma_{SERS}M_{laser}M_{stokes}I_{inc} \quad (1.5)$$

where N is the average number of molecules undergoing Raman scattering, σ_{SERS} is the *surface enhanced Raman scattering* cross-section (which is different from *Raman* cross-section σ_{raman}) and encapsulates the interaction of local electric field with the molecule and absorption enhancement, $M_{laser} = |\frac{\mathbf{E}_{loc}(\nu_{laser})}{\mathbf{E}_{inc}(\nu_{laser})}|^2$ is the field enhancement factor at the frequency of the incident light, $M_{stokes} = |\frac{\mathbf{E}_{loc}(\nu_{stokes})}{\mathbf{E}_{inc}(\nu_{laser})}|^2$ is the field enhancement factor at the frequency of the stokes scattered light, and I_{inc} is the intensity of the incident light. In most practical cases, the *Raman shift* is relatively small and the local electric field does not vary considerably in this range ($M_{stokes} \approx M_{laser}$). The electromagnetic enhancement factor can then be approximated as $|\frac{\mathbf{E}_{local}}{\mathbf{E}_{inc}}|^4$.

- *Chemical enhancement factor*: Another important, and *controversial*, enhancement factor come due to the alteration of polarizability of the molecule when adsorbed on metal surfaces. Chemical enhancement factors contribute much smaller amount to the overall enhancement compared to the electromagnetic enhancement factor.^[36] Most believed theory is the *charge transfer* mechanism, where the electron from the unoccupied orbital (LUMO) of the molecule adsorbed on the metallic surface is transferred to the metal or the electron is transferred from the metal to the HUMO of the molecule. This creates a change in the polarizability of the molecule and hence altering the intensity of the *Raman* signal.

1.4 Cavity architectures to engineer molecular emission

In the previous sections we briefly introduced two important molecular emission process *viz.* molecular fluorescence and Raman scattering and also their *enhanced* extensions. Enhancement factors in each case depends on the local electric field. Hence the design of strcutures to enhance the emission will be focused to maximize the local electric field in a very small area (called the mode volume). Cavity architectures play a

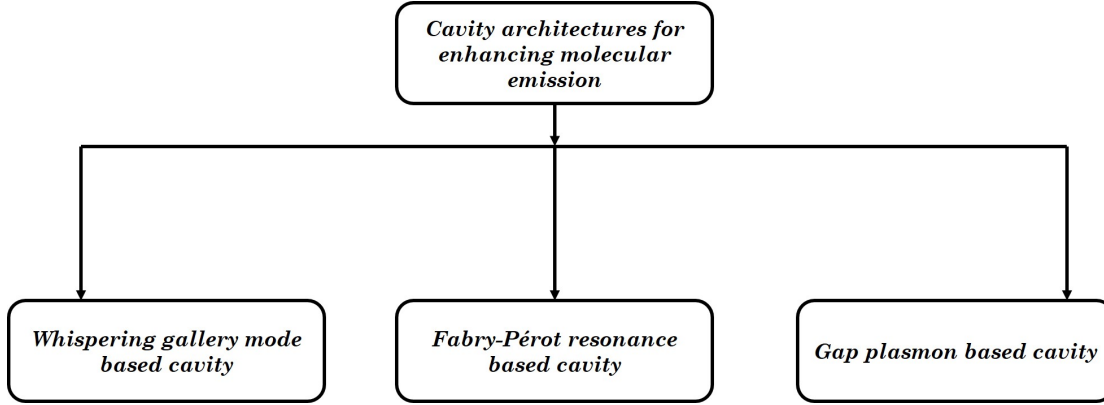


FIGURE 1.2: Schematic describing different types of cavities utilized for enhancing molecular emission.

critical role in addressing the above mentioned criterion. Quantification of the spontaneous emission enhancement of molecules inside cavity is done using *Purcell factor*. The magnitude of enhancement is given as,

$$F_{purcell} = \frac{3}{4\pi^2} \left(\frac{\lambda_{cavity}}{n} \right)^3 \frac{Q}{V} \quad (1.6)$$

where λ_{cavity} is the wavelength of emitted light inside the cavity of refractive index n , Q and V are the *quality factor* and *mode volume* of the cavity respectively. Quality factor of a cavity is given by the ratio $\frac{f_c}{f}$ (ratio of resonant frequency to the width of resonance). Larger the quality factor, finer the resonance and larger the purcell enhancement factor. Mode volume, broadly speaking, quantifies the spatial extent of electric field of any mode inside the cavity. Equation 1.6 clearly shows the importance of the ratio $\frac{Q}{V}$ for any cavity. The design of different cavity architectures aims to maximize this ratio.

Figure 1.2 shows the classification of cavity architectures utilized to enhance molecular emission. Now we discuss briefly the cavity architectures utilized to engineer molecular emission.

1.4.1 Whispering gallery mode based cavities

Whispering gallery modes (WGMs) are sharp resonances (eigen-frequencies) of a wave field (acoustic waves, electromagnetic waves) inside a resonator or a cavity with smooth edges. The waves circle around the cavity experiencing interference and hence certain frequency components gets enhanced due to the constructive interference. These resonances depend very critically on the structure of the cavity, hence they are called morphology dependent resonances. Concept of acoustic WGMs can be found in the classic architectures of 17th century like *the Gol Gumbaz of India* or the *St. Paul's cathedral*

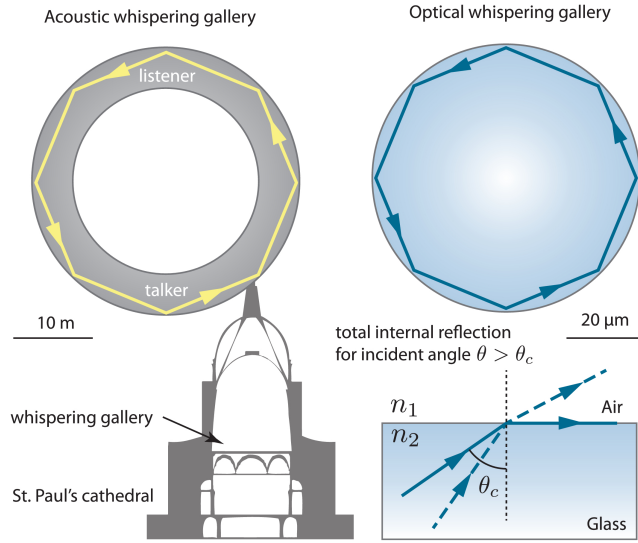


FIGURE 1.3: Schematic representing the whispering gallery modes in (left) acoustic wave and (right) optical wave regime . Figure reproduced from [37]

in London. In these architectural wonders, a *whisper* uttered at one end of the dome travels over the surface of the dome and can be heard at the other end. Only later this was experimentally discovered with light in micron sized particles, but the name WGM stuck on. This is represented in figure 1.3. Since the resonances in the WGMs depend on the structure of the resonator and the concept of interference, the Q factors in WGM based resonators are very large ($\sim 10^5$).

WGMs of a resonator are eigen-modes of the resonator and can be derived by solving wave equation with suitable boundary conditions. The complex amplitude of a wave (sound wave or a component of an electromagnetic wave) inside a cavity, u , satisfies the scalar wave equation given by,

$$\nabla^2 u - \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} = f(\mathbf{r}, t) \quad (1.7)$$

where v is the velocity of light in the cavity with refractive index n , and $f(\mathbf{r}, t)$ is any wave field source. The above equation can be solved by taking an ansatz $u(\mathbf{r}, t) = \psi_e(\mathbf{r})e^{-i\omega_e t}$ with $Re(\omega_e) > 0$. Using the ansatz, equation 1.7 can be written as,

$$\nabla^2 \psi_e + \frac{\omega_e^2}{v^2} \psi_e = f(\mathbf{r}, t)e^{i\omega_e t} \quad (1.8)$$

This is an eigen value equation with eigen value ω_e and eigen function $\psi_e(\mathbf{r})$. Given certain boundary conditions, one can solve the equation for discrete set of ω_e s. For a force field term $f(\mathbf{r}, t) = F(\mathbf{r})e^{-i\omega t}$, the wave amplitude u can be written as $u(\mathbf{r}, t) =$

$e^{-\omega t} \sum_e (\frac{B_e}{\omega^2 - \omega_e^2}) \psi_e(\mathbf{r})$. The expansion co-efficient B_e is independent of angular frequencies. Thus the energy of a specific eigen mode e can be expressed as,[38]

$$E_e \propto |\frac{B_e}{\omega^2 - \omega_e^2}|^2 \propto \frac{|B_e|^2}{[\omega^2 - \text{Re}(\omega_e^2)]^2 + \text{Im}(\omega_e^2)^2} \quad (1.9)$$

Energy of the eigen mode is maximum when $\omega = \sqrt{\text{Re}(\omega_e^2)} \approx \text{Re}(\omega_e)$. The frequency ω_e represents the central frequency of the cavity resonance and the line width of the resonance is defined by $\text{Im}(\omega_e)$. Q factor can then be expressed as $\frac{\text{Re}(\omega_e)}{2|\text{Im}(\omega_e)|}$. For dielectric cavities like microspheres one can have very small $\text{Im}(\omega_e)$ and hence very sharp resonances. In ray optics picture, WGMs can be treated as a ray traveling at the surface of a microcavity supported by total internal reflection.

WGMs can be excited by near-field coupling of a light carrying waveguide coupled to a microresonator [11] or through molecular emission.[39] When excited through broadband molecular emission like fluorescence, modes which are supported by the resonator will get enhanced due to the WGMs. This phenomenon has been used in various contexts including single molecule sensing,[12] lasers,[40] etc. WGMs also support very interesting polarization signatures which can be asserted to molecular emission.[41] Detailed discussion on WGM based cavities is presented in chapter 5 of the thesis.

1.4.2 Fabry-Pérot resonance based cavities

In the previous section, we discussed WGM based cavities and its applications. Now we focus on cavities based on Fabry-Pérot (FP) resonances. Originally it was devised in 1897 by A.Fabry and Ch.Pérot using two parallel mirrors placed apart. It has been modified and extensively used in production of mode locked lasers. An FP cavity consists of two partially reflecting mirrors placed at a distance, say d , from each other, as shown in figure 1.4. The light which gets reflected by the mirrors gets interfered inside the cavity. One gets resonances of the cavity when the waves interfere constructively. The Q factor of the cavity depends on the reflectivity of the mirrors at the operating wavelength. The difference between WGM based resonators and FP resonators is that former is based on total internal reflection while the latter on simple reflectivity of the mirrors. The mode supported in the cavity depends on the structure and material parameters of the mirror and the optical medium in between.

Intensity of optical beam in an FP interferometer and its dependence on different parameters of the cavity is beautifully explained in the classic *Born and Wolf*. [43]

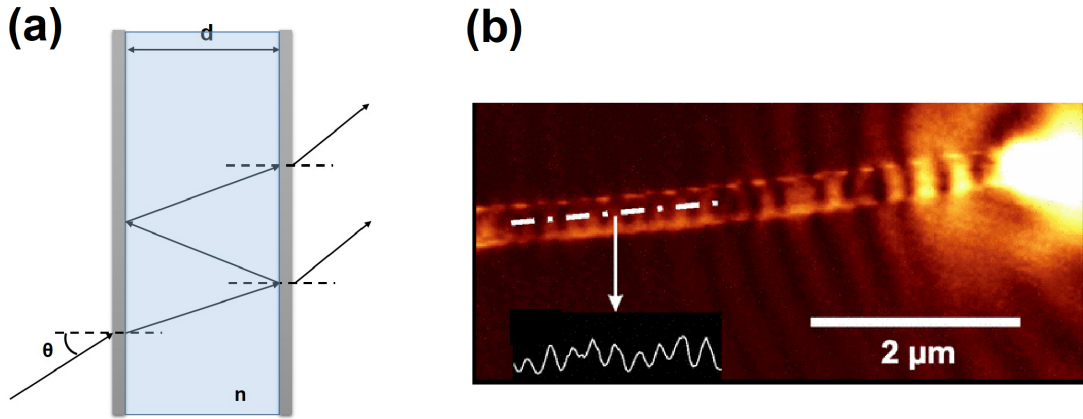


FIGURE 1.4: (a) Schematic of a conventional Fabry-Pérot resonator using two parallel mirrors. (b) Fabry-Pérot resonances in 18.6 μm long silver nanowire examined using near field optical microscopy. Figure adapted with permission from [42]

Output optical intensity, I , from an FP cavity can be shown as,

$$I = I_{inc} \frac{(1 - R)^2}{(1 - R)^2 + 4R \sin^2(\frac{2\pi d}{\lambda})} \quad (1.10)$$

where I_{inc} is the input intensity, R is the reflectivity of the mirrors, and λ is the wavelength of operation. One can see that the intensity spectra has sharp peaks around $\frac{d}{\lambda} = \frac{(2n+1)}{4}$.

The concept of FP resonances finds huge implications in nanophotonics. Thin metallic and semiconductor wires show this resonance.[42, 44] In the case of nano and micron sized wires, the ends of the wires act as mirrors and partially reflect the waves which gets interfered with the propagating modes resulting in FP resonances as shown in figure 1.4. Semiconductor nanowires show such resonances in *photoluminescence* regime, thus manipulating the molecular emission.[45] Molecular emission coupled to nanowires can be used to excite FP resonances. Advantage of such a configuration is that addition to the enhancement of molecular emission, the emission can be directed onto specific angles using antenna effect of the wire. Detailed discussion on FP resonance based cavities is presented in chapter 4 of the thesis.

1.4.3 Gap plasmon based cavities

Surface plasmons are surface electromagnetic excitation at metal-dielectric interface like thin metallic films, nanoparticles etc. If one brings another metal surface close to the former, new modes arise where the electric field is concentrated in between the metallic surfaces. Such modes are called gap plasmon modes or cavity plasmon modes. [46–48] Due very strong local electric field enhancement inside the cavity and ultra-low mode volumes such gap-plasmon cavities are used in single molecule fluorescence and Raman scattering measurements.[15, 49]

Nanoparticle aggregates were traditionally studied in harnessing the power of gap plasmons. Due to the large enhancement of near field electric field, nanoparticle aggregates were used to probe single molecule Raman signatures.[49, 50] The major issue with nanostructure aggregates is that they have random structural parameters. Hence systematic study of the gap plasmons in nanoparticle based aggregates should be based on controlling the number of particles and the distance between them.[51] This requires very complicated and sophisticated chemical techniques. An elegant alternative is to utilize nanoparticle on a metallic mirror geometry. This structure is conceptually similar to nanoparticle dimers and can be easily prepared and studied at single particle level. In metallic mirror based configuration, one can also create elongated cavities by placing nanowires on film, instead of nanoparticles.

Typical WGM based and FP based cavities are diffraction limited cavities. The minimum size of the cavity should be greater than the operating wavelength. Hence all the cavities mentioned in earlier sections are micron sized. Central advantage of diffraction limited dielectric based cavities is its capability to enhance the Q factor. On the other hand we lose our hold on the mode volume, as the cavities are spatially very large. To gain on the mode volume, one has to fabricate cavities which are extremely small in spatial dimensions, in other words: *sub wavelength cavities*. The development of *plasmonics* has propelled the research on cavities of size down to 1 nm.[52, 53] Such cavities can decrease mode volume less than $10^{-5}V_\lambda$ ($V_\lambda = (\frac{\lambda}{n})^3$) and are based on the concept of *gap plasmons*. Detailed discussion on cavity plasmons can be found in chapter 3.

1.5 Scope and outline of the thesis

This thesis focuses on understanding light-matter interaction in metal film based cavities, giving specific emphasis on polarization and wavevector of emitted light. Metal film based cavities are very important as they comprise combined effects of both plasmonic and dielectric parts. Also the idea can be extrapolated to study patterned meta

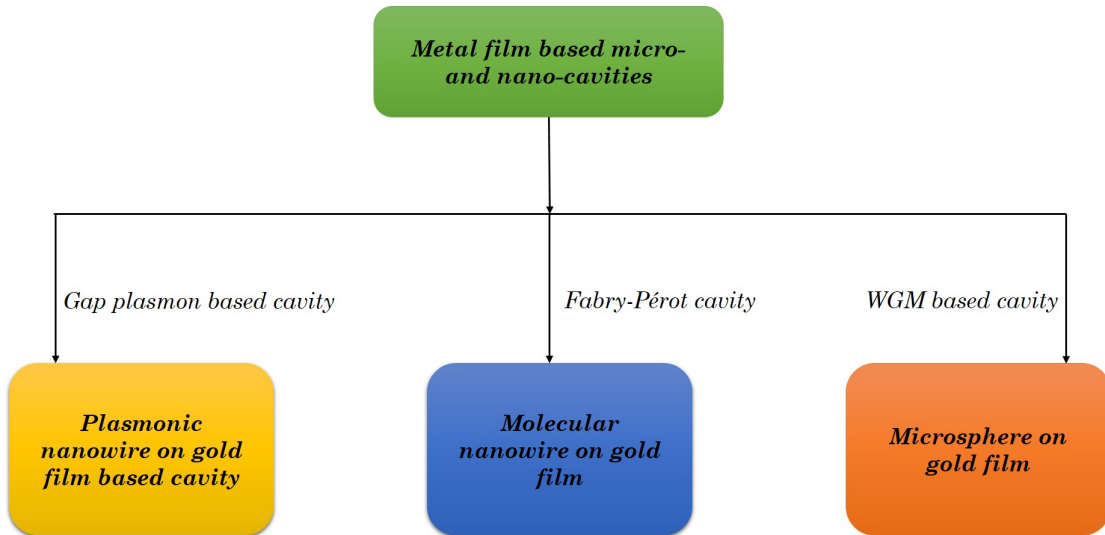


FIGURE 1.5: Schematic describing the outline of the thesis

surfaces and hence metamaterials. As discussed in previous sections, molecular emission can be manipulated by confining emitters inside an optical cavity. Our study provides a clear platform to understand the rich polarization and wavevector distributions achievable using different optical cavities. The scope of the thesis covers a wide umbrella of emission processes inside different cavity architectures with a momentum space analysis view point. Understanding them can have wide implications in applying the concepts of optical antenna, optical communication, molecular sensing, single molecule optics etc to the field of cavity optics. Figure 1.4 describes the outline of my thesis. The work can be seen in three different sections which emphasizes on a particular kind of cavity architecture.

Chapter 2: Here we focus on the experimental and numerical methods involved in probing polarization and wavevector information from optical cavities. Measurements techniques like Fourier plane optical microscopy and spectroscopy is introduced and its applications are elucidated. Then we discuss the numerical techniques used in the analysis (finite element method (FEM) and finite difference time domain (FDTD) based methods) of cavity architectures. Special importance is given to calculate the radiative and non-radiative decay rates and far field emission patterns.

Chapter 3: In this chapter, we discuss the effect of plasmonic nanowire on metal film cavity on molecular fluorescence and surface enhanced Raman scattering. This gap plasmon based cavity provides an opportunity to probe molecular emission in remote excitation configuration. We analyze the inelastic molecular emission from the distal end of the wire using Fourier plane spectroscopy. Detailed analysis of output polarization dependence of wavevectors of SERS and fluorescence is also provided. The results are then corroborated with 3D FDTD numerical simulations.

Chapter 4: Here we elucidate how a vertical Fabry-Pérot based cavity on a metal film shows doughnut shaped far field emission. The cavity architecture comprises of a molecular nanowire made of 1,5-Diaminoanthroquinone (DAAQ) grown vertically on a 50 nm thick gold film. Individual nanowires were excited using evanescent excitation and the out-coupled light is projected onto the Fourier plane (FP). We discuss the FP patterns in both elastic scattering and photoluminescence operational regimes. the results are corroborated with 3D FEM based numerical simulations.

Chapter 5: The main focus of this chapter is a WGM based cavity on a metal film. We discuss the FP emission pattern and polarization signatures of molecular fluorescence coupled to microsphere on a metal film. We show that the split WGMs, due to the interaction with the metal film, out-couples with vectorial polarization signatures. The instrumentation involved and a simple bi-sphere model to explain the observed results will then be discussed.

Chapter 6: We provide a meta-analysis of the advantages and limitations of the present study and then focus on the future aspects of the work. Hints towards coupling nanofabrication architectures and the optical cavities, coupling transition metal dichalcogenides (TMDs) and optical cavities are also discussed.

1.6 Where does this thesis stand ?

Cavity assisted molecular emission has been studied in great detail in the past using different probing techniques. In the past, metal film based cavities, in particular, were studied to understand the coupling mechanisms and enhancements as far as molecular emissions are concerned. We can broadly classify the existing literature on metal film based cavities into two categories: (i) Nanoparticle on mirror based cavities (Quasi-zero dimensional cavities) and (ii) Nanowire on mirror based cavities (Quasi-one dimensional cavities).

Nanoparticle on mirror cavities are extensively studied as far as the intensity enhancements and understanding coupling mechanisms are concerned. Recent developments include the demonstration of single molecule strong coupling, [15] Single molecule SERS, [49] molecular antenna [54], and many more. But rarely Fourier plane imaging has been utilized in probing the momentum space distribution of these cavities. The work presented in this thesis can be placed in this domain of understanding and probing molecular emission from such small cavities (chapter 5 of the thesis).

Nanowire on mirror is a recent development in the design of nanocavities. They provide a unique opportunity to probe guided modes as well as cavity enhancements. Nanowire on film has been studied previously with a cavity view point to understand the

modes of the cavity and enhancement factors involved. [55–57] But this thesis focuses on the effect of cavity on momentum states of the molecular emission, which has not been probed (chapter 3 and 4 of the thesis).

Talking about the technique, chapters 3 through 5 elucidates different cavities probed with Fourier plane imaging and spectroscopy techniques which have only been used to study SERS emission or emission from photonic crystals in the past. The work presented in the thesis finds itself comfortably in an important place as far as the techniques of probing and the questions probed are concerned.

Chapter 2

Basic strategies in Fourier plane imaging, Energy-momentum spectroscopy, and Numerical modeling

In the past, various methods have been utilized to understand light-matter interaction, particularly at subwavelength dimensions. Methods utilized purely depend on the questions asked and the practical applicability of the method to probe a relevant question eg: conventional real plane optical microscopy can give information about the spatial dimensions of the sample, but will not give any information about the energy structure. So one utilizes a number of scientific tools to probe a particular question. Since we were interested in the emission wavevectors of the micro/nanocavities, we utilized, prominently, Fourier plane imaging and energy-momentum spectroscopy as major tools. Fourier plane (FP) imaging is a unique experimental method which provides imaging in momentum (wavevector) coordinates. FP images can further be dispersed in a spectrometer to additionally acquire energy resolution. This chapter deals with the basic strategies in Fourier plane imaging, energy-momentum spectroscopy and the numerical modeling techniques utilized to understand the light-matter interaction. This chapter serves as a primer to the techniques utilized in probing the metallic film based nano and micro cavities.

2.1 Fourier plane imaging

Conventional real plane images, both bright and dark field images, have resolution in terms of spatial coordinates. In order to obtain the information about the angular emission/scattering pattern from the sample, one has to resort to Fourier plane imaging. Measuring angular emission pattern is of crucial importance and has been utilized in variety of applications including measuring angular emission pattern of single emitters,[58–62] optical antennas,[63–69] probing coupling mechanisms in cavities, [70] in

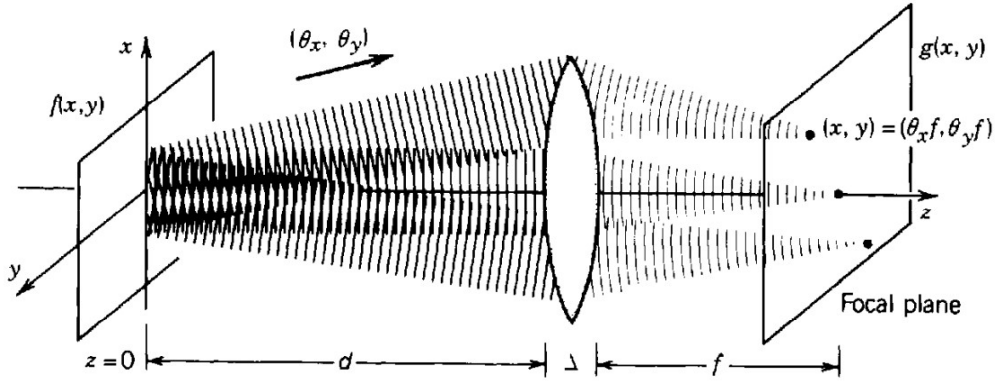


FIGURE 2.1: Conceptual schematic of Fourier transform using a lens.
Reproduced with permission [82]

cathodoluminescence, [71, 72] secondary emission, [73–78] scanning microscopy, [79] soft matter, [80] nonlinear scattering, [81] and many more. One uses the Fourier transform property of an optical lens to image the Fourier plane. The concept of Fourier transform using a lens is discussed first and then the full experimental setup will be explained.

Light emanating from the sample plane can be decomposed into a set of plane wave components $u^i(x, y)$ s traveling at different angles θ^i s. When this composite light is passed through an optical lens, different plane wave components gets focused to different points at the focal plane. Plane wave arriving at angle (θ_x, θ_y) gets focused to a point $(f\theta_x, f\theta_y)$, where f is the focal length of the lens. So imaging the focal plane of the lens will provide information about the wavevector distribution of the incoming beam. The angles θ_x and θ_y can be written as (see figure 2.1) $\theta_x = \lambda\nu_x$ and $\theta_y = \lambda\nu_y$ with $\nu_x = \frac{x}{\lambda d}$ and $\nu_y = \frac{y}{\lambda d}$ where d is the distance between the sample plane and the lens. A plane wave $U(x, y, z)$ having complex amplitude proportional to the Fourier transform $F(\nu_x, \nu_y)$ can be written at $z = 0$ as,[82]

$$U(x, y, 0) = F(\nu_x, \nu_y)e^{-i2\pi(\nu_x x + \nu_y y)} \quad (2.1)$$

and at $z = d$, $U(x, y, z)$ can be written as,

$$U(x, y, 0) = H(\nu_x, \nu_y)F(\nu_x, \nu_y)e^{-i2\pi(\nu_x x + \nu_y y)} \quad (2.2)$$

with $H(\nu_x, \nu_y) = H_0 e^{i\pi d(\nu_x^2 + \nu_y^2)}$ is the transfer function with $H_0 = e^{-ikd}$. Upon passing through the lens of thickness Δ , the complex amplitude will be multiplied by

the lens phase factor $e^{i\pi(\frac{x^2+y^2}{\lambda f})}$. The resulting equation can be simplified as ,

$$U(x, y, d + \Delta) = A(\nu_x, \nu_y) e^{i\pi \frac{(x-x_0)^2 + (y-y_0)^2}{\lambda f}} \quad (2.3)$$

where $x_0 = \lambda \nu_x f$, $y_0 = \lambda \nu_y f$, and $A(\nu_x, \nu_y) = H_0 e^{i\pi \lambda (d-f)(\nu_x^2 + \nu_y^2)} F(\nu_x, \nu_y)$. Equation 2.3 represents a paraboloidal wave converging to a point in the focal plane of the lens $z = d + \Delta + f$. Using $\int e^{\frac{i2\pi(x-x_0)}{\lambda f}} dx' = \lambda f \delta(x - x_0)$ one can write the complex amplitude as

$$U(x, y, d + \Delta + f) = h_0 (\lambda f)^2 A(\nu_x, \nu_y) \delta(x - x_0) \delta(y - y_0) \quad (2.4)$$

where $h_0 = \frac{i}{\lambda f} e^{-ikf}$, $x_0 = \lambda \nu_x f$, and $y_0 = \lambda \nu_y f$. Indeed equation 2.4 denotes a wave getting focused at point (x_0, y_0) on the focal plane of the lens. Now one can integrate over all ν_x and ν_y and using the sifting property of the delta function inside the integral, we can write total amplitude at the focal plane as

$$g(x, y) = h_l e^{\frac{i\pi(x^2+y^2)(d-f)}{\lambda f^2}} F\left(\frac{x}{\lambda f}, \frac{y}{\lambda f}\right) \quad (2.5)$$

where $h_l = H_0 h_0 = (\frac{i}{\lambda f}) e^{-ik(d+f)}$. When the sample is placed at the first focal plane of the lens ($d = f$), then the additional phase factor in equation 2.5 will vanish and the intensity at the back focal plane will be directly proportional to the Fourier transform of the complex amplitude at the image plane.

A typical experimental realization of the measurement of FP using a microscope is shown in figure 2.2. Emission from the sample plane is captured using objective lens and the collected light is routed to the camera using a set of relay lenses. Since the back focal plane (BFP) of the objective lens lies physically inside the case, it is difficult to directly image it. Hence, a set of relay lenses are used to project the BFP of the objective lens onto the imaging camera. In figure 2.2, the incoming laser is focused using a high numerical aperture objective lens and the backscattered light is collected using the same lens. The collected light is passed through set of lenses $L3 - L5$ and projected onto the CCD. The beam emanating from the objective lens is infinity corrected and will be focused using lens $L3$ to form a conjugate image plane. One can place any associated optics in the conjugate image plane like pinholes or apertures to spatially filter certain locations on the sample plane. Then the resulting light is passed through lens $L4$ which projects the Fourier transform of the light emanating from the conjugate image plane onto the CCD (the distance between lens and the image plane is equal to the focal length of the lens). Thus one can relay the BFP of the objective lens and image it using an external camera. Spectral filters like edge/notch filters can be placed in the optical path to reject the incident laser in performing secondary emission related experiments.

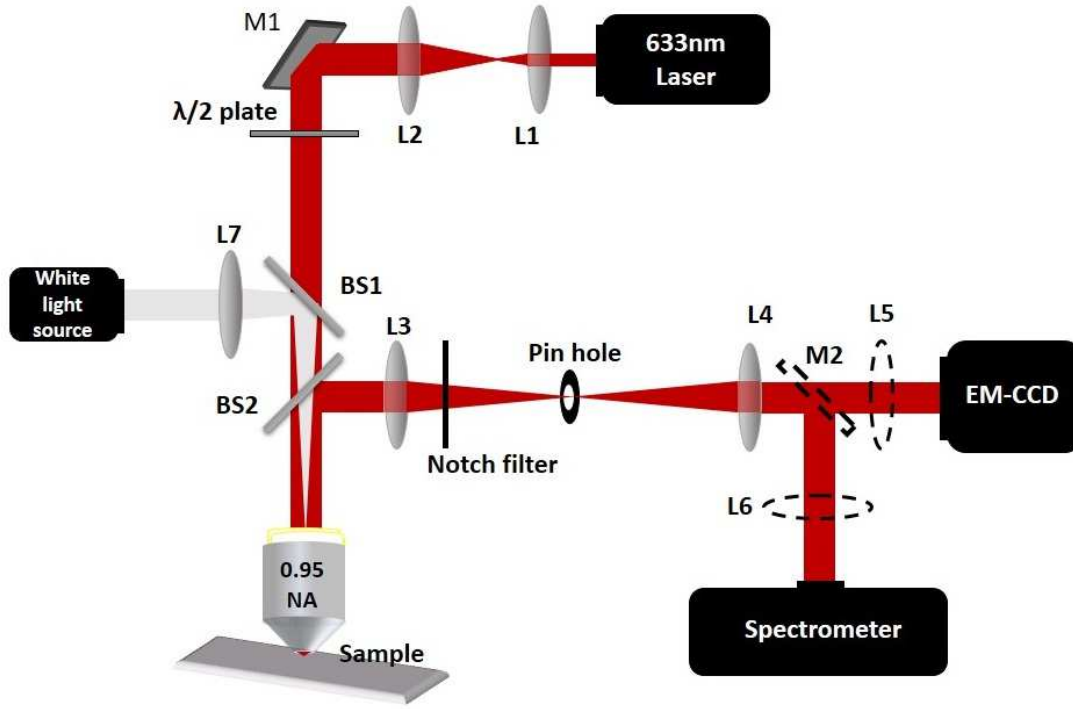


FIGURE 2.2: Schematic of imaging back focal plane using an optical microscope

2.2 Energy-momentum spectroscopy

In the previous section, the technique and importance of Fourier plane imaging has been explained. When the emission from the sample plane is broadband in wavelength, it would be necessary to have wavelength information in addition to the momentum information. This can be facilitated by energy-momentum spectroscopy. This technique finds enormous application in determining the wavevector spread of secondary emission like fluorescence and Raman scattering. Since Raman modes potentially support different wavevector signatures due to the different dipole moments of the vibrational modes, it is imperative to measure Fourier plane signatures in addition to the spectroscopic signatures. Here we project the FP image onto a momentum filter placed at the conjugate Fourier plane. The momentum filter can be a slit or a pinhole, which filters only certain range of k -vectors. The resulting light will be projected onto the spectrometer to provide wavelength information. Since the filter placed on the conjugate FP can be moved and placed accordingly, one can actually span the entire k -image. The resolution of the energy momentum (e-k) spectrum depends on the size of the momentum filter and the grating used. Figure 2.2 shows a simple way to perform e-k spectroscopy. Here, the FP image is projected onto the slit of the spectrometer. Now the slit defines the momentum vectors filtered and then further dispersed using the grating. The limitation is that one

can only have certain wavevectors filtered out as the orientation and position of the slit is fixed. If one requires to move the momentum filter across the FP image, one has to place the momentum filter in the conjugate Fourier plane.

2.3 Numerical modeling

¹ Another important technique to understand the light-matter interaction at nanoscale is to solve wave equation with suitable initial and boundary conditions. We utilize both finite element method (FEM) and finite difference time domain (FDTD) based numerical solutions to calculate the near field electric field around the structure and hence the far field signatures. To demonstrate the importance, we probe a single quantum emitter coupled to a plasmonic nanotriangle system. Plasmonic nanotriangle is an important probe system as it has an inherent spatial anisotropy, which can be harnessed in spatial dependent enhancements in molecular emission. In this context an important question to ask is, how does the spatial location of the quantum emitter with respect to individual anisotropic plasmonic nanostructure affect its radiative and non-radiative processes? This question is of direct relevance in designing optical antennas to control atomic and molecular emission. With the emergence of nanofabrication methods, accurate placement of single quantum emitters have been achieved,[83–85] which may open new avenues in quantum optics and quantum information processing.[86, 87]

Under the dipole approximation of particle-field Hamiltonian, one can represent the atom as an oscillating dipole for all practical calculations. [26, 88] The decay rate of a molecular or an atomic emitter can be expressed using Fermi's golden rule, considering weighted sum of all possible decay channels according to which, the total decay rate of an excited emitter is proportional to transition dipole moment $p_{trans}=i\hat{p}f$ where i and f denotes initial and final states of the emitter respectively and $\hat{p}$ represents the dipole operator. When a dipolar emitter is placed in the vicinity of a metallic nanostructure, the emitter will now have two channels to decay. One of those is to directly couple to the far field, γ_{fs} , and other is to couple to the near field of the structure, γ_{couple} . Thus coupled power, P_{couple} , can either get scattered away by the structure to far field or can get absorbed by the structure. Scattered power together with γ_{fs} forms the total radiative decay rate. That part of emitted power which ends up in getting absorbed by the structure is a measure of non-radiative decay rate of the emitter. So, in presence of

¹adapted version of the article *Opt.Commun.*381, 227-233 (2016) and *International Conference on Fibre Optics and Photonics*, W4D. 3 (2016)

nanostructure we can write the total decay rate of the emitter, γ_{tot} , as

$$\gamma_{tot} = \gamma_{couple} + \gamma_{fs} \quad (2.6)$$

Where, γ_{couple} , γ_{fs} are decay rates due to near field coupling with the nanostructure, free space radiative decay rate in the presence of nanostructure respectively. Now, γ_{couple} can further be expressed as a sum of absorptive decay rate, γ_{abs} , (which forms the non-radiative part) and scattered decay rate, γ_{scatt} , (which forms the radiative part) respectively. The scattered electric field and electric field of the emitter combine to give total radiated power in the far field. Depending upon the phase of the scattered field with respect to electric field of the dipolar emitter, one can have a destructive interference and hence excite optically dark modes which show complete radiation quench in the far field.

Now, the total radiation extraction efficiency, (modified quantum efficiency of the emitter in the presence of nanostructure) can be written in terms of γ_{abs} and γ_{rad} as

$$\eta = \frac{\frac{\gamma_{rad}}{\gamma_{rad}^0}}{\frac{\gamma_{abs}}{\gamma_{rad}^0} + \frac{\gamma_{rad}}{\gamma_{rad}^0}} \quad (2.7)$$

where γ_{rad}^0 is the radiative decay rate of emitter in absence of nanostructure.

2.3.1 Radiative and Non-radiative decay rates

Radiative decay rate for an emitter coupled to a nanostructure consists of two parts (i) Direct out-coupling of power by the emitter to the far field (ii) Scattered component of the coupled power by the scatterer. If the dimensions of the scatterer is less than emission wavelength, the scattered power from the structure will be majorly dependent on the induced dipole moment, ($\vec{p}_{induced}$), in the structure. Using this approximation, normalized radiative decay rate can be represented as [89],

$$\frac{\gamma_{rad}}{\gamma_{rad}^0} = \frac{|\vec{p} + \vec{p}_{induced}|^2}{|\vec{p}|^2} = \frac{P_{rad}}{P_{rad}^0} \quad (2.8)$$

where $\vec{p} = [p_x, p_y, p_z]$ is dipole moment of the emitter and P_{rad}^0 is power emitted by dipolar in the absence of nanostructure. Exact expression for the radiative decay rate will depend on morphology and polarizability of the structure.

Non-radiative decay rate from emitter is quantification of power absorbed by the nanostructure out of power coupled by emitter to its near field. For an emitter with

emission frequency ω and wavenumber $k=\omega/c$, to nanostructure with wavelength dependent dielectric permittivity $\epsilon(\omega)$ it can be expressed as [89],

$$\frac{\gamma_{abs}}{\gamma_{rad}^0} = \frac{3}{16} \text{Im} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} \frac{1}{k^3 z^3} \frac{(p_x^2 + p_y^2 + 2p_z^2)}{|\vec{p}|^2} = \frac{P_{abs}}{P_{rad}^0} \quad (2.9)$$

Neglecting edge and curvature effects equation 2.9 implies that non-radiant energy transfer is dependent only on the distance, z , between emitter and the structure and relative dielectric permittivity $\epsilon(\omega)$ of the structure. We used finite difference time domain (FDTD) method to calculate extinction spectrum, near field electric field and normalized decay rates using commercially available solver by Lumerical solutions Inc. The structure under study is a gold nanotriangle of edge length 160 nm and thickness of 30 nm placed over glass substrate (see figure 2.3(a)). Triangle was modeled to have rounded corners with corner radius of 20 nm to avoid field singularity at corners and also to mimic experimentally realizable object. The area near the triangle was discretized by a non-uniform conformal variant mesh with meshing size of 0.6 nm and rest of the simulation area with size of 1 nm. Simulation area was terminated by Perfectly Matched Layers (PMLs) to avoid spurious reflections from boundaries. Wavelength dependent dielectric permittivity of gold was taken from experimental details provided by Jhonson and Christy [90] and that of glass (SiO_2) from Palik. [91] For extinction spectrum calculation, a broadband Total Field Scattered Field (TFSF) source¹ (illumination wavelength, 400 nm-1200 nm) was used. Absorption and scattering cross sections were calculated using an in-built analysis group in Lumerical FDTD solver and extinction spectrum was calculated in the post processing step as sum of absorption and scattering cross sections. Atomic emitter is modeled as an oscillating classical dipole with current dipole moment 9×10^{-14} Am. It is representative in nature so as to model an excited atom. Decay rates (Radiative, Non-radiative and Total) were calculated using a broadband dipole emitter (emission wavelength, 400 nm-1000 nm), placed at 5 nm above the substrate in two different positions, (i) corner (ii) center of the nanotriangle. Radiative decay rate was calculated by enclosing both emitter and the nanotriangle by a rectangular surface and integrating time averaged Poynting vector over the surface, which gives power outflow from the system, and normalizing this with emission power of the dipole emitter, P_0 . For the non radiative decay rate calculation, similar procedure was followed with integrating time averaged incoming Poynting vector over a rectangular surface enclosing only nanotriangle, which gives the power inflow to the nanotriangle, followed by subtracting the power scattered off to far field. Intrinsic quantum yield of the emitter is considered to be unity in all calculations. Total decay rate was calculated

¹ A TFSF source uses a plane wave illumination and divides simulation area into total and scattering fields

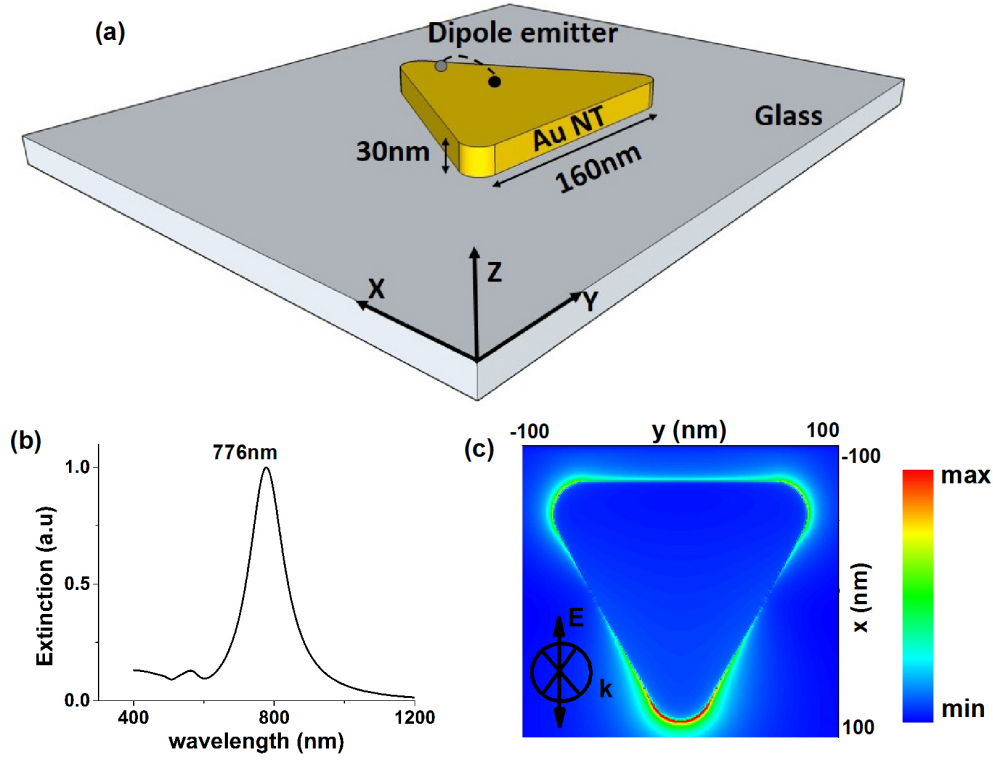


FIGURE 2.3: (a) Schematic of gold nanotriangle of thickness 30nm and edge length 160nm placed over glass substrate. Calculations were performed by placing a dipole emitter at a distance 5nm above triangle, either at the center or at the corner (represented by grey and black points in the figure). (b) Normalized extinction cross section of the nanotriangle showing a dipolar resonance at 776nm. (c) Near field electric field distribution at the glass-triangle interface for illumination wavelength of 776nm showing the corner mode. The k -vector was directed into the plane and the E field polarization is indicated by the double-sided arrow.

as sum of its radiative and non-radiative counterparts.

Plasmon modes of the nanotriangle

Schematic of the system under study is as shown in figure 2.3 (a). Typical dimensions of triangle were taken from experimental results of [92]. We have chosen nanotriangles for two major reasons. Firstly, nanotriangles have intrinsic structural anisotropy which shows geometry dependent modes of localization. [93] Depending on the energy of excitation, triangles show various modes of field localization such as corner, edge and center modes. The corner mode, being the lowest order mode, can be excited in visible and near infrared wavelengths. Secondly, electromagnetic resonances of these structures show a critical dependence on edge length and thickness. We have chosen edge length of triangle as 160 nm and thickness as 30 nm as we limit our discussion

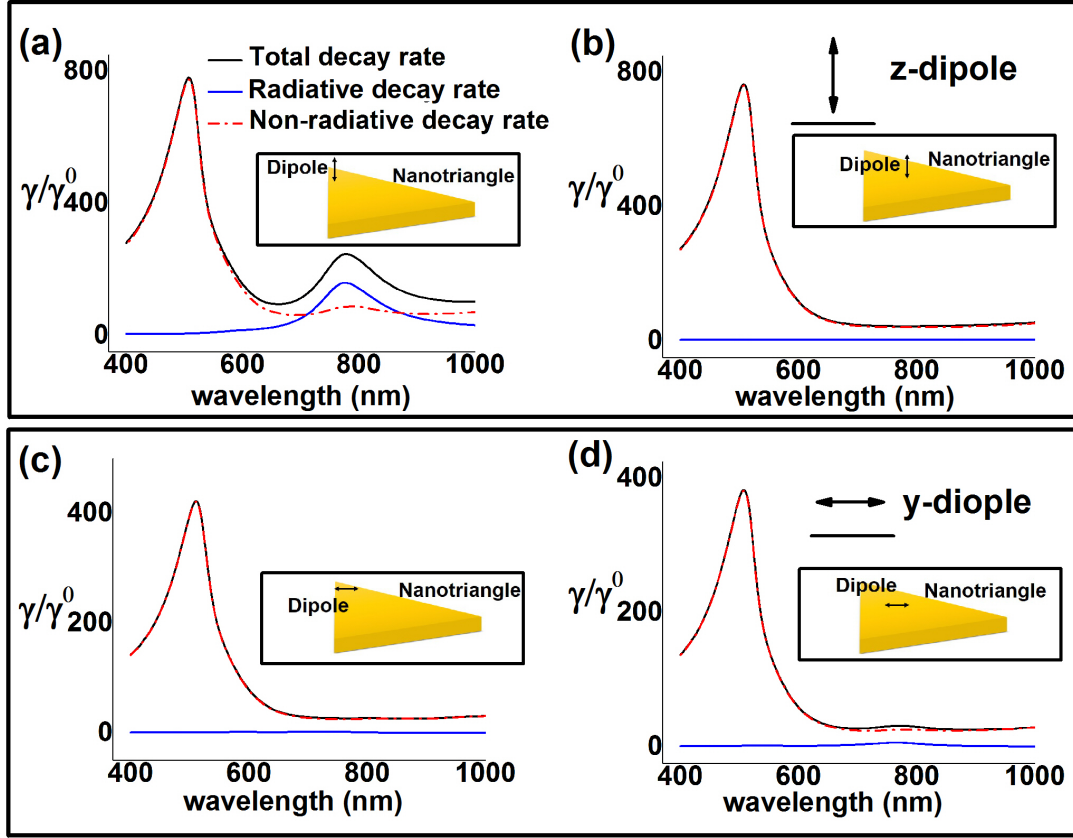


FIGURE 2.4: Normalized decay rates, γ/γ^0 , for z oriented dipole emitter coupled to nanotriangle calculated by placing a dipole at 5nm above (a) corner and (b) center of the triangle. Normalized decay rates, γ/γ^0 , for y oriented dipole emitter coupled to nanotriangle calculated by placing it 5nm above (c) corner and (d) center of the triangle. Insets show the orientation of position of the dipoles with respect to the structure.

to visible wavelength, since triangle with these dimensions is expected to show at least one mode of resonance in visible and near infra-red wavelength regime. Calculated extinction cross section of the triangle shown in figure 2.3 (b) shows a corner mode dipolar peak at 776 nm. There is also a weak, broad quadrupolar peak around 540 nm. The near field electric field map, calculated at the glass-triangle interface, at 776 nm illumination wavelength further clarifies the mode excited in the triangle (see figure 2.3(c)) as corner mode. Electric field is localized in the corners of the triangle and field intensity is minimum at the edges and center. Because of strong anisotropy in field localization, emitters placed near such nanostructures experience spatially dependent mode volume, which makes them emit differently depending on the placement with respect to the structure.

Calculation of decay rates

To probe effects of strong localized modes, decay rates were calculated by placing a dipole emitter 5 nm above the surface of the triangle in two different positions, above (i) corner and (ii) center of the triangle (see figure 2.3 (a)). Calculated normalized decay rates are as shown in figure 2.4. The total decay rate curve peaks at two different wavelengths, one can be attributed to radiative decay maximum and another to non-radiative energy transfer.

Radiative decay rate

For dipole oriented along z-axis, i.e., perpendicular to the surface of the triangle, dipole placed above corner shows a radiative decay peak at 776 nm, coinciding with the dipolar corner mode of the structure (see figure 2.3 (c)), which is absent for the dipole placed over center of the triangle as figure 2.4 (a) and (b) illustrates. This feature can be explained by the fact that dipole placed above center of the triangle cannot couple to corner mode, hence there will be radiation quenching while the one placed above corner shows radiative enhancement because of coupling with the resonant mode of triangle. Radiation extraction efficiency, η ($\gamma_{rad}/\gamma_{tot}$), for z-oriented dipole at 776 nm is 0.678 for placement of dipole over corner. When dipole orientation is changed to align along y-axis, parallel to the surface of the triangle, there is a total radiation quench in both the placements of emitter as shown in figure 2.4 (c) and (d). Normalized radiative decay rate for y-polarized dipole placed above center and corner shows considerable quench in emission. This quenching is due to the fact that dipole couples to optically dark quadrupolar mode. The decay rate in the presence of the nanotriangle (γ/γ^0) essentially represents the Purcell enhancement in the system. In particular, the radiative decay rate enhancement of 159.751 at the operating wavelength 776 nm signifies that the molecule near the triangle radiatively decays 159 times faster than a molecule placed in vacuum. This also shows the enhancement factor for the intensity of molecular emission.

Parameters of radiative enhancement

Radiative enhancement of an emitter coupled system is closely knit with two important parameters, (i) Spatial modal range of the resonance and (ii) Dipolar moment orientation and positioning of emitter. Because of sharp corners, modal range of triangles are limited and hence will enhance only those emitters which lie in its range and will not affect molecules which are away from the range of the mode. Secondly, dipolar orientation will play a very critical role in exciting certain dark optical modes and hence quenching the emission from emitters even though, emitter is in modal range of the

resonance [94]. Structural asymmetry allows to probe both concepts together. Hence, nanotriangles offer an interesting platform to study spatial switching and modulation of fluorescence.

Non-radiative energy transfer

In all four configurations, there is a strong non-radiative decay peak at 507 nm, which can be attributed to the energy transfer by emitter to structure (See figure 2.4). At this particular emission wavelength, power coupled to the structure, P_{couple} , is mostly absorbed by the nanostructure and very small amount of power will be radiated to far field resulting in a radiation quench. As given by equation 2.9, the non radiative energy transfer is independent of morphology of structure. It depends only on distance between emitter and the nanostructure and relative dielectric permittivity of the structure. For nanostructures made of gold, it occurs around 510 nm (Equation 2.9 qualitatively explains this fact, using wavelength dependent dielectric permittivity). Non-radiative decay rate for dipole orientations parallel to the surface of nanostructure is half as that of orientation perpendicular to structure (see equation 2.9). Also, equation 2.9 neglects curvature and edge effects. This is evident in the case of emitter placed above corner of triangle, where there is a slight change in non-radiative decay rate with respect to the same when placed above center of the triangle in both the dipole orientations. Probing and quantifying non-radiative decay peak is very crucial to understand surface enhanced emissions and also in design of nano sources of heat which act away from their electromagnetic resonances.

2.3.2 Far field signatures

k-space scattering diagrams were plotted using Near to Far Field Transformations (NFFT) following reciprocity arguments.[95] Near field for NFFTs were calculated using commercially available Finite Element Method solver by COMSOL. Simulation geometry was terminated by scattering boundary conditions to avoid spurious reflections from the boundaries. For all FEM based simulations a broadband plane wave illumination was used (illumination wavelength, 400-1200 nm). Nanotriangle was illuminated by broadband plane wave through glass and scattering towards glass was visualized using NFFT mechanism. Triangles, due to inherent structural anisotropy, show different electromagnetic modes. Extinction spectra of gold nanotriangle of chosen dimensions shows a dipolar mode at 776 nm and a weak quadrupolar mode around 540 nm (see section 2.3.1). The dipolar mode is a low energy fundamental mode and is characterized by a strong electric field localization around its corners.

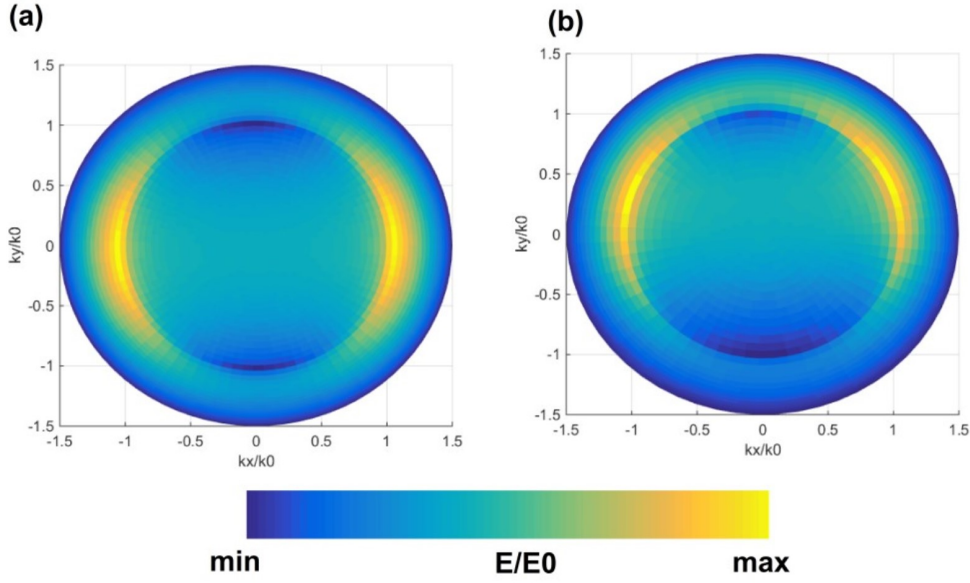


FIGURE 2.5: k-space scattering patterns of nanotriangle for illumination wavelength (a) 776 nm and (b) 540 nm. Color bar shows normalized far field electric field intensity (E/E_0) in V/m..

To probe the far field scattering patterns of the nanotriangle, we calculated the k-space diagram using NFFT at both resonances of the nanotriangle viz., dipolar and quadrupolar resonances. Figure 2.4 shows the scattering radiation pattern of the nanotriangle at two different resonances. Polarization of the illuminating wave is kept along x-axis (see figure 2.3 (a)). At illumination wavelength 776 nm, the far field diagram shows dipolar nature as depicted in figure 2.4 (a). This corroborates the dipolar nature of resonance. Using the fact that angular intensity in the k-space diagram is represented by the azimuthal angle ϕ and $n \sin \theta$, where n is the refractive index of the medium and θ is the polar angle. Also with $k_{||} = k_0 n \sin \theta$ for all azimuthal angles (ϕ), where k_x and k_y are wavevectors of the light scattering by the nanotriangle resolved with respect to x and y axes respectively, k_0 is the wavenumber of light in vacuum and $k_{||}$ is parallel wavevector of incoming light, intensity in the k-space diagram directly depict the radiation pattern. In the present case, the scattering is dominant at k_x/k_0 around 1 which corresponds to scattering angle of $\sim 42^\circ$ i.e., critical angle of glass-air interface.

At illumination wavelength 540 nm, quadrupolar resonance of the nanotriangle, the k-space diagram shows a typical pattern around critical angle of glass-air interface. Polarization of the incident wave is kept along x-axis (see figure 2.3 (a)). The far field projection resembles distribution of a point quadrupole placed on glass air interface. Modification in the far field distribution is due to spatial anisotropy and different modes

of the charge distribution supported by the nanotriangle. So the local electromagnetic resonances bear a very intricate relationship with the far field scattering patterns. Since the far field patterns are easily measured using back focal plane microscopy, such k-space analysis becomes very crucial for understanding electromagnetic resonances.

2.4 Conclusion

In summary, a brief discussion on different experimental and numerical techniques utilized in the wavevector analysis from a subwavelength sized system has been presented in this chapter. Fourier microscopy and spectroscopy techniques are not just limited to probe individual nanostructures and can be extended to periodic structures like metamaterials. Recently Fourier microscopy has been applied to probe soft matter and related topics. The numerical techniques outlined in the chapter are robust and finds applications in varied fields like finding electromagnetic responses of complex structures, etc.

Chapter 3

Directing molecular fluorescence and SERS using nanowire on gold film cavity

Chapter 3 is an adaptation of the research article " Nano Lett.,18,650-655,(2018)". The article describes the effect of plasmonic nanowire on metal film cavity in imparting directionality to molecular emission processes like surface enhanced Raman scattering and molecular fluorescence.

3.1 Introduction

Nanoscale cavities have been utilized in understanding a variety of emission processes including molecular fluorescence,[15, 64, 96–99] metal photoluminescence,[100–103] SERS,[17, 49, 50, 104, 105] etc. Very large electric field densities in such extremely small spatial dimensions have been utilized to probe strong molecule - cavity coupling,[15] detect single molecules,[49] etc. Understanding cavity mediated molecular emission processes has implications not only in fundamental physics of cavity electrodynamics [106, 107] and molecular optics [108–112], but also in emerging applications. Molecular emission processes such as molecular fluorescence and Raman scattering can be enhanced and directed into specific momentum vectors by coupling molecules to nanoscale cavities.[15, 64, 96–99]

In the past, various nano/micro cavities [106, 113, 114] have been utilized to study molecule-cavity interactions including nanoparticle over mirror,[15, 115–117] nanoparticle dimers,[47] nanowire dimers,[118, 119] nanowire-nanoparticle junction cavity,[120–122] bowtie antennas,[54], nanogrooves, [123] nanowire on metal film,[56, 57, 124] etc. Out of these configurations, single crystalline nanowire on metal film cavity provides a unique opportunity to study molecule-cavity interactions in remote excitation configuration. Since the nanowire supports propagating plasmon modes[96, 125,

[126], one can couple molecular emission to the propagating modes of the nanowire and simultaneously enhancing the molecular emission due to the presence of gap plasmons. The elongated cavities possess complex polarization structure and thus affect molecule-cavity interaction. Fourier plane analysis of such cavities can provide rich information not only about the molecule-cavity interaction, but also about the polarization and mode structure of the cavity itself.

Motivated by this, here we try to understand the momentum signatures of molecular emission (both molecular fluorescence and SERS) coupled to elongated cavities in remote excitation configuration. Relevant questions in this context are: *What will be the wavevector distribution and polarization structure of waveguided secondary emission from the molecules confined to the gap?* Answers to these questions can impact engineering molecular electronic and vibrational relaxation inside a nanocavity. In this chapter, the hybridized cavity modes and the polarization structure of the nanowire on gold film geometry in the absence of dye molecules will be discussed first and subsequently momentum distribution of molecular emission in the geometry will be elucidated.

3.2 Architecture of the system

The architecture of the system under study is as shown in figure 3.1. 170 nm thick gold film was deposited onto a glass coverslip using thermal evaporation method. Nile Blue A (10^{-6} M in ethanol) dye was drop-cast on the film, let to dry and then washed off using ethanol to remove excess molecules from the film surface. Silver nanowires were synthesized using known polyol process [127]. These wires have a pentatwinned cross-section, and are about 10 - 15 μm long and 300-400 nm thick (see inset of figure 3.1). A dilute solution of these wires in ethanol was drop-cast onto the film coated with Nile Blue A to form film coupled plasmonic nanowire (FPN) cavity, and was used for experiments after drying. The silver nanowires have a coating of polyvinylpyrrolidone (PVP) of about ~ 4 nm. When silver nanowires were placed on dye coated Au substrate, the molecules will be arrested in the cavity between PVP coated silver nanowire and Au film, with cavity thickness being ~ 4 nm.

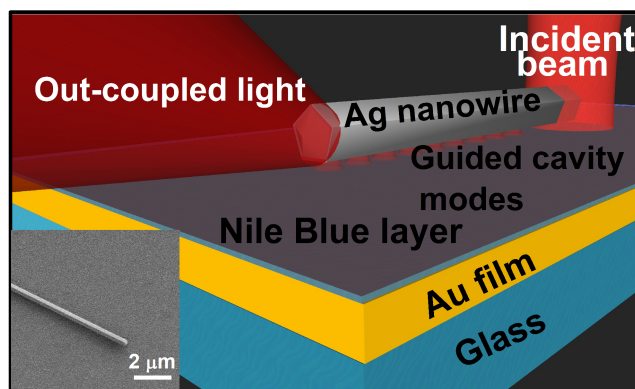


FIGURE 3.1: Schematic of an Ag nanowire (NW) coupled to a 170 nm thick Au film. The film was deposited over a glass coverslip. Nile blue (10^{-6} M) molecules were sandwiched between Ag NW and Au film. The FPN is excited at one end using a focused 633 nm He-Ne laser beam. The out-coupled light is collected from the distal end using a spatial filtering approach and then analysed for its energy and momentum states. *Inset* Scanning electron image of an individual nanowire.

Home built upright microscope was used for capturing Fourier space images and energy-momentum spectra from Ag NW-Au film system (see figure 3.2). The 633 nm He-Ne laser was expanded using lenses L1 and L2 and was focused onto one of the ends of Ag NW using 0.95NA 100X objective lens. Backscattered light was collected using the same objective lens. Lenses L3 and L4 form a telescopic arrangement, and a pinhole was placed in the conjugate image plane formed by the tube lens L3. Pinhole acts as a spatial filter and was used to filter distal end of the Ag NW spatially. Bertrand lens L4 takes the optical Fourier transform of the image formed at the image plane (created by L3), which can either be focused to EM-CCD or slit of the spectrometer depending upon the flip mirror (M2) position. Lenses L5 and L6 are focusing lenses, and are used to switch from Fourier plane to image plane which is focused on the CCD or spectrometer respectively. Energy-momentum spectra are obtained by filtering the Fourier space image using the slit (200 μm wide) of the spectrometer and then dispersing it using 1200 grooves/mm grating. Acquisition time was kept at 40 s.

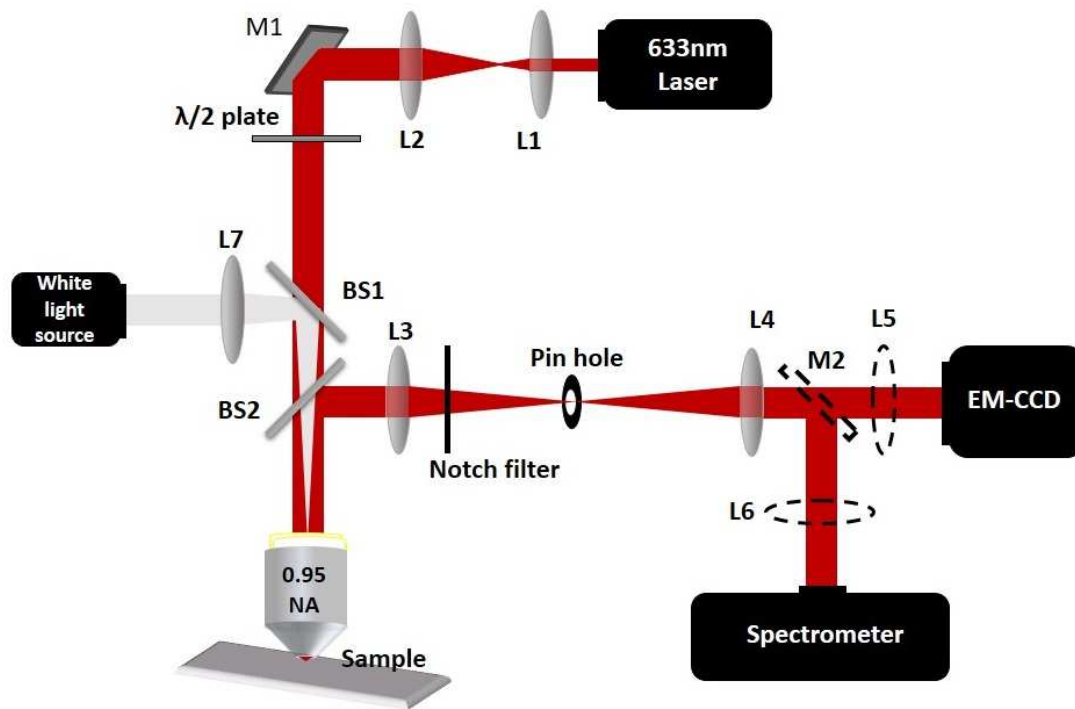


FIGURE 3.2: Schematic of the experimental setup used to probe FPN cavity

3.3 Analyzing modes and polarization of FPN cavity

Silver nanowires used in the experiments have pentagonal cross-section and have shown to support multiple propagating modes[128, 129]. When silver nanowires are placed on metallic substrate, the propagating modes hybridize[47]. To understand the modes supported by the FPN cavity, numerical simulations were performed using finite element method (FEM)¹. Ag NWs of diameter 400 nm were placed on Au film with a gap of 5 nm. The length of the wire is considered infinite to calculate the possible modes due to the pentatwin symmetry of the structure. Figure 3.3 shows the supported modes in the FPN cavity. Modes in the FPN cavity are similar to the modes in Ag NW on glass substrate case, except considerable amount of the electric field is localized in the cavity between Ag NW and Au film.

¹see appendix A for details on modes in silver nanowire and the simulation methodologies utilized here

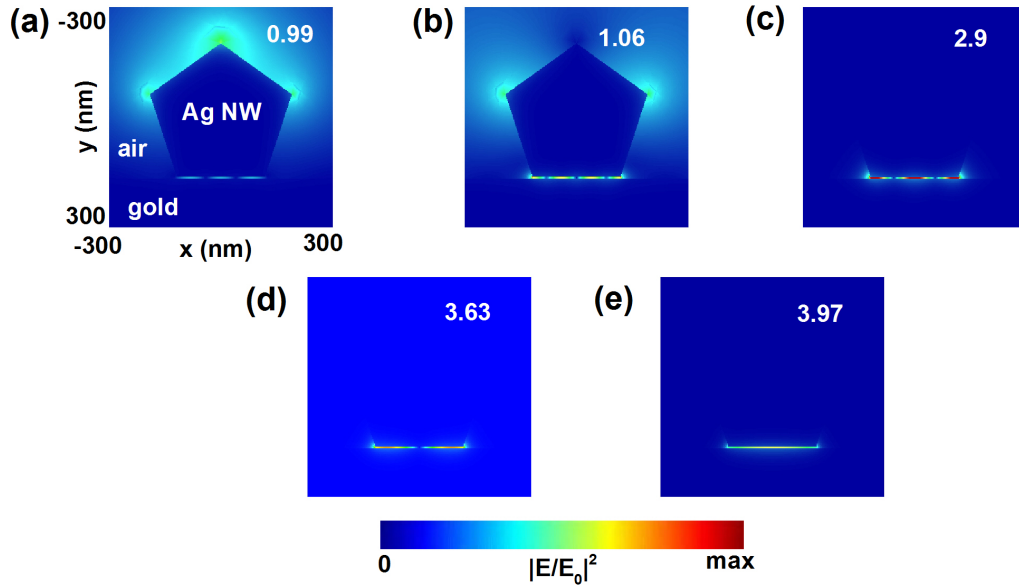


FIGURE 3.3: Modes supported by the FPN cavity. (a)-(e) show the near field electric field distributions for Ag NW on Au film system excited at 633 nm. The effective mode index is written as inset in each of the sub-figures.

To understand the polarization structure of the FPN cavity, output polarization resolved real and Fourier space measurements on Ag NW on Au film were performed and the results are as shown in figure 3.4. The Ag NW was excited using longitudinal polarization (along the axis of the NW) and the out-coupled light at the distal end was collected and analysed. Figure 3.4 (a) and (b) show the real plane image with the longitudinal and transverse output polarizations respectively. They clearly indicate that the majority of the Surface Plasmon Polaritons (SPPs) out-couple with the longitudinal polarization. Figure 3.4 (b) and (c) show the corresponding Fourier space images of the out-coupled light with longitudinal and transverse output polarizations respectively. The Fourier space image for the longitudinal output polarization is sharp and unidirectional.

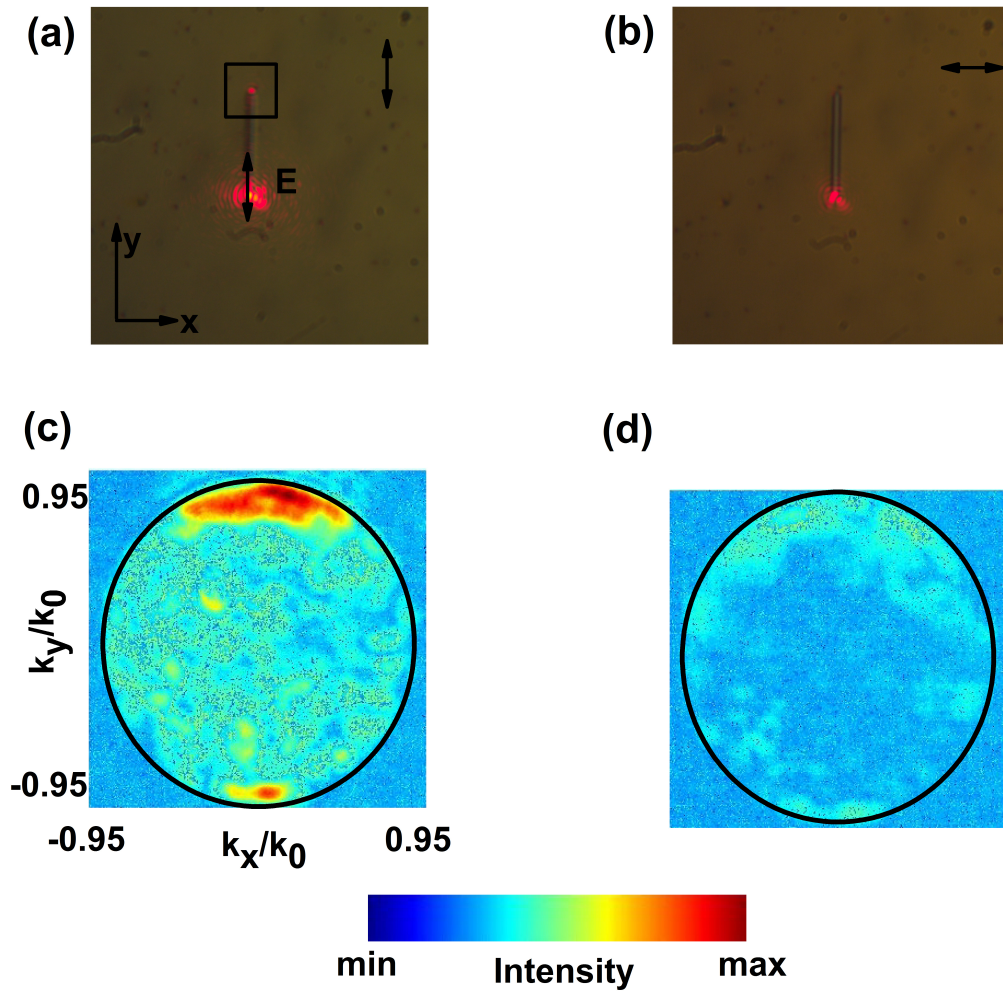


FIGURE 3.4: Output polarization resolved real plane bright-field images for the Ag NW on Au film. The wire was excited using longitudinal polarization to excite the propagating SPP modes. The output light was resolved for (a) longitudinal and (b) transverse polarizations respectively. (c) and (d) are corresponding Fourier space images.

3.4 Enhancing and directing of molecular fluorescence and SERS in FPN cavity

In the previous sections, the modal and polarization characteristics of FPN cavity in the absence of dye molecules. In the present section, the effect of FPN cavity on the molecular emission of nile blue A sye molecules will be discussed. Figure 3.5 (a) shows the optical image of a film-coupled Ag NW excited by a focused 633 nm laser light at one of the ends. The arrow mark indicates the polarization of the excitation beam. Input polarization was longitudinal and along the axis of the nanowire, which excites

a propagating mode in the FPN cavity giving maximum out-coupling at the distal end. The square region indicated at the distal end is the location from which the out-coupled emission was spatially filtered and resolved in terms of energy and in-plane momentum. Note that the location of excitation and signal collection are spatially separated.

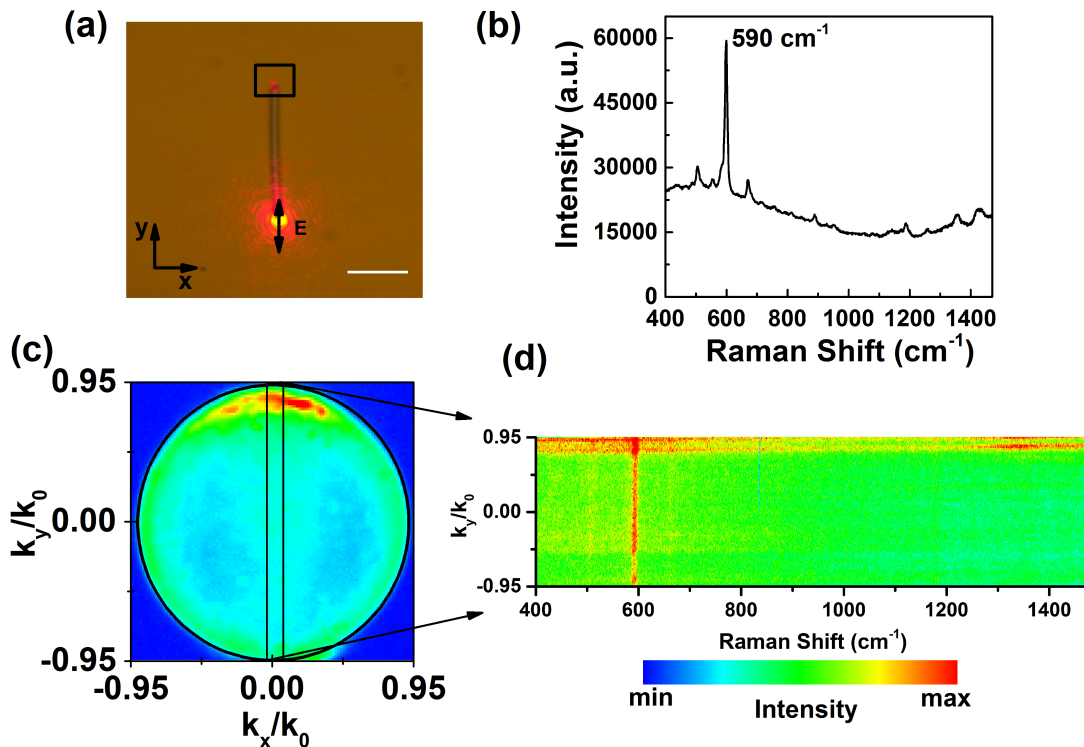


FIGURE 3.5: Fourier space imaging and E-k spectroscopy of a single Ag nanowire. (a) Bright field image of a single Ag nanowire on Au film. The incident light is polarized along the axis of the nanowire as shown. (b) Nile Blue spectrum collected from the distal end showing Raman modes overriding fluorescence. (c) Fourier space image of the out-coupled light collected from the distal end of the Ag NW–Au film system after rejecting the Rayleigh component using a notch filter, which shows that emission is biased toward higher k_y/k_0 values. Here, k_x and k_y are in-plane momentum vectors of the out-coupled light, and k_0 is wavenumber of light in vacuum. (d) A small portion of the Fourier image around $k_x/k_0 = 0$ was filtered using the slit of the spectrometer (200 μm wide) and dispersed to obtain the spectral information. The energy–momentum spectrum clearly shows the difference in momentum states of the out-coupled Raman and fluorescence photons.

In Figure 3.5 (b), the optical spectrum obtained from the spatially filtered region is shown. There are two characteristic features of the spectrum: first, a sharp line around 590 cm⁻¹ due to the Stokes Raman mode of the NB molecule. The second feature is a broad background spectrum due to fluorescence of NB molecules.

We were interested in knowing how these two spectral features distribute themselves in momentum or equivalently wavevector (k) space. To this end, we performed k -resolved optical imaging (Figure 3.5 (c)) by capturing the Fourier space image of the emitted light from the spatially filtered distal end of the geometry. An important feature of Figure 3.5 (c) was that the emission intensity was dominant at high values of k_y/k_0 . Such dominant emission can be attributed to a unidirectional antenna-like emission process,[65, 130] where the Ag NW essentially directs the light in specific angles.

Of greater interest to us was to resolve the spectrum along k_y/k_0 indicated by the rectangular region in Figure 3.5 (c). To this end, we performed energy-momentum (E - k) spectroscopy, the result of which is shown in Figure 3.5 (d). There are two interesting features of the E - k spectrum: (1) The broad fluorescence-like emission was mainly confined to high values of k_y/k_0 . (2) The sharp, 590 cm^{-1} Raman mode appears equally distributed along all values of k_y/k_0 . This data indicates that the fluorescence background and the SERS emission for the given geometry distribute themselves in different ways in the k -space.

3.5 Input and output polarization dependence of fluorescence and SERS from FPN cavity

Since the FPN cavity has strong polarization sensitivity (see section 3.3), it is imperative to study the polarization dependence of the molecular emission from the geometry. Probing polarization dependence in such systems can give important information about the molecule-cavity interaction and modes excited in the cavity.

3.5.1 Input polarization dependence

Figure 3.6 shows the effect of input polarization on the intensity of Nile blue molecular emission captured from the distal end of the nanowire. Enhancement factors of Raman and fluorescence depend on the mode generated in the wire-film system. Longitudinal input polarization (along the axis of the wire) excites long range propagating modes thus providing high enhancement factors at the distal end of the wire, which is not the case for transverse polarization (perpendicular to the axis of the wire). Observation of Raman photons even in the absence of long range SPPs (in case of transverse input polarization) can possibly be due to propagating modes generated in the cavity, which out-couple at the distal end.

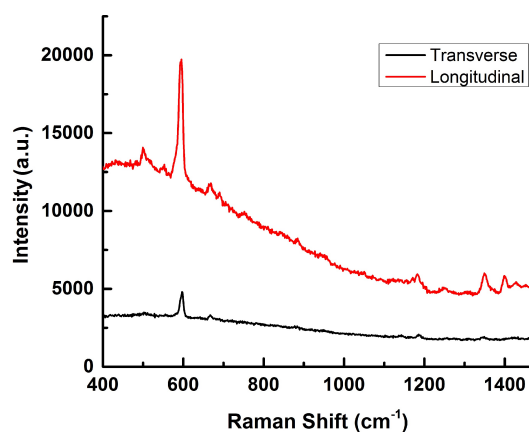


FIGURE 3.6: Input polarization dependence of spectra at the distal end of the Ag NW on Au film for Transverse and Longitudinal polarizations.

3.5.2 Output polarization dependence

Out-coupled light from the FPN cavity carries specific polarization signatures which can be probed to understand the coupling of molecules to the cavity modes. To understand the polarization dependence of the molecular emission from the FPN cavity, we resolved the out-coupled light in two orthogonal polarization components, viz., longitudinal and transverse. Figure 3.7 (a) shows the output polarization resolved spectra of the FPN system collected from the distal end of the Ag NW. To understand the emission process further, we measured output polarization resolved E-k spectra which are shown in Figure 3.7 (b),(c).

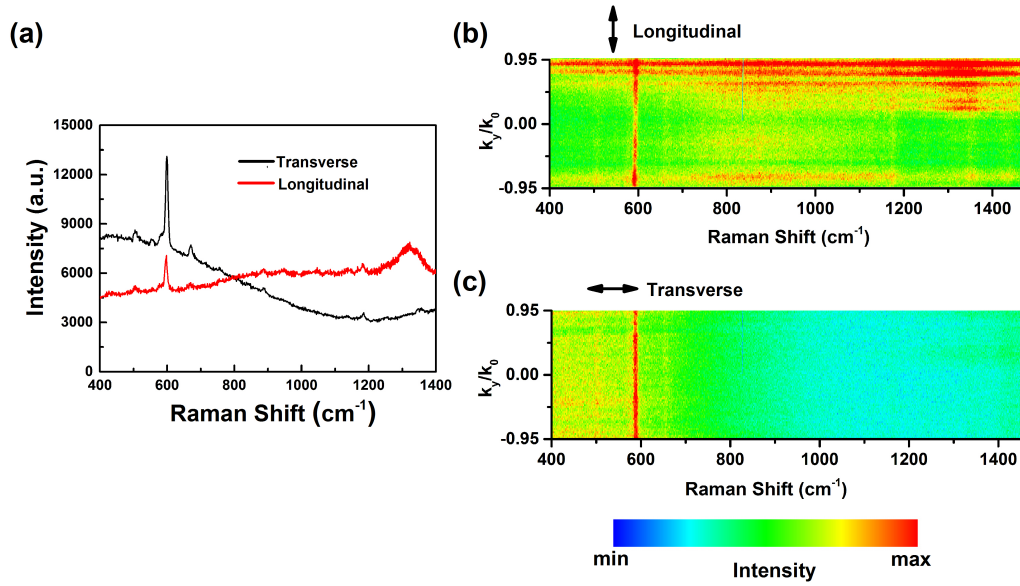


FIGURE 3.7: Output polarization resolved analysis of out-coupled light from distal end of a single Ag NW. (a) Out-coupled light from the Ag NW was resolved along (longitudinal) and perpendicular to (transverse) the nanowire. (b, c) Full energy-momentum spectra of out-coupled light from the distal end of the nanowire resolved along longitudinal and transverse directions, respectively. See text for explanation.

For the longitudinal output polarization (Figure 3.7 (b)), both the fluorescence and SERS signals directionally scatter to higher k_y/k_0 values. For transverse output polarization (Figure 3.7 (c)), both the fluorescence and SERS signals are distributed uniformly over all k_y/k_0 . To understand the polarization dependence of the molecular emission, we further analyzed the output polarization resolved spectra from FPN cavity. Figure 3.8 shows the output polarization resolved spectra collected from the distal end of the wire. The fluorescence was assumed to vary smoothly and was fit using a smoothly varying polynomial function. Intensity of fluorescence was calculated by considering the area under the curve between 400 cm^{-1} and 1100 cm^{-1} (where fluorescence counts are predominant) for both transverse and longitudinal output polarizations. The same procedure was repeated for SERS (between 580 cm^{-1} and 610 cm^{-1}). The calculations show that the ratio of SERS intensity ($\frac{(I_{Ram})_T}{(I_{Ram})_L}$) for transverse to longitudinal polarization is 2.5 times larger than that for fluorescence ($\frac{(I_{flu})_T}{(I_{flu})_L}$).

$$\frac{(I_{Ram})_T}{(I_{Ram})_L} = 2.5, \frac{(I_{flu})_T}{(I_{flu})_L} = 1.1 \quad (3.1)$$

This large transverse polarized SERS outcouples at a range of k-vectors (see figure 3.6 (c)). Fluorescence at the other hand is almost polarization independent and outcouples with both the polarizations equally.

We calculated $(\frac{I_{flu}}{I_{flu}})_T$ and $(\frac{I_{Ram}}{I_{Ram}})_T$ near 590 cm^{-1} (between 580 cm^{-1} and 610 cm^{-1}) and we find that,

$$\frac{(I_{Ram})_T}{(I_{Ram})_L} = 2.5, \frac{(I_{flu})_T}{(I_{flu})_L} = 1.5 \quad (3.2)$$

This shows that the SERS has more transverse component than fluorescence and hence it is more distributed in momentum space (Figure 3.5 (d)).

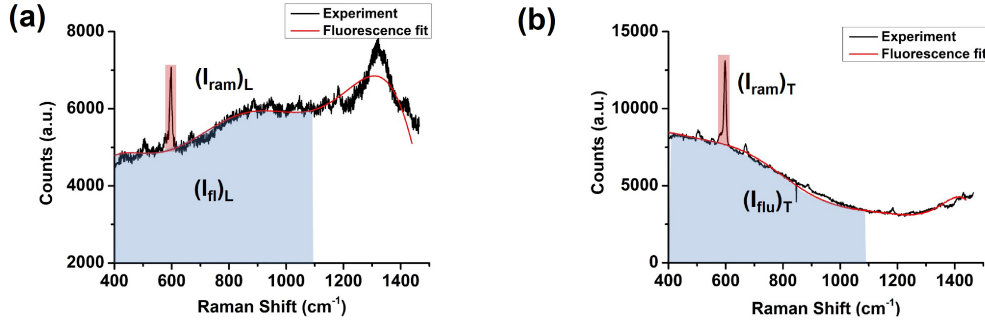


FIGURE 3.8: (a) Longitudinally polarized spectrum collected from the distal end of the wire with the fluorescence fit. (b) Transversely polarized spectrum collected from the distal end of the wire with the fluorescence fit

3.6 Dependence of cavity parameters on SERS and molecular fluorescence

In order to understand the effect of cavity parameters like presence of a spacer layer, length and width of the nanowire, we performed similar set of experiments by varying the length of the nanowire, substrate, thickness of the nanowire.

3.6.1 In the absence of the cavity

To ascertain the effect of gold substrate, we placed silver nanowire on Nile blue dye ($10^{-6} M$) coated glass substrate and excited one end of the nanowire. The distal end of the wire was spatially filtered and analyzed. Figure 3.9 (a) shows the FP image of the secondary emission from the system. The emission occupies a broad range of wavevectors unlike the FPN cavity (see figure 3.5). The spectral information from the system is shown in figure 3.9 (b). One can clearly notice the absence of Nile blue Raman mode.

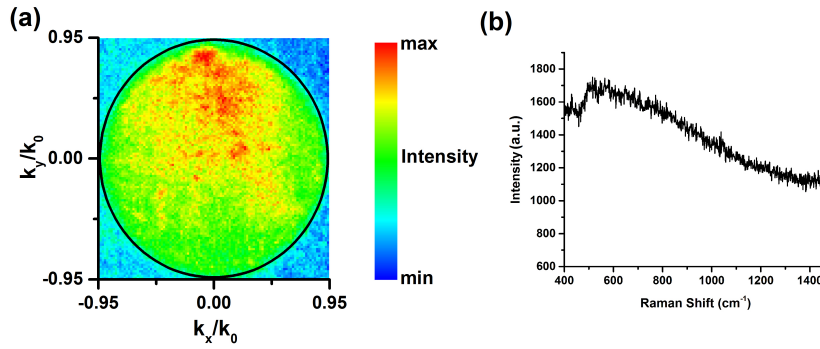


FIGURE 3.9: Characterization of Ag NW placed on Nile Blue coated glass substrate. (a) Fourier space image of the out-coupled light from the distal end. (b) Spectrum as collected at the distal end. The spectrum shows the absence of Raman modes in this configuration. Fluorescence emission from the system is greatly influenced by the excited Surface Plasmon Polariton (SPP) modes in the Ag NW and tailors the emission directionality as shown in the Fourier space image.

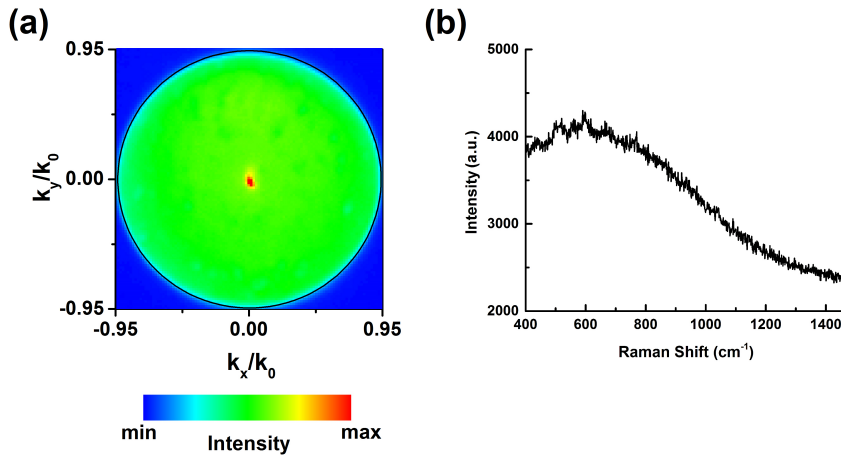


FIGURE 3.10: (a) Fourier space image and (b) Spectrum of Nile Blue on bare gold film. The spectrum shows the outcoupled light consists of fluorescent photons in dominance and is distributed uniformly in the Fourier space.

Also Nile Blue emission was collected from dye coated ($10^{-6} M$) bare gold substrate (figure 3.10). The molecular emission is largely uniform in the k -plane as shown in figure 3.10 (a). The spectrum also clearly shows the absence of the Raman mode, indicating the role of FPN cavity in obtaining both Raman scattering and fluorescence simultaneously.

3.6.2 FPN cavity with spacer layer

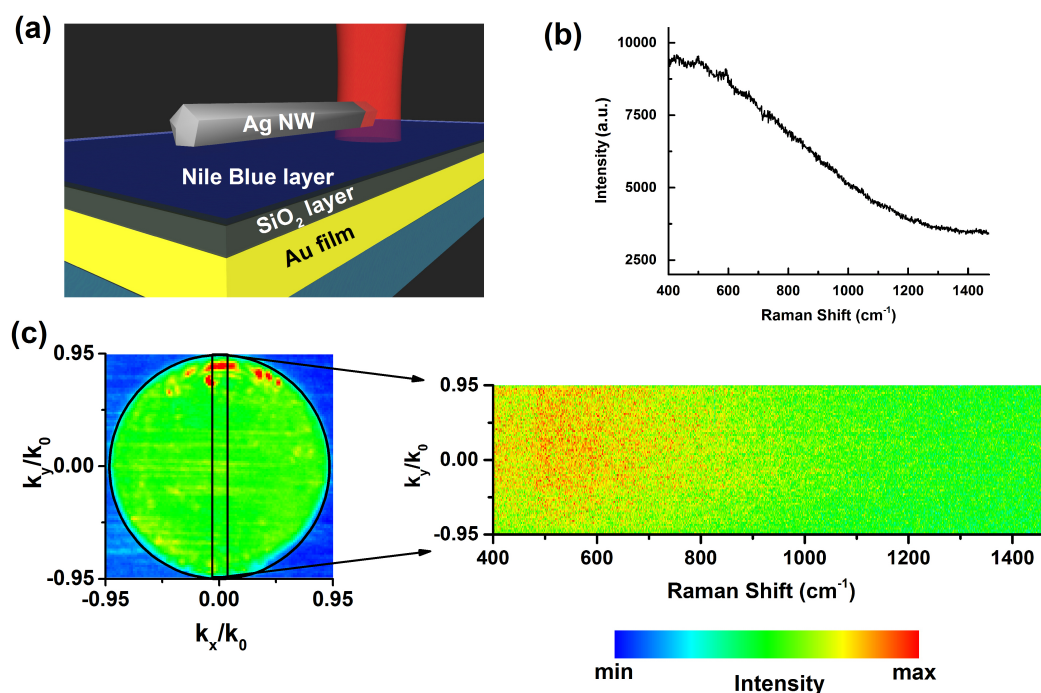


FIGURE 3.11: (a) Schematic of an Ag NW coupled to 170 nm thick Au film with a ~ 10 nm SiO₂ layer. SiO₂ was deposited using thermal vapour deposition mechanism (b) Spectrum collected at the distal end of the wire, showing the absence of Raman modes. (c) Fourier space image and energy-momentum spectrum of the out-coupled light at the distal end. The emission of fluorescence is spread of all values of k_y/k_0 , unlike the case of wire on Au film. This indicates towards the role of the film (or the gap) in directing fluorescent photons to high values of k_y/k_0 .

Cavity length in the FPN system can be altered by increasing or decreasing the distance between the bottom plane of silver nanowire and the Au film. To understand the effect of the cavity an SiO₂ layer of thickness ~ 10 nm was introduced between the Au film and the Ag nanowire. The configuration is as shown in figure 3.11 (a). Nile blue molecules were dropcasted above SiO₂ coated Au film and the silver nanowires were drop-cast over it. The distal end of the nanowire was spatially filtered and analyzed. Now, as molecules are not in the close proximity of both the film and the wire, Raman enhancement is expected to decrease.^[131] This is exactly what we observed in our experiments which is shown in figure 3.11 (b). Inclusion of a 10 nm SiO₂ spacer between the Au film and Ag NW drastically decreased the Raman enhancement, however the fluorescent signal was pronounced and easily detected. The FP image shown in figure 3.11 (c) shows that the emission (molecular fluorescence) occupies higher k_y/k_0 values,

which is also seen in E-k spectrum (figure 3.11 (d)). These results clearly demonstrate that molecules should be in the close proximity both Au film and Ag nanowire to get simultaneous SERS and molecular fluorescence signals.

3.6.3 Dependence on diameter and length of the silver nanowire

To understand the effect of thickness of nanowires on propagation, Ag NWs of three different thickness were drop-casted on the 170 nm thick Au film. All the wires were excited with the longitudinal input polarization as shown in the figure 3.12 (a). Thin wires (diameter ~ 100 nm) do not propagate when they were placed on Au film, but they do propagate when placed over glass substrate (see figure 3.12 (a) and (b)). The wires ranging from 150 nm to 400 nm propagate both on Au film and glass (see figure 3.12 (c) – (g)). This also provides a rationale to use relatively thicker wires for the remote – excitation measurements.

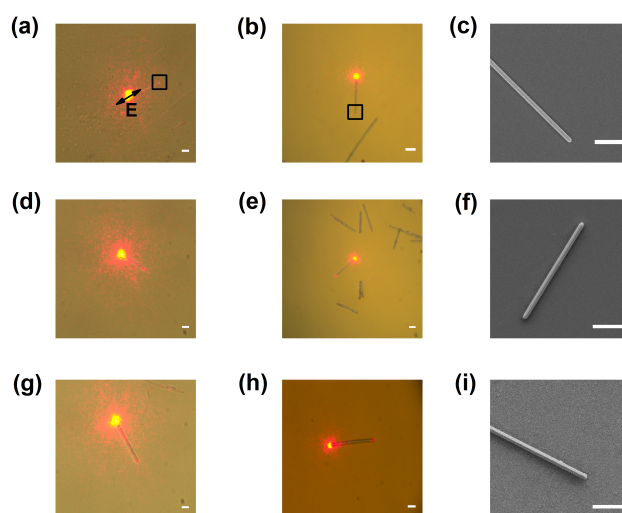


FIGURE 3.12: Propagation of light in wires of varying thickness. (a) and (b) shows the Ag wire of thickness ~ 100 nm placed on glass substrate and Au film respectively and excited with the longitudinal input polarisation. (c) is the typical SEM image. (d) and (e) shows the Ag wire of thickness ~ 200 nm placed on glass substrate and Au film respectively. (f) is the typical SEM image. (g) and (h) shows the Ag wire of thickness ~ 400 nm placed on glass substrate and Au film respectively. (i) is the typical SEM image. Scale bars are $2 \mu\text{m}$.

The propagation length of the 400 nm Ag NWs on 170 nm thick Au film was found to be $6.2 \pm 0.9 \mu\text{m}$. To calculate propagation length, 400 nm thick NWs were drop-casted on Au film and the light from distal end of an individual wire was spatially filtered and output power was measured. This was repeated for wires of different lengths.

Thus calculated propagation lengths were found to be lesser than the typical propagation length of Ag NWs of similar diameter when placed on glass substrate.[132, 133] When Ag NWs were placed on Au film, the propagation length reduces because of the change in effective refractive index and power dissipation.

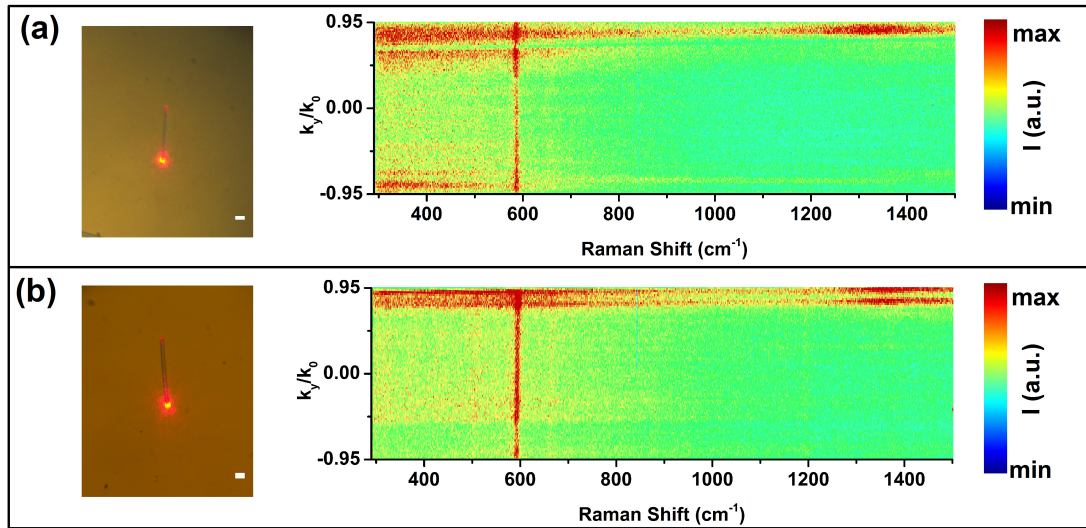


FIGURE 3.13: (a) Real plane image of the Ag NW of diameter ~ 200 nm on Au film and corresponding measured E-k spectrum from the light out-coupled from the distal end of the Ag NW. (b) Real plane image and E-k spectrum for Ag NW of diameter ~ 400 nm. Scale bar is $2 \mu\text{m}$.

To understand the dependence of diameter of the wires on the collected energy-momentum spectrum, we studied Ag NWs of diameter ~ 200 nm on Au film. The obtained energy – momentum spectrum is as shown in figure 3.13 (a). The broadband fluorescence is limited to higher k -vectors, but the k -spread of fluorescence has increased. This increase in the k -spread is a feature of thin wires.[65] As the diameter of the wire increases, the k -spread of the out-coupled light decreases as shown in figure 3.13 (b). Also there is a considerable emission at near $k_y/k_0 = -0.95$. These are representative images and we found that the measurements are repeatable over a variety of wires. This boosts the fact that the thick wires (~ 400 nm diameter) is suitable for remote-excitation SERS/SEF measurements.

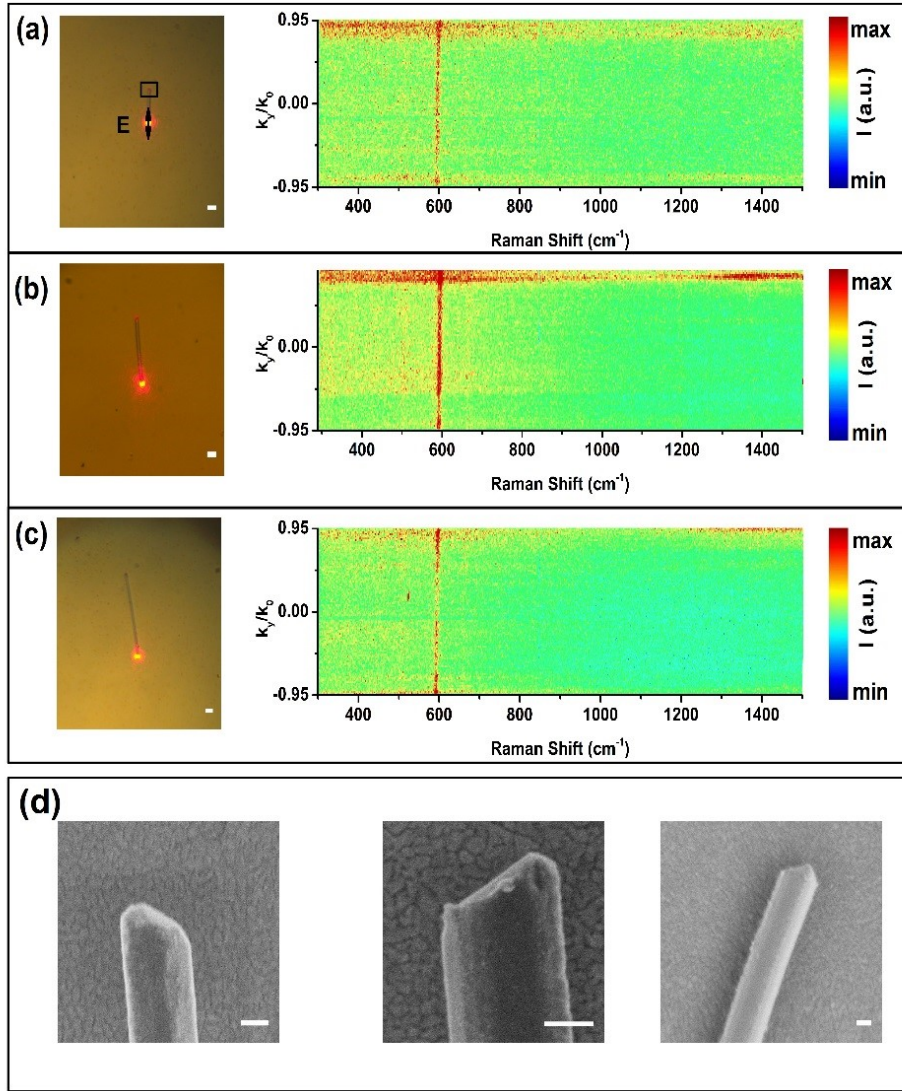


FIGURE 3.14: (a) – (c) Real plane images of the Ag NW of length 6 μm , 10 μm and 18 μm on Au film respectively and the corresponding measured E-k spectrum from the light out-coupled from the distal end. Scale bar is 2 μm . (d) SEM images of typical Ag NWs showing the end termination. Scale bar is 200 nm.

We collected energy-momentum spectra from Ag nanowires of different length on the Au film. Ag NWs from thickness varying from 6 μm to 18 μm were observed and the collected E-k spectra are shown in figure 3.14. The E-k spectra have similar features and they do not appear to change drastically with the length of the wire. Figure 3.14 (a) shows real plane image of the Ag NW of length 6 μm and its corresponding E-k spectrum respectively. The wire was excited using longitudinal input polarization. Similar measurements were performed with wires of length 10 μm and 18 μm . The results are shown in figure 3.14 (b) and (c). As the length of the wire increases, the intensity of out-coupled light reduces. This makes the E-k spectrum look hazy. These

spectra show the repeatability of the obtained results.

Since the Ag NWs are chemically prepared, and the end terminals of the wires show variations in the morphology and are shown in the figure 3.14 (d). Figures 3.14 (a) – (c) indicate that the structure of the E-k spectrum does not vary drastically, with the choice of wires (of similar diameter). This shows that the end termination of the Ag NWs have negligible effect on the structure of the E-k spectrum. The termination of the wires may affect local scattering from the end of the wire, which should be dealt in a more precise way with all its nuances and is currently explored in our laboratory.

3.6.4 In the absence of nile blue dye molecules

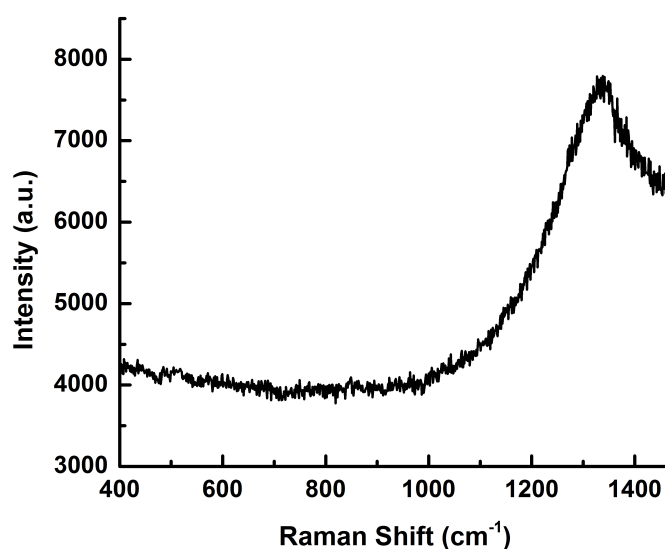


FIGURE 3.15: Spectra from the distal end of the Ag NW- Au film system in the absence of NB molecules.

To ensure that the signatures captured from the dye doped FPN cavity is indeed from nile blue molecules, we performed remote-excitation measurements on bare FPN cavity (dye absent). Figure 3.15 shows the spectrum collected from the distal end of the FPN cavity. The input polarization was maintained as longitudinal. One can clearly notice the absence of any metal photoluminescence contribution or contribution of PVP Raman scattering at the wavelength of interest (here: near 590cm^{-1}). The peak near 1300cm^{-1} is due to Raman scattering of PVP (present in the coating of silver nanowires).

3.7 FDTD simulations

To understand the origin of differential wavevector dependence of SERS and fluorescence from the FPN cavity, we performed full-wave 3D numerical simulations based on the finite-difference time-domain (FDTD) method. The Finite Differences Time Domain (FDTD) simulations were performed using Lumerical Solutions Inc. A 5000 nm length (in the y direction) silver nanowire with pentagonal cross section in the XZ plane (distance from center to a vertex is 100 nm, edge length is $2 \times 100 \times \sin(36) = 117.557$ nm), is located at $z = 4$ nm above a wide gold plate where the gold plate thickness is 170 nm (in the negative z direction) The 4nm gap and the entire silver NW are covered with SiO_2 . Fine meshes of 1 nm resolution are used to describe the gap and the bottom part of the NW. To mimic the emission from molecules throughout the cavity, broadband dipoles, with 3 different orientations, were placed in 6 different positions along the cavity separately. The outcoupled light at the distal end was collected for each instance and then summed up. Dipoles in the gap have broadband emission pattern extending well around the measurement frequencies. The fields are measured in a frequency-band corresponding to sampling every 2 nm in the wavelength.

The far field pattern is calculated using the near to far field transformation, where the near field is measured on a large plane located above the NW. The k_x - k_y far field patterns are generated by summing the intensity over all frequencies, while the Raman shift spectra is calculated by taking the middle column of the far field patterns corresponding to $k_x = 0$ from every frequency far-field pattern, and arranging them side-by-side.

To simulate the excitation of NB molecules through the propagating hybridised modes, the FPN cavity was excited by placing a y-oriented excitation dipole at one end of the wire. We found that the out-of-plane component of the electric field, E_z , is very strong throughout the cavity and enhances the excitation of z-oriented molecular dipoles (see figure 3.16).

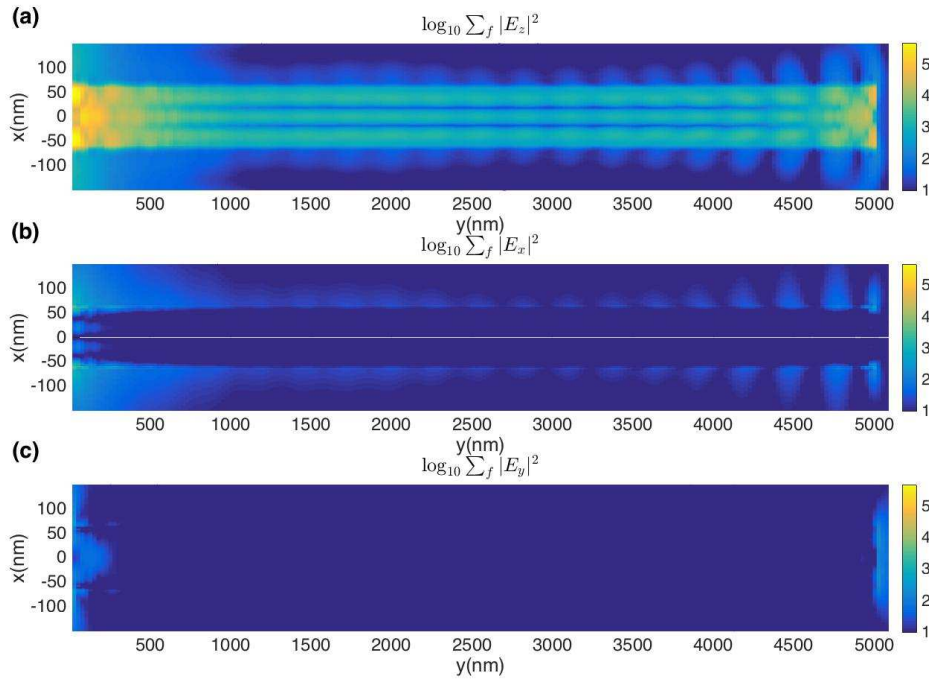


FIGURE 3.16: Calculated component-wise near field electric field map inside the cavity for (a) E_z , (b) E_x and (c) E_y . Intensity is plotted in log scale.

3.7.1 Simulation of E-k spectra based on broadband dipole placed at the location of excitation.

Also such excitation results in emission of light with large k_y/k_0 values with longitudinal output polarization (see figure 3.17).

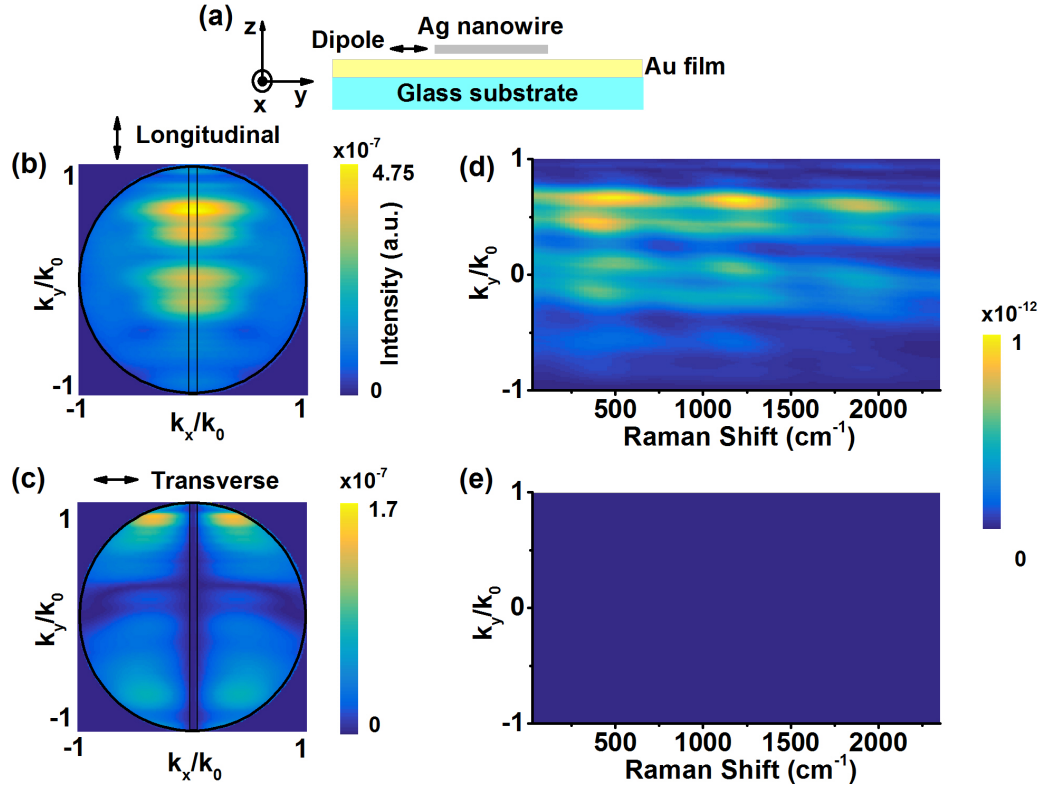


FIGURE 3.17: Numerically simulated far field image and energy-momentum spectra for two orthogonal output polarizations. (a) Schematic of the simulation geometry. The FPN was excited using a broadband dipole oriented along the axis of the wire placed at the excitation end. The light out-coupled from the distal end of the wire was filtered and projected onto the far field. (b) and (c) are output polarization resolved Fourier space images along longitudinal and transverse directions respectively. Small portion around $k_x/k_0=0$ was filtered, shown as black rectangular box, and dispersed to probe the wavelength resolution. (d) and (e) are the corresponding polarization resolved E-k spectra.

To probe the polarization signatures of such configuration, output polarization resolved Fourier plane images were calculated and are shown in figure 3.17 (a) and (b). E-k spectra were calculated by filtering the Fourier plane image around $k_x/k_0=0$ and resolving it in wavelength domain, which are shown in figure 3.17 (d) and (e). The simulated spectra in figure 3.17 (d) indicates that the out-coupled emission for longitudinal polarization is more intense at higher values of wavevectors, but does contribute at other wavevector values. The SERS and fluorescence signal that we experimentally observed in figure 3.7 (b) does have a similar behavior, except for the uniform distribution of SERS signal for all values of the filtered wavevectors. It was interesting to observe no contribution towards intensity of the simulated E-k spectrum due to transverse polarization (figure 3.17 (e)). This result is in contrast to the experimentally observed data

shown in figure 3.7, where the SERS and fluorescence signal was uniformly distributed over all the wavevectors. These results imply that molecular emission in the cavity is not completely defined by the hybridized gap mode of the system, but may also depend on other factors such as orientation and location of the broadband dipole. To capture the directionality of the SERS and fluorescence emission, we next performed a separate set of simulations by placing an x- or z-oriented dipole within the gap. The z-oriented dipoles emit with longitudinal polarisation near $k_x/k_0=0$ line (Figure 3.17). This longitudinal polarized emission is directional and couples through the same propagating modes as the excitation.

3.7.2 Effect of orientation and position of broadband dipole on E-k spectra.

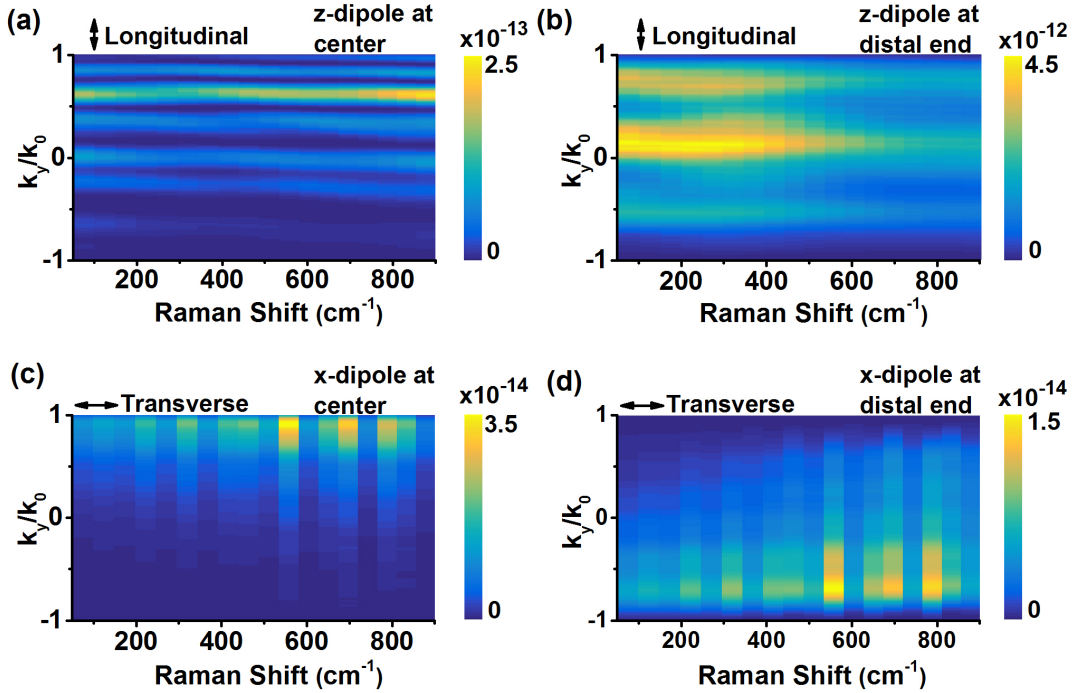


FIGURE 3.18: Output polarization resolved E-k spectra for different dipolar positions and orientations along the cavity. Longitudinally polarized energy-momentum spectra for z-oriented dipoles placed near (a) the center of the cavity and (b) distal end of the cavity. Transversely polarized energy-momentum spectra for x-oriented dipoles placed near (c) the center of the cavity and (d) distal end of the cavity.

Molecular emission collected at the distal end of the wire is a cumulative result of molecular emission throughout the cavity. The molecules are randomly orientated and can couple to any of the cavity modes in the geometry. [134] SERS and fluorescence

radiation patterns are sensitive to the orientation of the molecular dipole moments.[135] With this hindsight, we explored the dependence of polarized E-k spectra on orientation and position of broadband dipole in our geometry. We simulated individual E-k spectra for two different orientations (z and x) of dipoles placed at two different positions (center and distal end of the cavity) whose results are shown in figure 3.18. The z-oriented dipoles at center contributes towards longitudinally polarized emission mainly at higher value of wavevectors (figure 3.18 (a)), and the z-oriented dipoles at the distal end has a contribution that spans over large range of wavevectors (figure 3.18 (b)). This indicates z-oriented dipoles if present throughout the cavity, can cumulatively contribute towards emission along all k-vectors, and hence contribute towards the observed SERS emission presented in figure 3.7 (b). The x-oriented dipoles at the center contributes towards transverse polarized emission mainly at higher values of wavevectors (figure 3.18 (c)), and the x-oriented dipoles at the distal end contribute mainly towards lower value of wavevectors (figure 3.18 (d)). This further indicates that x-oriented dipole if distributed along the cavity can cumulatively contribute towards transversely polarized emission along all wavevectors.

3.7.3 Modeling molecules throughout the cavity

Further refining our argument, to account for the emission of molecules positioned throughout the gap between the nanowire and gold film, we considered broadband classical dipoles at six evenly distributed points within the gap structure with orientations along the x, y, and z directions, resulting in 18 different simulations. Here y is the longitudinal direction relative to the nanowire, and x and z are in-plane and out-of-plane transverse directions, respectively. Calculations were performed separately for each combination of orientation and dipole position, and the resulting field intensities were added together in order to mimic the incoherent emission from randomly oriented molecules in the nile blue film (see also [130]). The out-coupled light was then projected into the far-field and resolved in terms of the transverse and longitudinal polarization components.

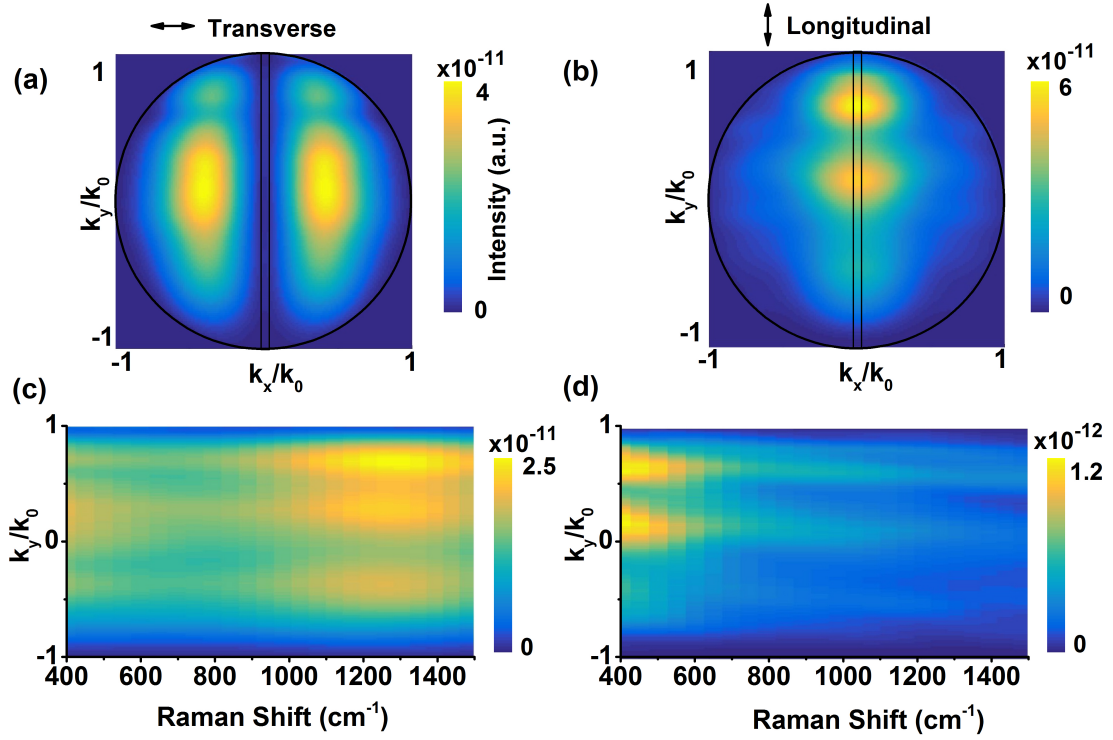


FIGURE 3.19: Numerically simulated far-field image and energy-momentum spectra for two orthogonal output polarizations. (a, b) Simulated Fourier space images for the light out-coupled from distal end of the FPN cavity for transverse and longitudinal output polarizations, respectively. Excited dipoles were placed at six different positions, with x , y , and z orientations, inside the cavity separately and the resulting field intensities were added together to mimic the incoherent emission from random oriented molecules. The out-coupled light was then analyzed for two orthogonal output polarizations. (c, d) Corresponding energy-momentum spectra.

The calculated images in figure 3.19 correspond to the far-field transverse (x) and longitudinal (y) intensities in the Fourier plane, respectively, integrated over the energy range corresponding to 350 to 1500 cm^{-1} Raman shift. It is significant that the longitudinal case, figure 3.19 (b), shows a strong degree of directional emission (much larger $k_y/k_0 > 0$ content) along $k_x/k_0 = 0$, which is qualitatively consistent with the experimental result of Figure 3.7 (c). In contrast, the transverse emission pattern appears relatively isotropic along the k_y/k_0 direction but exhibits lobes at nonzero k_x/k_0 values. This is a result of the symmetry of the coupled nanowire-gold film; transverse-polarized dipole emission is suppressed along the y - z symmetry plane. We can also consider just the $k_x/k_0 = 0$ region and plot the corresponding spectra resolved as a function of k_y/k_0 and emission frequency, i.e., no longer frequency-averaged as in figure 3.19 a,b.

Figure 3.19 c,d presents the corresponding E-k spectra for the transverse and longitudinal cases, respectively. We should note that it is not possible to achieve an E-k spectrum such as in figure 3.7 c,d with a distinct and narrow Raman emission feature using FDTD, owing to the non-quantum-mechanical nature of the calculations. Rather, these spectra should be construed as what to represent a spatially averaged out-coupling for dipole emission from within the gap. This out-coupling should be independent of the nature of the emission process, as it is simply a result of the FPN geometry, and should apply to both SERS and fluorescence. We see again in figure 3.19 c,d that the longitudinal polarization case is more directed in the far-field, whereas the transverse polarization is less so, consistent with the results of figure 3.7. This indicates that the longitudinal-polarized dipole emission couples through propagating plasmon modes within the FPN geometry, similar to what is observed in the Rayleigh scattering from samples without Nile blue (see figure 3.4).

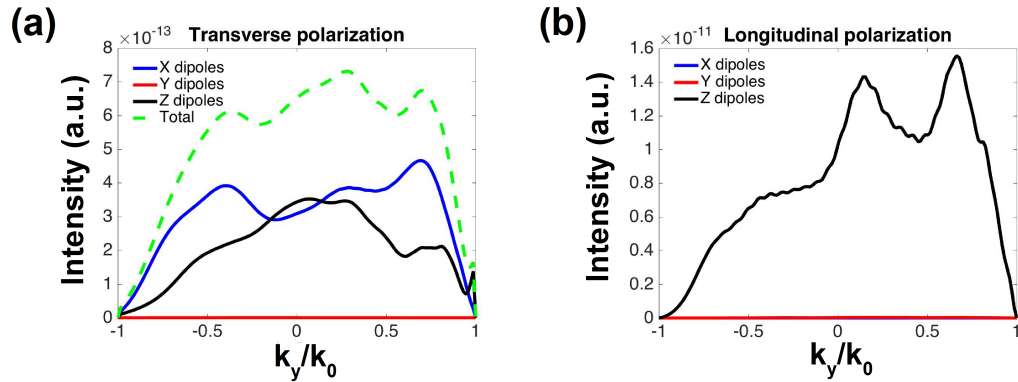


FIGURE 3.20: Variation of emission intensity as a function of k_y/k_0 for three dipolar orientations at Raman shift of 590 cm^{-1} for (a) transverse and (b) longitudinal output polarizations.

Until this point we have focused on the directionality of the emission as it relates to the far-field polarization. We now consider the relation between dipole orientation and the far-field emission pattern. Figure 3.20 shows the emission intensity as a function of k_y/k_0 for three dipole orientations taken at Raman shift of 590 cm^{-1} . In figure 3.20 (a) the transverse polarization has a broad and flat total emission pattern (green dashed curve). We can decompose this signal into contributions from dipoles with x (blue), y (red), and z (black) orientations. As might be expected, the longitudinal or y-polarized dipoles do not contribute, and both x- and z-polarized dipoles do contribute. In the case of the longitudinal polarization, figure 3.20 (b), the signal is dominated by z-oriented dipoles (black curve), with very small contribution from the x and y orientations. Thus, the far-field, longitudinal (y-polarized) signal arises almost exclusively from z-polarized

near-field dipoles in the gap. Consistent with what has been previously noted and in the experiments, the longitudinal polarization case in figure 3.20 (b) is also significantly more directional than the transverse case. As discussed previously, the longitudinal fluorescence emission appears relatively stronger, and hence more directed, than the SERS emission at 590 cm^{-1} . The ratio of the peak heights at this energy indicates that SERS is more enhanced for transverse-polarized emission than fluorescence. As the out-coupling is identical for both processes, this would imply that x-oriented dipoles are preferentially enhanced for SERS in the FPN geometry. This may explain why we observe differential wavevector distributions for fluorescence and SERS and warrants further investigation.

3.8 Limitations of the adopted procedure

The major limitation of the discussed work is that there is no control on the molecular orientation or the thickness of the sandwiched molecular film. The molecular film was prepared by dropcasting Nile blue solution in ethanol on the surface of the cleaned gold film. Thus the uniformity of the thickness of the molecular film over the surface of the substrate is not controlled. Also, the molecules orient themselves randomly. Nevertheless the arguments made in the previous sections are still valid, as the observed result is the convolution of all the orientations of the molecule. To overcome these limitations, one has to prepare a molecular film with controllable thickness and known orientation on the Au film. An easy way to achieve this is to sandwich layers of transition metal dichalcogenides (TMDs) like MoS_2 , WS_2 etc. This gives clear control over the orientation of the molecules and the thickness of the molecular layer and is currently underway.

3.9 Conclusion

To conclude this chapter, we have shown how surface-enhanced Raman scattering and fluorescence emission from molecules confined to a nanowire gap-plasmon cavity differentially distribute themselves in momentum space. This differential out-coupling has a strong dependence on emission polarization, which was revealed by energy–momentum spectroscopy experiments and numerical simulations. Our analysis not only shows the role of hybridized modes in influencing and enhancing the emission process, but also explicitly reveals an intricate connection between the out-coupled wavevectors and the orientation and location of the molecular dipole in the geometry. All these results highlight the capability of the nanowire gap-plasmon cavity to influence and discriminate

competing molecular emission processes such as Raman scattering and fluorescence, without having to utilize any time-gating techniques. It would be interesting to extend our experiments to include oriented molecular layers and two-dimensional materials such as MoS_2 , where the dipole orientation is fixed, and hence the emission processes can be precisely controlled and varied by engineering the cavity parameters. It would also be interesting to look at the strong coupling effects in the FPN cavity. These effects will be dominant when the nanowire diameter is small enough to produce a large field localization, rather than propagation of light. Such studies, if done at the single emitter limit and under controlled experimental conditions, can be potentially harnessed to explore cavity molecular quantum electrodynamics effects.

Chapter 4

Probing emission profiles from vertical organic nanowire on metal film cavity

This chapter is an adapted version of the research article "Opt. Lett. 43, 923-926 (2018)". The article reports emission directionality of a vertical organic nanowire over a metallic film in both elastic scattering and photoluminescence operational regimes.

4.1 Introduction

In the previous chapter, the effect of complex polarization structures of a nanocavity on directionality of molecular processes like SERS and fluorescence was discussed. Plasmonic nanowire on gold film was utilized as the probe system. Plasmonic nanocavities have been utilized to enhance,[55] modify,[97, 136] and direct molecular emissions[64] to specific directions. A similar system utilized to study both nano-waveguiding and cavity effects is a dielectric nano and mesowire (both inorganic and organic molecular wires).[45, 68, 137–141] Specifically organic waveguide platforms offer low losses, support exciton-polaritons¹ and can have very large propagation lengths[45] keeping the strong Fabry-Perot cavity resonances intact. This makes them an important candidate to study in the context of waveguide cavities.

Coupling organic cavities to plasmonic systems provide opportunity to study plasmon-exciton coupling in both weak and strong coupling regimes.[142–145] Such coupling schemes may be harnessed to use the properties of both plasmonic and excitonic systems. An important architecture to probe coupling of a molecular cavity to plasmonic architecture is vertical nanowire on a plasmonic film. The advantages of probing such geometry are,

- The usual coupling mechanisms for plasmonic and dielectric (organic and inorganic) cavities are done in *horizontal* geometries.[146, 147] The vertical nanowire

¹see appendix B for a brief discussion on exciton-polaritons

cavity coupled to plasmonic film can be used to probe energy transfer perpendicular to the substrate and hence can be used to understand the coupling mechanism of 2D film plasmons and 1D exciton-polaritons at a single point of contact.

- Vertical oriented nanowires have shown to possess complex polarization structures,[148, 149] near field profiles,[150], and interesting radiation patterns [68, 149, 151–154]. Studying momentum space distribution of light from metal-organic hybrid system in vertical configuration may lead to interesting observations.
- Organic nanowires can be operated in two operational regimes: (i) *Active regime*, where the emission is dominated by the Frenkel exciton-polaritons. (ii) *Passive regime*, where organic wire act as a dielectric waveguide.

Motivated by these, we probed single vertical organic nanowire made of 1,5-diaminoanthroquinone (DAAQ) grown on a thin gold film. The nanowire was probed in both active and passive operational regimes using evanescent excitation. The relevant question in this context is: "What is the momentum space distribution of the light outcoupled from a vertical organic nanowire coupled to a thin plasmonic film?" Answer to this question can provide wide view in understanding coupling mechanisms in metallo-organic hybrid cavity. We show that the organic nanowire cavity coupled to a plasmonic film shows a doughnut shaped emission profile in both passive and active operational regimes. These results can have relevance in designing subwavelength light-emitting devices,[155, 156] nano-optical sources carrying orbital angular momentum,[157–160] etc.

4.2 Preparation of organic nanowire cavity on plasmonic film

Vertical organic nanowires were prepared by physical vapor deposition methods. 30 mg of 1,5-diaminoanthroquinone (DAAQ) powder was dissolved in 200 ml of ethanol. This solution was kept in a round bottom flask. The solution was evaporated using rota-evaporator. In this process, DAAQ molecules get coated on the walls of the round bottom flask. This DAAQ coated flask is kept in a silicon oil bath at $\sim 170^\circ\text{C}$. 50 nm thick gold film was prepared using thermal vapor deposition on glass coverslip. The gold film coated coverslip was suspended in the flask in such a way that the film faces the bottom of the flask. DAAQ molecules get vaporized and nucleates over the gold film. The substrate was removed from the flask after 6 - 8 min.

4.3 1,5-diaminoanthroquinone

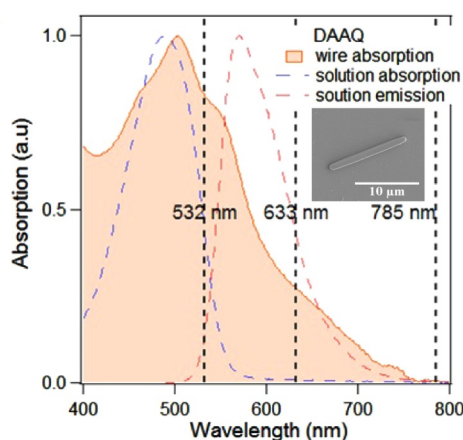


FIGURE 4.1: Absorption spectra of DAAQ solution and DAAQ wire and emission spectra of the DAAQ solution. Figure reproduced with permission from [139]

The absorption spectra of DAAQ solution and wires placed on substrate are shown in figure 4.1. The absorption spectrum of the DAAQ wires is red shifted with respect to the molecular absorption of DAAQ. This is due to aggregation of the molecules into the crystal. The absorption maximum of DAAQ is around 500 nm. If one excites the nanowire around the absorption maximum (532 nm laser), one can excite Frenkel exciton-polaritons in the nanowire. [45, 139] In this case, the exciton-polaritons out-couple at the distal end as photoluminescence, hence the wavelength of the outcoupled light is red shifted compared to the excitation wavelength ($\lambda_{out} > \lambda_{in}$). This operational regime is called active regime. If one excites the wire off-resonance (633 nm), the wire behaves as a dielectric waveguide. Now, $\lambda_{out} = \lambda_{in}$ and this operational regime is called passive regime. This operational regime tunability makes organic nanowire distinct from its plasmonic counterpart.[148, 161, 162]

4.4 Probing individual vertical nanowire on thin plasmonic film

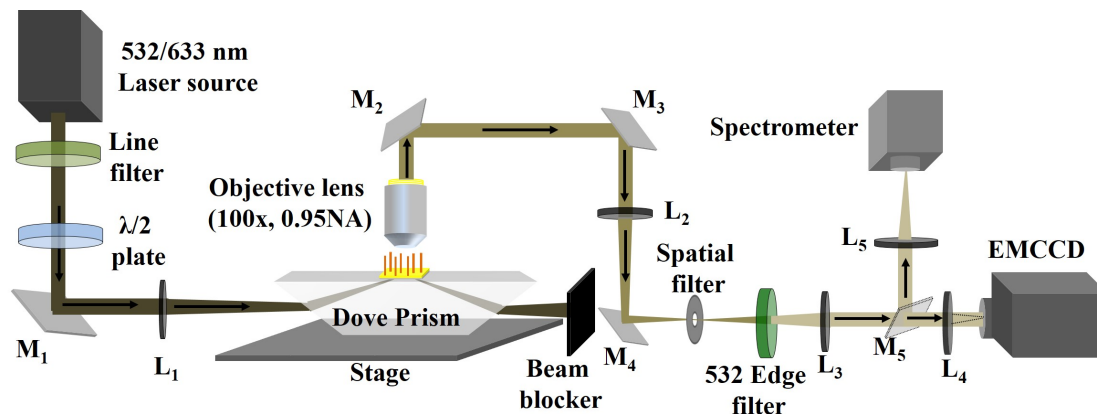


FIGURE 4.2: Schematic of the home built optical setup used to probe individual organic nanowire on thin plasmonic film

The optical setup used to probe individual organic nanowire on plasmonic film is shown in figure 4.2. The plasmonic film on which organic nanowire was grown was coupled to a dove prism using index matching oil. Individual nanowires were excited using evanescent excitation geometry. To ensure the single wavelength excitation, we introduced a laser line filter in the excitation path (for both 532 nm and 633 nm excitation). Incident beam polarization was varied by using a $\lambda/2$ plate in the excitation path. The outcoupled light from a single vertical organic nanowire was captured using a high NA (100x, 0.95) objective lens using a spatial filter placed in the conjugate image plane and routed to engaged EMCCD/spectrometer by utilizing 4- f configuration. 4- f transformation was performed using the lens combination of L_2 and L_3 . Real plane imaging was performed by introducing flippable lens L_4 . The spectral signature of emission was recorded by routing the captured light toward the spectrometer using flippable mirror M_5 . For the photoluminescence microscopy, elastically scattered light was rejected by introducing a 532 nm edge filter. With 633 nm laser excitation, the outcoupled light is dominated by elastic scattering with practically no contribution from photoluminescence.

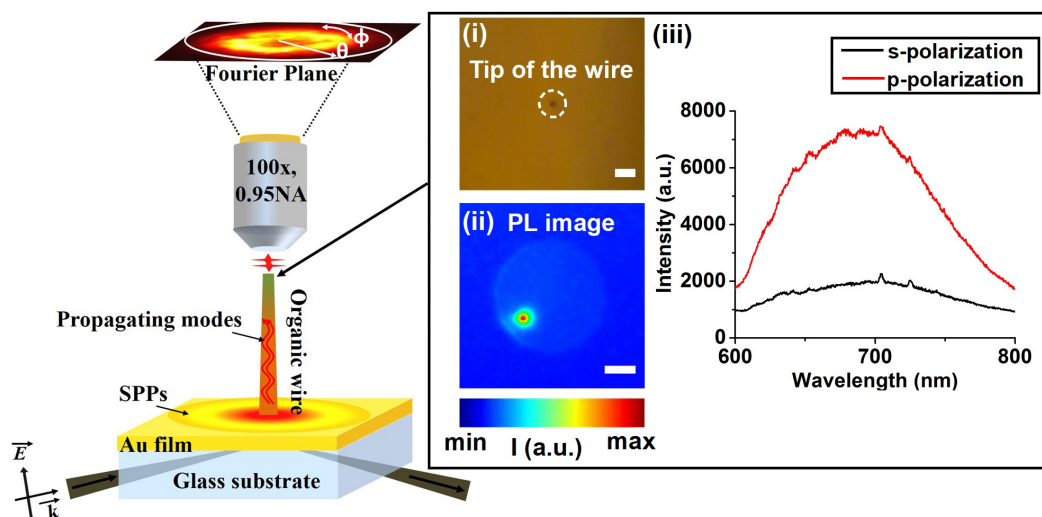


FIGURE 4.3: (a) Conceptual schematic of plasmonic (Au) film coupled single, vertical organic (DAAQ) nanowire. Surface plasmon polaritons (SPPs) in Au-film (thickness $\sim$ 50 nm) were generated using evanescent excitation with 532 nm / 633 nm laser beam. This field facilitates the excitation of the propagating modes in the organic nanowire, which outcouple at the distal end of the wire. By changing the excitation wavelength from 532 nm to 633 nm, we switch between active and passive operating regimes of the nanowire. The light from the distal end was collected and projected into the Fourier plane and analyzed. Figure not to scale. *Insets* : (i) Real plane brightfield image of the tip of the organic nanowire. (ii) Real plane photoluminescence image captured by focusing the tip of the nanowire. (iii) Photoluminescence spectra collected from an individual organic nanowire for different input polarizations. Scale bars are $2\mu\text{m}$.

Figure 4.3 (a) shows the conceptual schematic of the experiment. Surface plasmons in the film can be efficiently excited using evanescent excitation, which in turn couples the energy to the vertical wire by exciting propagating modes. The coupled light travels through the length of the wire and outcouples radiatively. Insets (i) and (ii) of figure 4.3 show real plane brightfield and photoluminescence images captured by focusing the tip of an individual organic nanowire. Photoluminescence spectral information collected from the vertical nanowire shows very strong input polarization dependence as shown in inset (iii) of Fig. 1(a). When the input was *p*-polarized, we get considerably more photoluminescence compared to *s*-polarized input. Passive emission also shows strong elastic scattering for *p*-polarization (data not shown here). This was mainly due to the fact that the efficiency of excitation of surface plasmons on the film is large for *p*-polarized light. This in turn couples to the propagating mode of the wire, hence showing pronounced emission. This makes the vertical nanowires act as an input polarization sensitive switch.

4.5 Fourier plane imaging of an individual vertical organic nanowire

Given these facts, an important question in this context is what is the wavevector distribution of outcoupled radiation in both active and passive regime, for plasmon coupled organic hybrid system? To answer this, we performed Fourier plane (FP) microscopy on individual vertical nanowire coupled to Au thin film. The excitation wavelength was chosen corresponding to the operational regimes: 532 nm for active regime (exciting near absorption maximum, as the absorption maximum of DAAQ wires is around 520 nm [139]), to probe photoluminescence and 633 nm for passive regime (exciting away from absorption maximum [139]), to probe elastic scattering. The light outcoupled from a single vertical wire was collected using an high numerical aperture objective lens and projected into the Fourier plane.

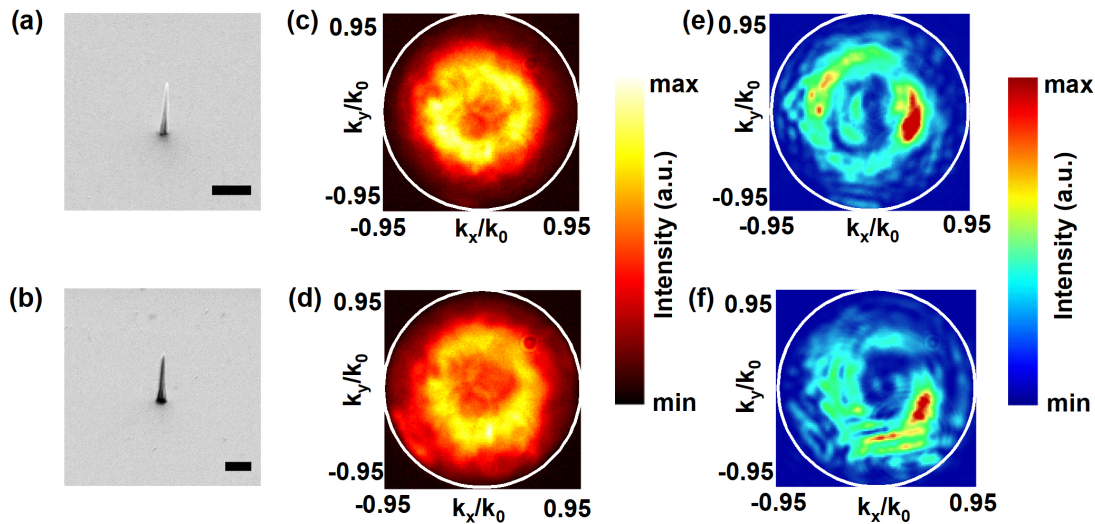


FIGURE 4.4: (a) and (b) are representative scanning electron micrographs showing vertical nature of the organic nanowires with respect to the substrate. Scale bar is $2\ \mu\text{m}$. The wires are typically $2\text{-}3\ \mu\text{m}$ in length and the radius at the tip is $\sim 200\ \text{nm}$. (c) and (d) are photoluminescence Fourier plane images captured from two individual nanowires showing doughnut emission pattern. (e) and (f) are corresponding elastic scattering Fourier plane images.

Figure 4.4 (a) and (b) show the representative SEM images of the vertical organic nanowires on Au film. They clearly indicate that the wires are grown vertically over the substrate. The typical length of the wire was $\sim 2\text{-}3\ \mu\text{m}$. The base radius of the wire was $\sim 300\ \text{nm}$ and that of the tip was $\sim 100\ \text{nm}$, thus making the wire a continuous taper.

Equipped with this, we collected the outcoupled light from an individual organic wire and projected it into the Fourier plane. The vertical nanowires on thin Au film were excited using *p*- polarized laser beam through evanescent excitation. We performed measurements with 532 nm and 633 nm laser separately on the same nanowire to probe photoluminescence and elastic scattering FP images. Figure 4.4 (a) and (b) show the measured photoluminescence FP images from two individual nanowires. We can see clear doughnut like pattern in both the images. This emission pattern is repeatable, as long as wires are vertical to the substrate and the images shown here are representative in nature. Further we measured elastic scattering FP images by same wires by exciting them using 633 nm laser beam. Figures 4.4 (c) and (d) show the corresponding FP images. It is interesting to note that the elastic scattering FP images are qualitatively similar to the corresponding photoluminescence FP images. Due to spurious scattering from the substrate, the elastic scattering FP image has irregular speckles. But the overall feature of doughnut is clearly visible.

Doughnut type emissions are seen typically in dipole over mirror configurations[72, 163, 164], which is further affected by the presence of an organic semiconductor medium, here. The nanowire acts as a waveguide for the propagating modes of the organic wire. The free end of the nanowire now acts as an effective radiating dipole oriented along the z -axis and outcouples the guided modes.

4.6 Numerical simulations

To understand the emission process further, we performed finite element method (FEM) based full-wave numerical simulation using COMSOL software (version 5.1). Near field to far field transformation were carried out using reciprocity arguments [95]. Nanowire geometry was taken as a tapered cone with dimensions derived from SEM images, mimicking the realistic situation. DAAQ wires were modelled using lorentzian oscillator model and wavelength dependent refractive indices were taken from [139, 165] and that of gold from [90]. The radius of the base of the wire was taken to be of 300 nm and that of the tip to be 100 nm, thus making the wire to have a continuous taper. The wire was placed on a 50 nm gold film over the glass substrate. To simulate the photoluminescence emission from vertical nanowires, vertical dipole source oscillating at 700 nm (wavelength at which photoluminescence emission is maximum) was placed inside the nanowire at nanowire - Au film interface [68, 166]. The simulation region was terminated by scattering boundary conditions to avoid spurious reflections. The system was

meshed using free tetrahedral mesh with maximum element size of 20 nm to ensure accuracy. The light out coupled from the nanowire was collected and projected to the far field. To model elastic scattering from vertical nanowires, the vertical dipole oscillating at 633 nm was placed at the gold - glass interface right below the nanowire [167]. The oscillating dipole excites the propagating plasmons in the film, which in turn excites the wire. The light outcoupled from the wire was collected and projected to the far field.

4.7 Quantifying Fourier plane images

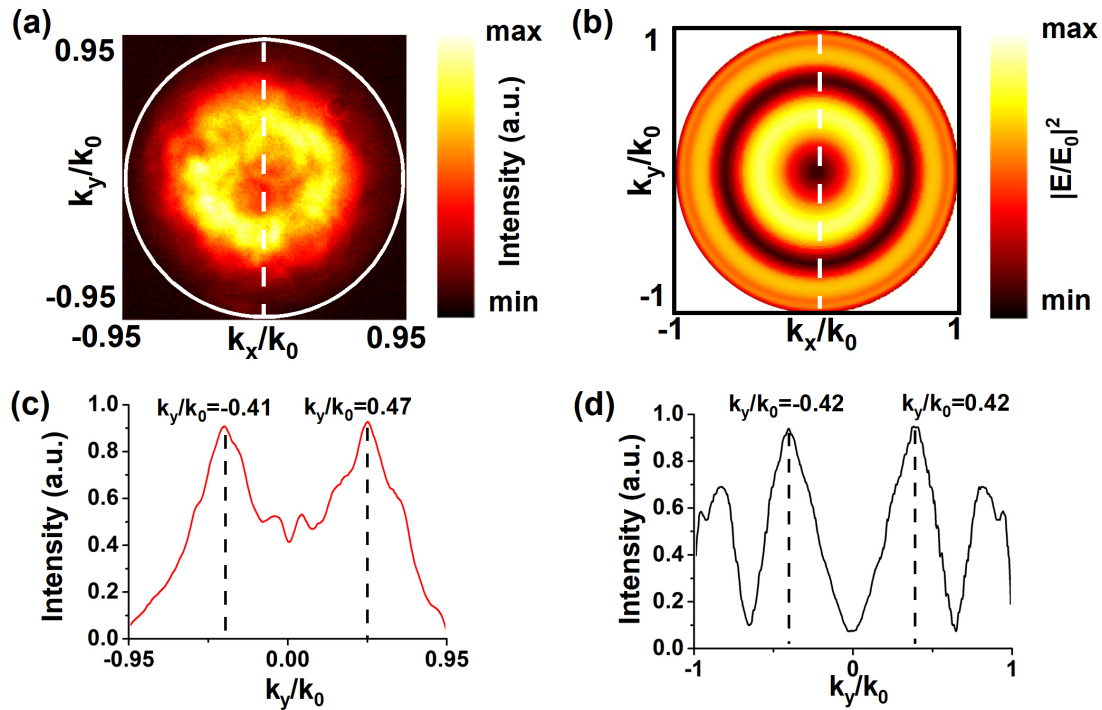


FIGURE 4.5: (a) Measured Photoluminescence Fourier plane image captured from an individual vertical organic nanowire, showing doughnut typed emission. (b) Simulated photoluminescence Fourier plane image captured from individual vertical organic nanowire at 700 nm wavelength. (c) and (d) are intensity profiles along the dashed line shown in Fourier plane images.

Figure 4.5 (a) and (b) show the measured and simulated photoluminescence FP images respectively. The simulated FP image is similar to the measured FP pattern. To further quantify the emission, we further plot the intensity profiles of the emission along the dashed line for $k_x=0$ (figure 4.5 (a) and (b)) and are shown in figure 4.5 (c) and (d) respectively. The emission is maximum near $k_y/k_0=-0.41$ and 0.47 for measured

photoluminescence emission. Also emission occurs at $k_x/k_0 = -0.44$ and 0.42 (graph not shown). For the simulated FP image, emission occurs at $k/k_0 = \pm 0.42$, which is in good agreement with the measured photoluminescence angular emission values.

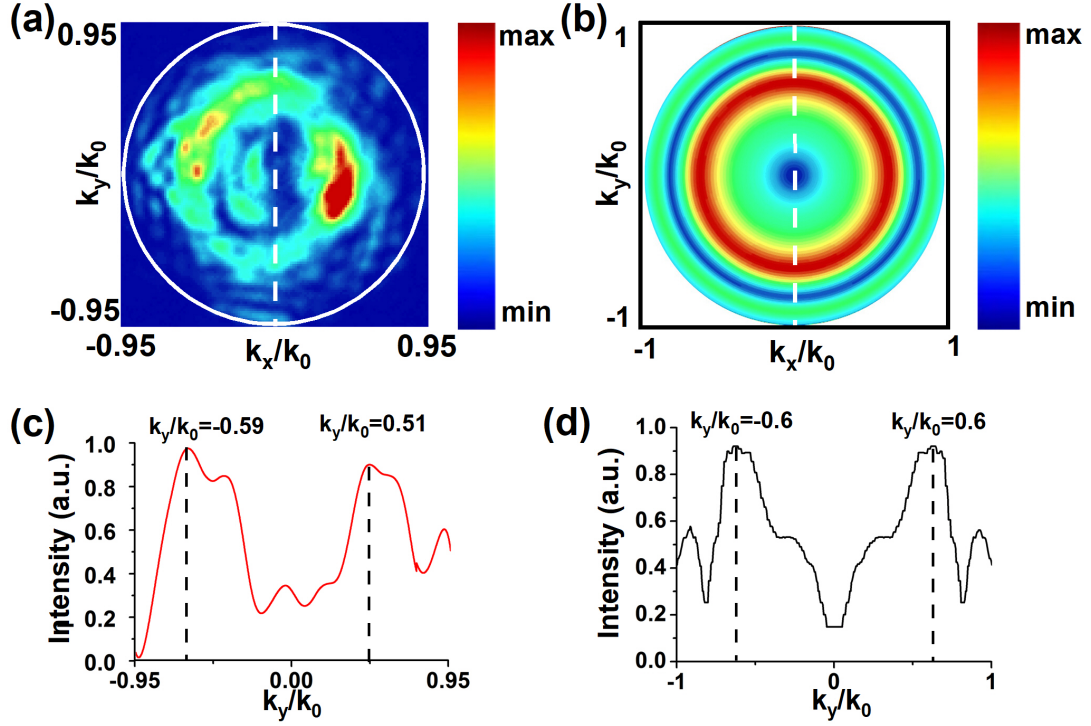


FIGURE 4.6: (a) Measured elastic scattering Fourier plane image captured from an individual vertical organic nanowire, showing doughnut typed emission. (b) Simulated elastic scattering Fourier plane image captured from individual vertical organic nanowire at 633 nm wavelength. (c) and (d) are intensity profiles along the dashed line shown in Fourier plane images.

Figure 4.6 (a) and (b) show measured and simulated elastic scattering FP images respectively. The angle of scattering were calculated by plotting the intensity profiles along the dashed line in figure 4.6 (a) and (b). Experimentally measured FP image shows that the k -vectors of scattering are $k_y/k_0 = -0.59$ and 0.51 . Also emission occurs at $k_x/k_0 = -0.54$ and 0.46 (graph not shown). For simulation FP images, maximum elastic scattering happens at $k/k_0 = \pm 0.62$ which is similar to the values observed in the measurements. So qualitatively photoluminescence and elastic scattering FP images show similar FP images with slightly different emission angles, which warrants further investigation. The FP images show a slight asymmetry which may be due a small tilt in the vertical nanowire with respect to the normal to the substrate.

By measuring the wavevector distribution of multiple vertical nanowires, we calculated the average emission vectors k_x/k_0 and k_y/k_0 for both photoluminescence and elastic scattering. For photoluminescence average value of emission wavevector was $k_x/k_0 = -0.425 \pm 0.02$; 0.435 ± 0.01 and $k_y/k_0 = -0.423 \pm 0.03$; 0.435 ± 0.01 . For elastic scattering it was $k_x/k_0 = -0.482 \pm 0.06$; 0.5 ± 0.04 and $k_y/k_0 = -0.53 \pm 0.08$; 0.56 ± 0.02 . The values are similar to that observed in the numerical simulations.

4.8 Further questions

The chapter addressed wavevector distribution of the outcoupled light from an individual vertical organic nanowire grown on plasmonic thin film in both elastic and inelastic operational regimes. The system can be easily extrapolated to study the effects of array of such structures on wavevector distributions by growing such wires on patterned metallic films. This will give an opportunity to study the interaction of lattice plasmon modes and the exciton-polaritons, which may give rise to interesting effects. Also, this study can be extended to study the effect of spin locking and adiabatic nanofocusing which have been studied in plasmonic nanotapers.

4.9 Conclusions

To conclude, we experimentally and numerically demonstrate doughnut shaped emission from a single vertical organic nanowire excited via surface plasmons. We studied Au film coupled vertical organic nanowires in both active and passive operational regimes and corroborated our experimental observations with numerical simulations. We anticipate that the obtained results can have implications in realizing efficient light sources carrying orbital angular momentum. These organic wires can be driven to get doughnut pattern in both coherent scattering and incoherent emission regimes. Hence, it provides unique opportunity to devise nano optical sources which can carry angular momentum states in two different operational regimes. Simultaneously, the same system can be further extrapolated to probe the quantum (weak or strong) spin-orbit coupling effects in plasmon - organic hybrid system.

Chapter 5

Metallo-dielectric microsphere antennas: guiding molecular fluorescence

This chapter is an adapted version of the research article " Adv. Opt. Mater., 2018, 1801025." The article explores the effect of metal film based microsphere cavity on the polarization signatures of molecular fluorescence from the hybrid-cavity.

5.1 Introduction

Till now, the discussion was mainly on gold film based elongated cavities. The momentum space distribution of molecular fluorescence and SERS coupled to plasmonic nanowire based cavity (chapter 3) and elastic scattering and photoluminescence from vertical organic nanowire cavity on metal film (chapter 4) was elucidated. They exhibit strong localization of electromagnetic fields, support multiple cavity modes, etc but without large Q-factors. On the other hand dielectric microsphere based cavities have shown to support morphology dependent resonances called whispering gallery modes (WGMs) with large Q-factors. [37, 168, 169] They have also been used in the context of probing molecule-cavity interaction.[11, 170, 171]

By combining plasmonic and dielectric structures, hybrid metallo-dielectric cavities have also been realized.[172–174] Hybrid plasmonic–photonic cavities have shown to manipulate morphology-dependent resonances,[175, 176] engineer light–matter interactions,[177, 178] detect molecules,[179] etc. In an essence, such hybrid cavities can potentially bring together the ‘best of both worlds’, and there is an imperative to study them in detail, especially in the context of understanding how molecules emit in such cavities. Specifically, interesting questions arise, such as: how is the fluorescence of molecule influenced in such hybrid cavities? What is the spectral, wavevector

and polarization features of far-field molecular fluorescence in such cavities? Addressing them can lead to some unexpected insights into molecule-cavity interaction, and can potentially lead to some important applications including novel, orbital angular momentum-carrying molecular light sources and chiro-optical sensors.

An important aspect of microsphere based cavity is that WGMs are very sensitive to the morphology of the structure and can be split by perturbing the morphology. Strong coupling of the microsphere modes can be easily achieved by placing two microsphere side-by-side.[180, 181] The WGMs of the microsphere strongly interact and hence split into bonding and anti-bonding modes. Strong coupling in microresonators has also been studied in semiconductor microdiscs, [182, 183] microspheres, [184, 185] epitaxial heterostructures, [186] etc. One way to create strongly coupled microresonator system is to utilize sphere-image sphere interaction by placing microsphere on a metallic mirror. This configuration has been utilized with metal/dielectric nanoparticles and nanowires in various prospects, [15, 70, 174, 187, 188] but has not been studied extensively in understanding polarization structure of strong coupling physics. This configuration is advantageous over in-plane coupling of microspheres as the size mismatch problem between microspheres is solved.

Motivated by these issues, herein we report our experimental studies on in-plane momentum and polarization-resolved fluorescence emission from dye molecules in microsphere coupled to a gold mirror[189, 190] One of the important findings from our study is that the far-field fluorescence emission. from the cavity is vectorial in nature. That is, the far-field fluorescence spectra have strong polarization dependence with respect to radial and azimuthal co-ordinates in the emission profile.

5.2 Architecture of the system

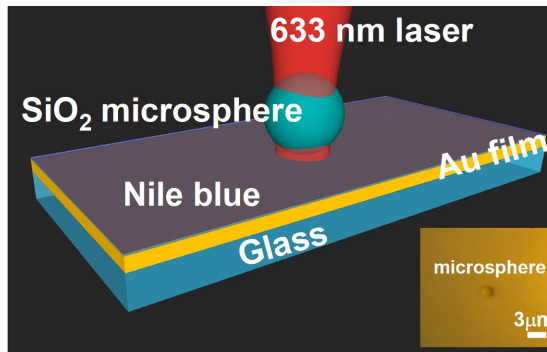


FIGURE 5.1: (a) Conceptual schematic of metal film coupled SiO_2 micro-resonator system. The SiO_2 microsphere of diameter $3\ \mu\text{m}$, placed on 100 nm thick Au film was excited using a high numerical aperture objective lens. Nile Blue molecules were sandwiched between microsphere and Au film. *Inset*: Real plane bright-field image of an individual microsphere on gold film.

Figure 5.1 (a) shows the schematic of the experiment. A gold film of 100 nm thickness was deposited using thermal vapour deposition method on glass coverslip. Nile blue (NB) molecules (10^{-4}M) were dropcasted on the metal film and allowed to dry to form a thin molecular film. The number of molecular layers in the focal volume is more than one for this concentration and hence the molecular fluorescence from the layers not in contact with the metal film will be screened and not quenched strongly. SiO_2 microspheres of diameter $\sim 3\ \mu\text{m}$ (with 5% variation in diameter) were dropcasted over it. This experimental configuration is an important one as this can be easily extrapolated to study molecular emissions coupled to the WGMs of the structure both in the reflection geometry and transmission geometry. An individual microsphere was excited by focusing 633 nm laser beam using high numerical aperture objective lens. Microsphere acts as a micro-lens and focusses the incoming laser to a very small region through photonic nanojet effect.[191, 192] This creates large electric field at the junction of the microsphere and the metal film. NB molecular fluorescence was enhanced due to this strong localization of the electric field. The generated molecular fluorescence couples to WGMs of the microsphere and emits in specific directions. Inset of figure 5.1 shows the brightfield optical image of microsphere on thin Au film. Individual microspheres were excited using 100x, 0.95 NA air immersion objective lens and the backscattered light was collected from the same objective lens. The collected light was projected onto the Fourier plane and then analyzed for spectroscopic information (see section 3.2 for the experimental setup to probe spectroscopic and Fourier plane information).

5.3 Splitting of WGMs in metal film coupled microsphere system

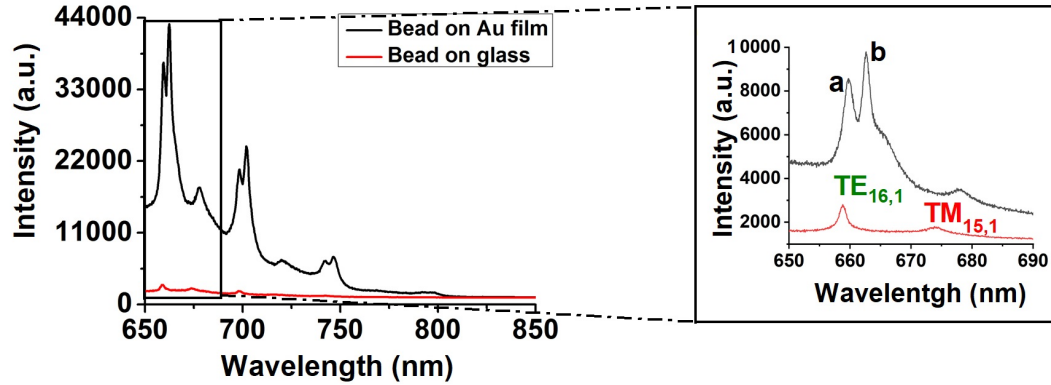


FIGURE 5.2: Nile Blue fluorescence spectra collected by exciting an individual microsphere placed on Au film and glass substrate separately. *Inset*: Molecular fluorescence spectrum collected by exciting single microsphere placed on glass substrate and Au mirror captured at higher resolution (1200 grooves/mm). The mode numbers were assigned using analytical theory for single isolated microsphere. The red curve indicates the molecular fluorescence captured by placing microsphere on glass substrate and the black one indicates that on Au film.

The NB fluorescence spectrum collected from individual SiO_2 microsphere is shown in figure 5.2. One can clearly see the enhancement of WGM coupled NB fluorescence from the microsphere coupled Au film when compared to that on the glass substrate ($I_{\text{gold}}/I_{\text{glass}} \sim 5$ with Q of individual split mode ~ 300). This is essentially due to the very high electric field generated at the metal-microsphere interface which enhances the WGM coupled molecular fluorescence. Also the WGMs in the molecular fluorescence show clear splitting when the microsphere is coupled to Au film, [193] as shown in the inset of figure 5.2 (energy of splitting: 8.27 meV).

5.3.1 Coupling molecular fluorescence to WGMs

To understand the effect of the coupling of microsphere to Au film, we performed finite element method (FEM) based numerical simulations using COMSOL 5.2 software. The diameter of the microsphere was fixed at $3 \mu\text{m}$ and was placed on a 100 nm Au film. The simulation area was meshed using free tetrahedral mesh and was terminated using perfectly matched layers (PMLs) to minimize spurious reflections from the boundaries. Wavelength dependent refractive index of gold was taken from [90]. The microsphere was excited using dipole source placed at the substrate – microsphere interface.

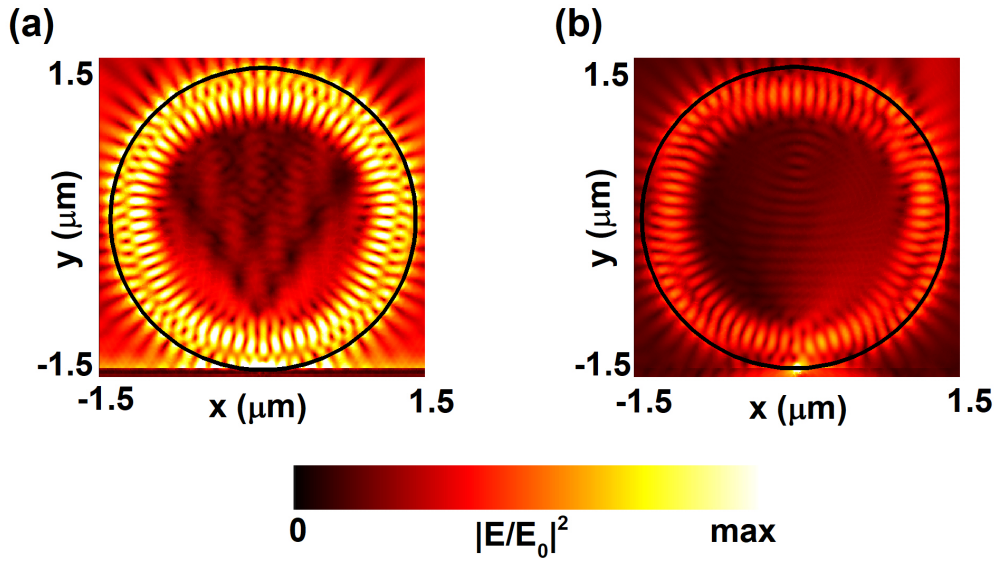


FIGURE 5.3: Calculated near field electric field distribution for (a) microsphere on Au film and (b) glass substrate respectively.

Figure 5.3 (a) and (b) shows the near field electric field distributions for microsphere placed on Au film and glass substrate respectively. Figure clearly shows enhancement of local electric field for the microsphere on film geometry. This enhancement of the electric field will be manifested in the enhancement of the molecular signatures coupled to the system (see figure 5.2).

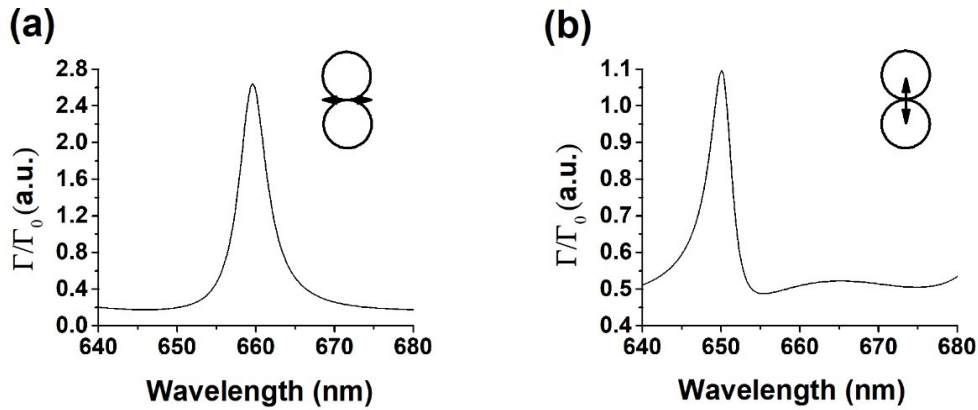


FIGURE 5.4: Calculated decay rate for bisphere system by placing dipole oriented along (a) x-axis and (b) y axis respectively.

To understand the decay rate modification by coupling the molecule to microsphere on Au film, we calculated decay rates for individual dipoles using 2D FEM methodologies (COMSOL). Microsphere over metallic film was modeled as bisphere system

(sphere-image sphere) and the dipolar source was placed at the junction of spheres. The power radiated by the bisphere was integrated over a circle $4 \mu\text{m}$ away from the system and normalized by power radiated by the individual dipole. The radiative decay rate is enhanced for dipolar orientation along x-axis as shown in figure 5.4.

WGMs were characterized using radial (n), orbital (l) and azimuthal (m) quantum numbers. The WGMs of the microsphere, are computed using classical Mie theory and are labelled by two polarizations, Transverse Magnetic (TM) and Transverse Electric (TE) and three quantum numbers n , l and m . n is the radial quantum number and corresponds to the number of intensity maxima along the radius of the sphere. l is equal to half the intensity maxima along the great perimeter of the sphere and is termed as the orbital quantum number whereas m , which is the azimuthal quantum number, is the projection of l on the quantization axis. The mode number were assigned using the MATLAB code provided by [194]. The extinction crossection (Q_{ext}) for a microsphere interacting with an electromagnetic field is given by,

$$Q_{ext} = \frac{2}{(ka)^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}(a_n + b_n) \quad (5.1)$$

Where k is the wavenumber and a_n and b_n are Mie coefficients to calculate the amplitude of the scattered fields. When b_n is zero, a_n dominates and modes corresponding to this are assigned as TM modes. Similarly, b_n dominates when a_n is set to zero and these modes are assigned as TE modes. Furthermore, the assignment was verified using finite difference time domain (FDTD) simulations.

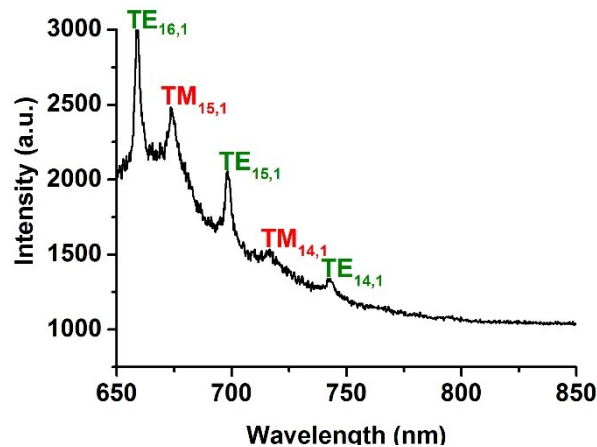


FIGURE 5.5: Molecular fluorescence spectra collected from microsphere coupled to glass substrate with mode assignment.

To understand and identify the Mie modes, the spectrum collected by placing microsphere on glass substrate is shown in figure 5.5. Individual peaks of the spectrum

corresponds to different Mie modes of the microsphere. The mode numbers were assigned using analytical mie theory outlined previously. For an isolated microsphere in vacuum, azimuthal quantum number (m) has $2l+1$ degeneracy. This degeneracy can be lifted if the azimuthal symmetry of the resonator is broken. This can be achieved by coupling it to another microsphere, presence of material inhomogeneity and existence of scatterer at the periphery of the resonator, [195–197] deviation of morphology of the microresonator from that of perfect sphere, [196] etc. The lifting of degeneracy will be manifested as spectral split in the mie modes. In the present case, the splitting is mainly due to the presence of metal film which alters the azimuthal symmetry of the microsphere. Inset of figure 5.2 clearly shows the Mie mode $TE_{16,1}$ is split into two modes when microsphere is placed on Au mirror.

5.3.2 Optical energy-momentum spectroscopy of fluorescence emission from the geometry

To analyze the momentum space signatures of WGMs, the outcoupled fluorescence from the the system was projected onto the Fourier space. Figure 5.6 (a) shows the Fourier space image of the captured light from the microsphere coupled to Au film. The FP image clearly shows that the emission is ring shaped. To understand the effect of coupling to the metal film, we measured FP image from microsphere coupled to NB coated glass substrate. Figure 5.6 (b) shows the measured FP image. On comparison with the FP image obtained by coupling to the Au film, one can note that the emission of microsphere on glass occupies a relatively broad range of wavevectors.

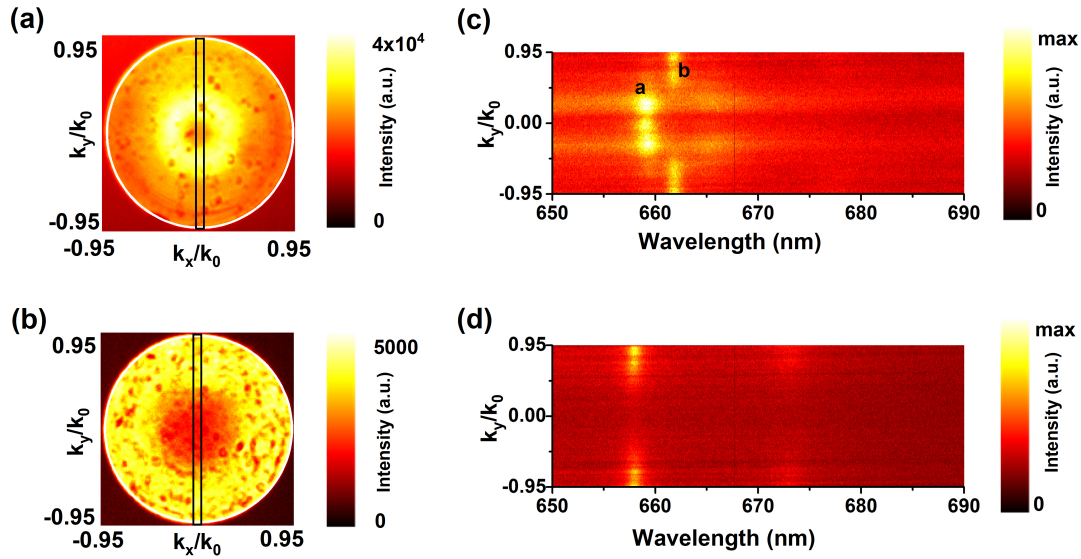


FIGURE 5.6: (a) Fourier plane fluorescence image captured from microsphere coupled Nile Blue coated Au film. (b) Fourier space image captured from microsphere coupled Nile Blue coated glass substrate showing that emission is ring-like with large wavevector spread. A narrow range of wavevectors around k_x/k_0 was filtered (shown as a rectangle in (a) and (b)) and dispersed in wavelength to understand momentum signatures of individual Mie modes. (c) and (d) are measured E-k spectra for microsphere placed on Au mirror and glass substrate respectively.

To further quantify the emission, we plot the intensity of fluorescence emission along $k_x/k_0=0$ and is shown in figure 5.7. For microsphere on Au mirror majority of emission happens at $k_y/k_0 = -0.33$ (Full width at half maxima (F.W.H.M)=0.32) and 0.29 (F.W.H.M=0.32). And for the microsphere on glass substrate the intensity of emission across $k_x/k_0=0$, figure 5.7 (b), shows that emission maximum is at $k_y/k_0 = -0.67$ (F.W.H.M=0.55) and 0.75 (F.W.H.M=0.64). Hence coupling to the Au mirror not only affects the spectral shape and causes the spectral split but also affects the emission wavevectors of the WGMs both in terms of emission wavevector maxima and wavevector spread.

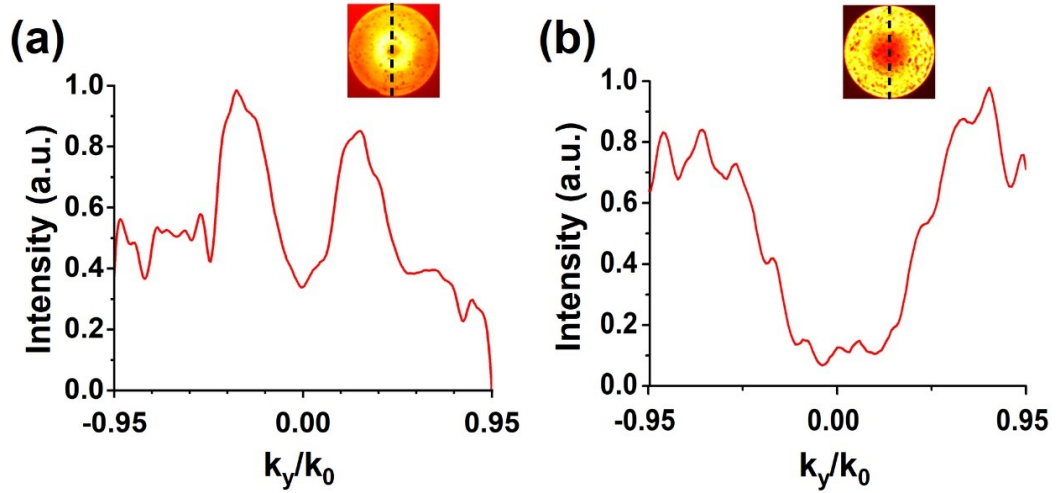


FIGURE 5.7: Intensity profiles along $k_x/k_0=0$ line for Fourier plane images captured from microsphere coupled to (a) Au film (b) glass substrate respectively. Insets show Fourier plane images

Note that the FP images shown in figure 5.6 (a) and (b) are convoluted images of all the excited WGMs in the microsphere. If one filters specific k/k_0 values in the FP image and then disperse to provide wavelength resolution, then momentum distribution of individual WGMs can be studied using wavevector resolved spectroscopy. The energy-momentum (E-k) spectroscopy measurement is very important for microsphere coupled to thin Au film, as coupling introduces split in WGMs and the E-k spectrum sheds light on the momentum distribution of the split modes in such situation. With this hindsight we performed E-k spectroscopy on microsphere coupled to NB coated Au film and glass substrate. A thin slice of the FP image (see figure 5.6 (a) and (b)) around $k_x/k_0=0$ was filtered using the slit of the spectrometer and dispersed using 1200 grooves/mm diffraction grating to obtain the E-k spectrum. Figure 5.6 (c) and (d) show the corresponding E-k spectra for microsphere coupled to Au film and glass substrates respectively. The Mie mode split observed near 660 nm wavelength (originally $TE_{16,1}$ for unperturbed microsphere) clearly shows different momentum distributions (see figure 5.2). We observe emission at lower k_y/k_0 values for peak 'a', while that for peak 'b' at higher values of k_y/k_0 . The trend is repeatable and the data shown here is representative in nature. While for the microsphere on glass substrate case, there is no split in the WGMs observed and this translates to the E-k diagram as well. Both modes emit at larger values of k_y/k_0 (see figure 5.6 (d)). This shows that the coupling of microsphere to thin film not only splits the WGMs in wavelength domain but also in momentum domain, showing anti-crossing. This anti-crossing behavior of Mie modes is a result of coupling of the microresonators.

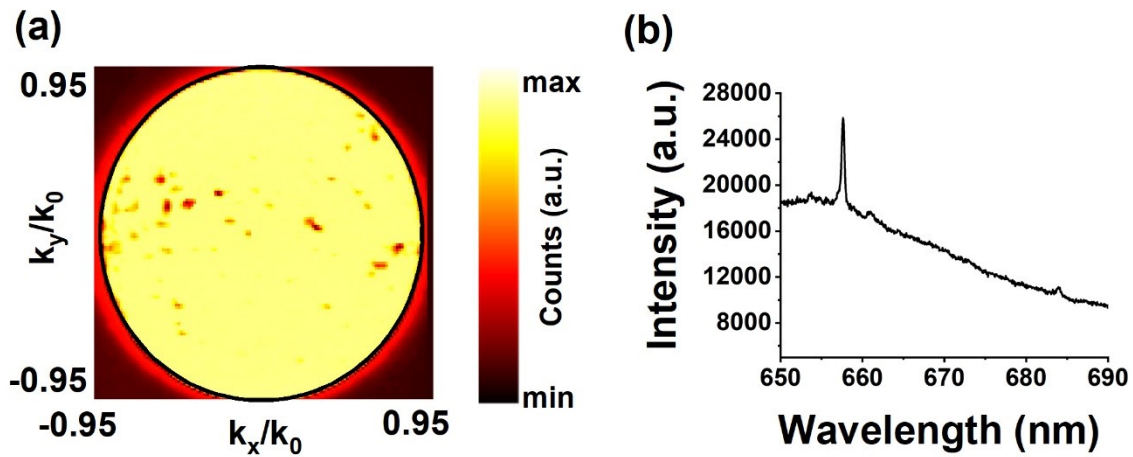


FIGURE 5.8: (a) Fourier plane image of an individual $1\ \mu\text{m}$ diameter SiO_2 bead on Nile blue coated Au film, showing uniform emission. (b) Nile blue molecular emission spectrum from $1\ \mu\text{m}$ diameter SiO_2 bead on Au film.

To ascertain this, we performed similar experiments on $\sim 1\ \mu\text{m}$ diameter SiO_2 microsphere on Au mirror. At this operational wavelength, WGMs were not excited, but the molecular emission (both fluorescence and Raman) were enhanced. The FP image shows that the emission is uniform over a broad range of wavevectors, unlike the present case. Figure 5.8 (a) denotes the Fourier plane image of the molecular emission captured by coupling it to microsphere of size $1\ \mu\text{m}$ on Au film. FP image clearly shows that emission is uniform over a broad range of wavevectors. Also, the molecular emission does not excite WGMs in the microsphere (see figure 5.8 (b)).

5.4 Determining polarization structure of split modes

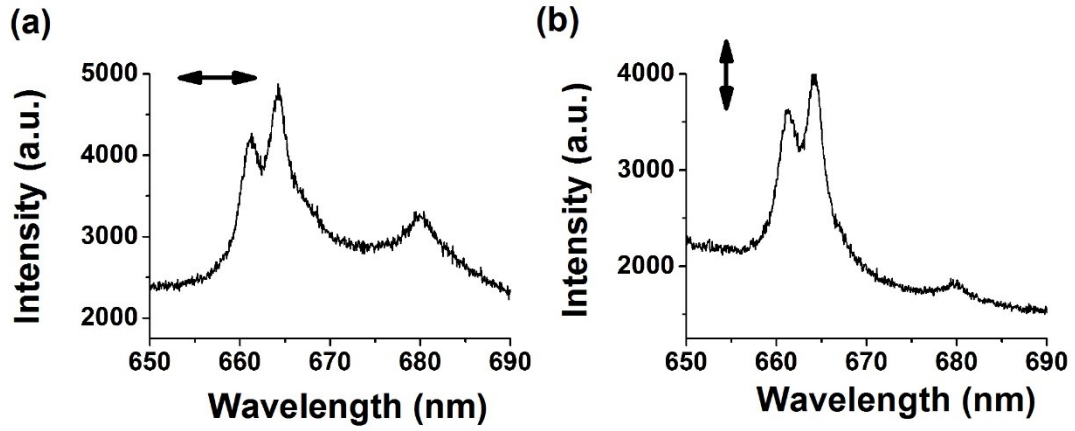


FIGURE 5.9: Output polarization resolved spectra collected from strongly coupled optical microresonator system in real plane for (a) 0° and (b) 90° analyzer positions respectively. The spectra show no significant differences between two different analyzer positions

We were interested in understanding the polarization signatures of the split whispering gallery modes due to strong coupling. To this end, we performed output polarization resolved real plane spectroscopy. Output resolved spectra for two orthogonal polarizations are shown in figure 5.9 (a) and (b). There seem to be no pattern intensity variation for two different output polarizations.

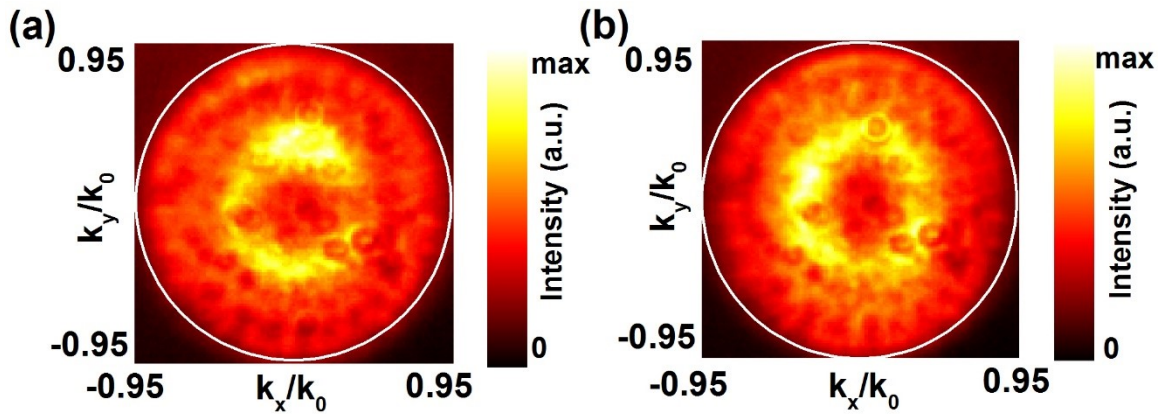


FIGURE 5.10: Output polarization resolved fluorescence FP images for microsphere on Au film along (a) k_x/k_0 and (b) k_y/k_0 axes respectively.

To further probe the polarization of modes in momentum domain, we performed polarization resolved BFP imaging. Polarization resolved BFP images did not show any clear evidence of a polarization structure. Output polarization resolved FP images for molecular emission along k_x/k_0 and k_y/k_0 are shown in figure 5.10 (a) and (b) respectively. Polarization resolved FP images do not provide simultaneous information of momentum and polarization of split modes as the wavelength information is integrated out.

WGMs can potentially possess orbital angular momentum with azimuthal polarization signatures and cannot be detected in real plane spectroscopy. This suggests that one has to perform polarization resolved E-k spectroscopy to understand the polarization information of strongly coupled optical microresonators. Hence we probed individual WGMs using polarization resolved E-k spectroscopy. The FP image was projected onto the slit (width = 200 μm) or a square pin hole (200 μm x 200 μm) placed at the conjugate Fourier plane. The slit (pinhole) was used to filter narrow range of k_y/k_0 and k_x/k_0 . This requires modification to the optical setup shown earlier.

5.4.1 Optical setup to study polarization resolved energy-momentum spectroscopy

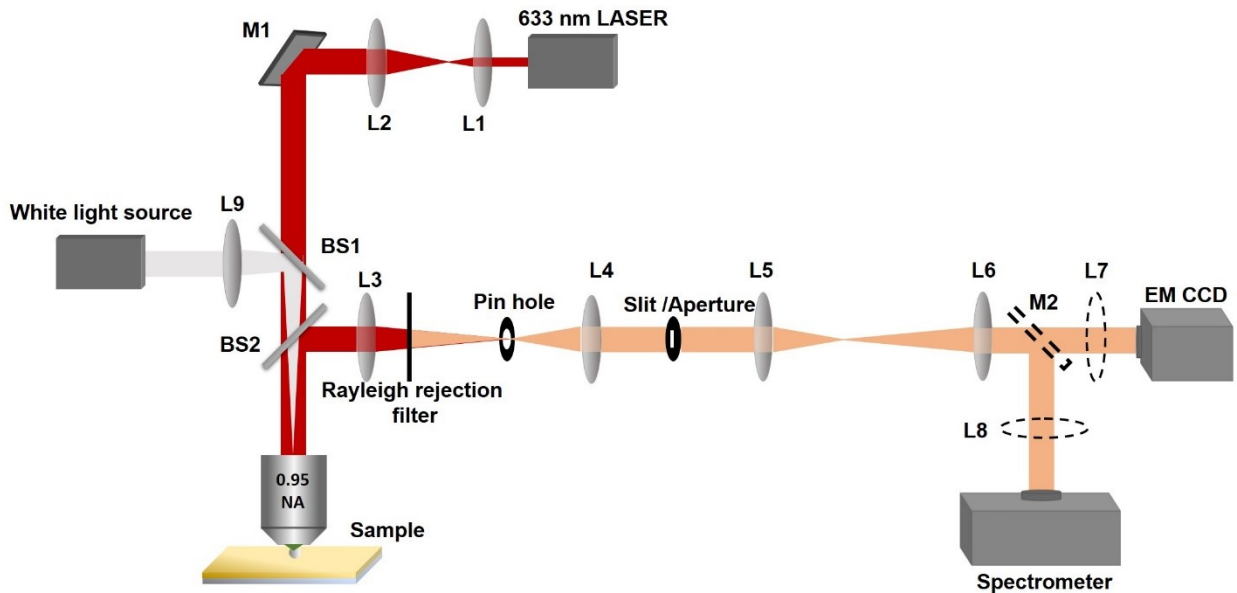


FIGURE 5.11: Schematic of the experimental setup used to perform Fourier plane imaging and spectroscopy on microsphere coupled to Au film.

The experimental setup used to probe microsphere coupled to Au film is as shown in figure 5.11. Individual microspheres were excited using 100x, 0.95 NA air immersion

objective lens and the backscattered light was collected from the same objective lens. The collected light was projected onto the Fourier plane using combination of lenses L3-L6 after rejecting the Rayleigh scattered component using 633 nm edge filter. Slit/aperture was placed at the conjugate FP created by lens L4 to filter narrow range of wavevectors. Flippable mirror, M2, was used to direct light to the spectrometer. Lenses L7 and L8 were used to focus the light to the EMCDD and to the spectrometer respectively. Using this setup, one can filter very narrow regions of momentum vectors (both in k_x and k_y) using pinholes and then analyze using polarizers.

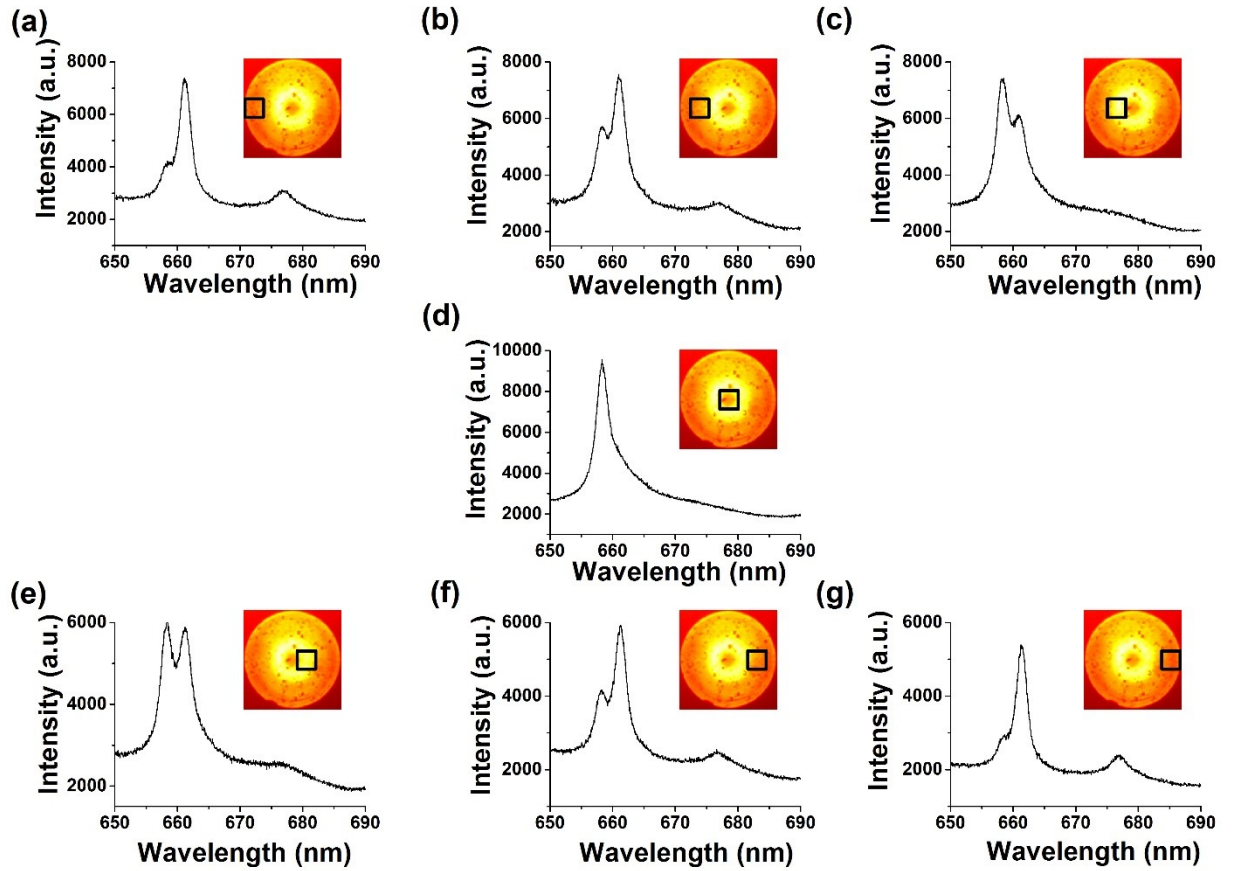


FIGURE 5.12: Momentum resolved spectra collected from the microsphere coupled to Au mirror system. The outcoupled light was filtered using a square pinhole of size $200\ \mu\text{m}$ to understand spectral signatures at different k -points. (a) - (g) are k resolved spectra by placing pinhole at points along $k_y/k_0 = 0$ as shown in the insets.

Figure 5.6 (c) shows the energy-momentum spectrum collected by filtering a narrow range of k_x using the slit of the spectrometer. Now, using the experimental setup discussed above, we performed energy-momentum for microsphere on gold film by placing a square pinhole of size $200\ \mu\text{m}$ at the conjugate back focal plane. Figure 5.12 shows series of momentum resolved spectra by filtering different ranges k_x/k_0 near

$k_y/k_0=0$ (shown in insets). It clearly establishes the differential momentum distribution of split modes. As one moves from $k_x/k_0=-0.95$ to 0.95 , different modes can be probed by restricting the range of momentum vectors filtered. This is a very powerful method to understand strong-coupling phenomenon in nanophotonics. Also note that figure 5.12 corroborates the E-k spectrum shown in figure 5.6 (c), in the context of differential momentum distribution of split modes.

5.4.2 Polarization resolved E-k spectroscopy using a slit

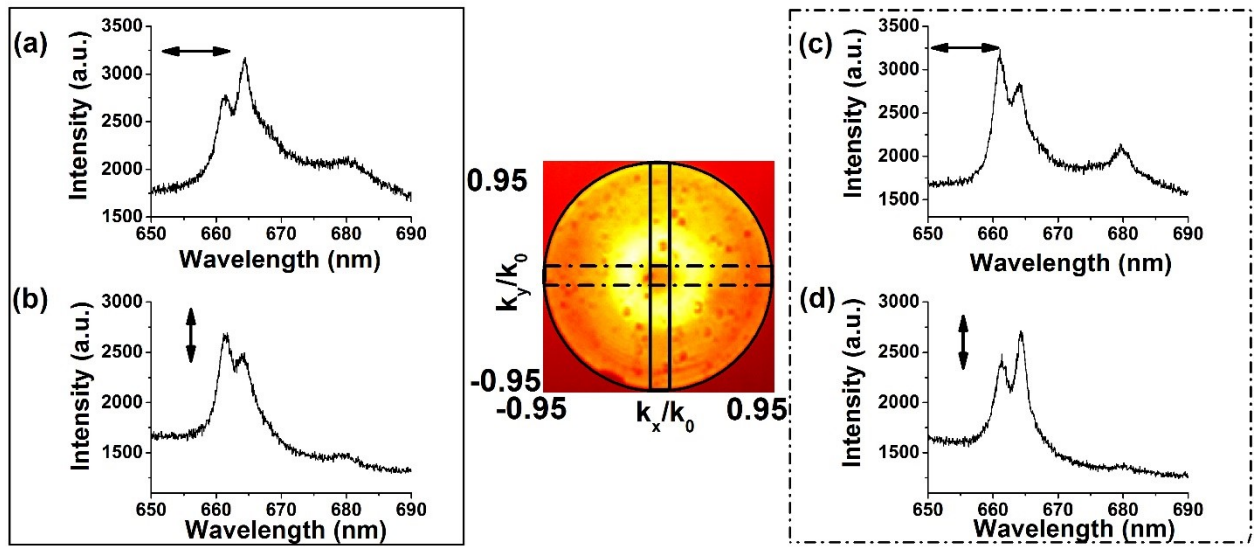


FIGURE 5.13: Momentum resolved spectroscopy of individual WGMs. (center) FP image of emission from microsphere coupled to Nile Blue film coated Au film. Momentum resolved spectroscopy was performed by filtering out a narrow range of wavevectors along $k_x/k_0=0$ and $k_y/k_0=0$ (shown as rectangles on the FP image). The resulting light was analyzed for its output polarization. (a) and (b) are output polarization resolved spectra along k_x/k_0 and k_y/k_0 axes respectively after filtering narrow range of wavevectors near $k_x/k_0=0$ using a narrow slit of width $200\ \mu\text{m}$. (c) and (d) are output polarization resolved spectra along k_x/k_0 and k_y/k_0 axes respectively after filtering narrow range of wavevectors near $k_y/k_0=0$ using a narrow slit of width $200\ \mu\text{m}$.

Figure 5.13 shows the importance of momentum resolved spectroscopy. When a slit is introduced in the conjugate FP and then the polarization of the light is analyzed, we start to see hidden features in the polarization structure. Figure 5.13 (a) and (b) shows the output polarization resolved spectrum, for slit placed along $k_x/k_0=0$ line, along k_x/k_0 axis and k_y/k_0 axis (0° and 90° analyzer positions) respectively. In this case, one can clearly see the difference of intensities in the split modes for two orthogonal analyzer positions. When the similar experiment was conducted for slit placed along $k_y/k_0=0$

line (figure 5.13 (c) and (d)), we get exactly opposite signatures. Looking carefully at figure 5.13 (a) and (c), one can easily notice that the polarization of the mode ‘b’ has been rotated by 90° and so is the polarization of mode ‘a’. But they are orthogonal in nature. Over the full k-plane the polarization of the modes, then, will rotate 360° , making the modes azimuthally and radially polarized.

5.4.3 Polarization resolved E-k spectroscopy using a pinhole

In the previous section, we discussed E-k spectroscopy by placing a slit in the conjugate FP. This experiment can be further extrapolated by placing a pinhole in the conjugate FP, which provides greater control over the filtering of momentum vectors.

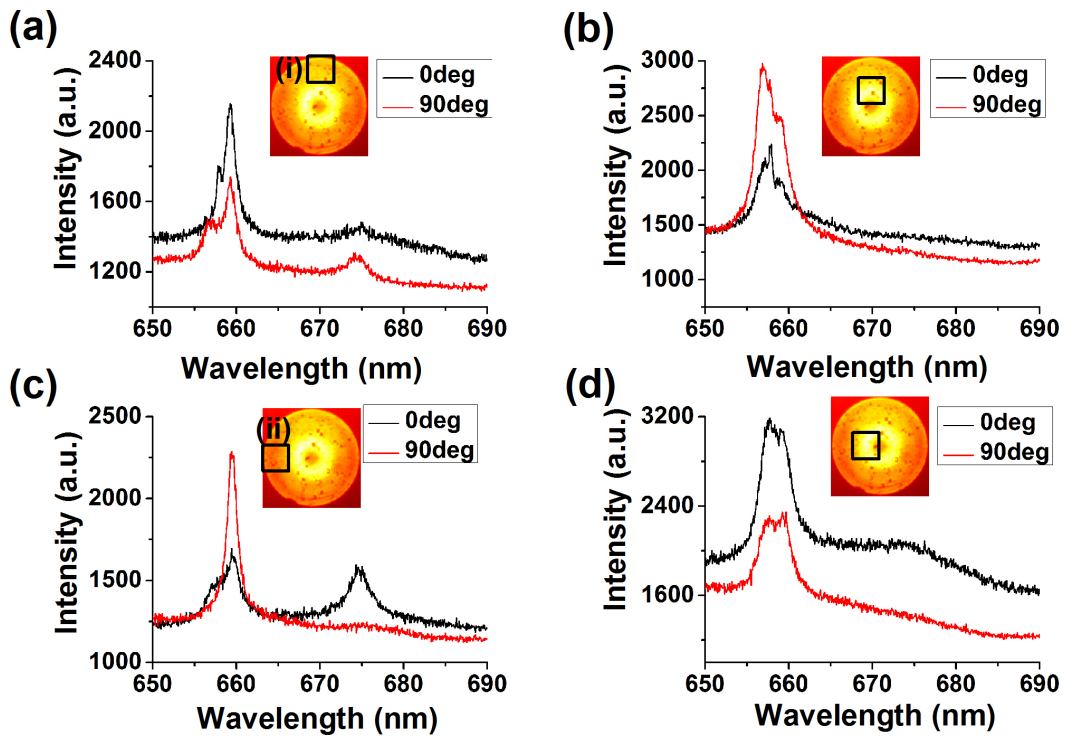


FIGURE 5.14: Momentum resolved spectra collected from the microsphere coupled to Au mirror system. The outcoupled light at the conjugate back focal plane was filtered using a square pinhole of size $200 \mu\text{m}$ and was analyzed to understand the polarization signatures at different k-points. (a) and (b) are polarization resolved spectra by placing pinhole at points along $k_x/k_0 = 0$ as shown in the insets. (c) and (d) are polarization resolved spectra by placing pinhole at points along $k_y/k_0 = 0$ as shown in the insets.

Figure 5.14 shows polarization resolved E-k spectra of individual WGM from strongly coupled microresonators. Square pinholes were placed along $k_x/k_0 = 0$ (figure 5.14 (a))

and (b)) and along $k_y/k_0 = 0$ (fig. 5.14 (c) and (d)) to filter narrow range of wavevectors and the output polarization was analyzed. As seen in figure 5.12, the split modes outcouple at different wavevectors. So, it is easy to understand them by filtering narrow range of k -vectors where only one of the two split modes exist in the k -space. As the peak ‘b’ of the split modes outcouple at higher wavevectors (see figure 5.14 (c)), we filtered out two points (along $k_y/k_0 = 0$ and $k_x/k_0 = 0$) as shown in figure 5.14 (a) and (c). At point (i) the polarization of the mode was predominantly along k_x/k_0 (0° in analyzer). But along $k_y/k_0 = 0$ line (point (ii)), the polarization has rotated by 90° and the mode is polarized along $k_y/k_0 = 0$ (90° in analyzer). Thus, it shows that the polarization of the Mie mode rotates as one moves along the momentum plane making it an azimuthally polarized beam.

Interestingly the peak ‘a’ of the split modes behaves exactly the same (see figure 5.14 (b) and (d)). But the polarization signatures are orthogonal to that of split mode ‘b’, making it radially polarized. Split modes due to strong coupling of microresonators, thus, possesses vectorial polarization signatures and are azimuthally and radially polarized respectively. This result can potentially have wide relevance in understanding the angular momentum mechanics inside strongly coupled cavities. Since both the modes outcouple at different wavevectors, one can easily filter out specific mode. Under far field real plane spectroscopy/imaging direct observation of vectorial polarized emission is not possible and have to be resorted to wavevector based spectroscopy.

5.5 A plausible model to explain observed results

We can understand the momentum and polarization signatures of the WGMs by looking at the electromagnetic field of a WGM. For simplicity, we consider electromagnetic field of an individual microsphere. The results can then be extrapolated to microsphere over mirror. Electromagnetic field of a WGM of an isolated sphere is concentrated at a distance of $r(1 - \sqrt{1 - |m/l|^2})$ from the substrate, where r is the radius of the microsphere [196, 198] (see figure 5.15 (a)). The equatorial plane of the sphere corresponds to $|m| = l$. In non-degenerate case, the states are filled in the order of increasing energy and mode $|m| = l$ will have lowest energy. Also, one can find that the distance increases as the mode number l decreases for any m . So modes with lower l value are farther away from the substrate and will be nearer to the equatorial plane.

For the microspheres with relatively lower textitl values (large distance from the substrate), which is the present case, the electric field of WGMs will be concentrated near the equatorial plane. The local electric field of the mode is ring-shaped. Hence its projection onto the Fourier plane will also be a ring-like structure (see figure 5.6 (a) and

(c)). The k_x and k_y values of any mode will then be intimately related to the distance from the substrate. Larger the distance of substrate, the ring in the FP will have large (k_x, k_y) values.

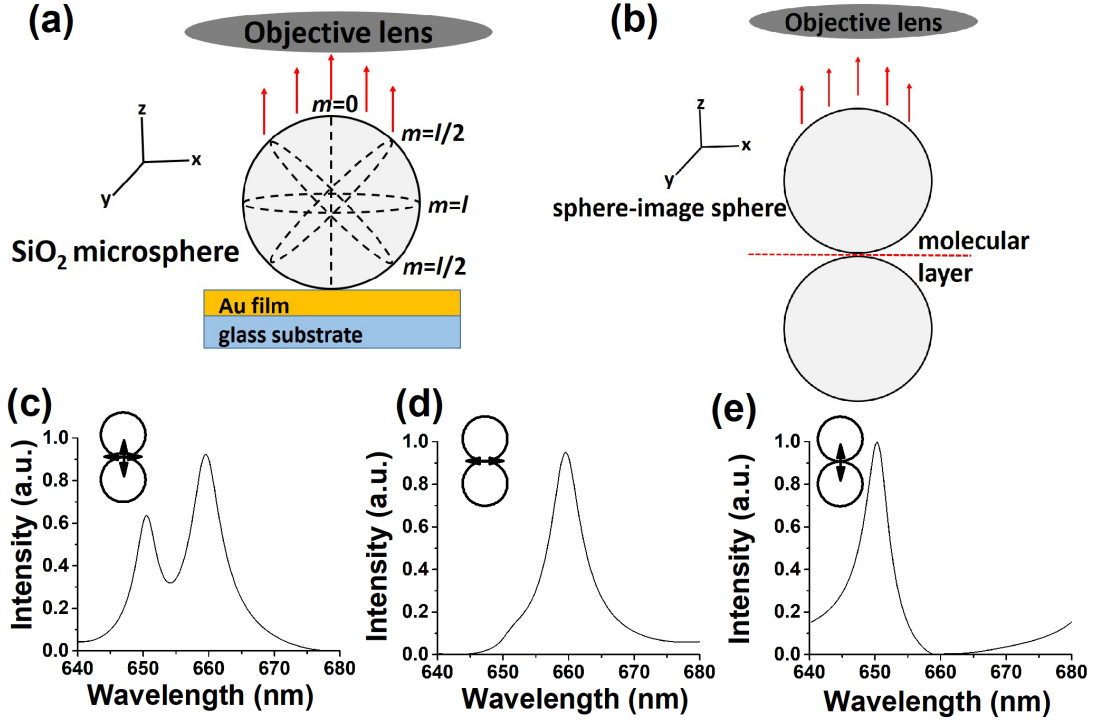


FIGURE 5.15: (a) Schematic representation of whispering gallery modes in an Au film coupled microsphere system. (b) Model system, bisphere in contact, considered to represent microsphere on mirror. Calculated spectra for bisphere system by placing (c) two orthogonal dipoles (d) single dipole along x axis (e) single dipole along y axis.

E-k spectrum gives information about the momentum distribution of the individual mie modes. Modes with degenerate $|m|$ ($-l$ to l) will span a range of wavevectors at a particular value of wavelength. This is seen in figure 5.6 (d), where wavevector distribution of individual modes are shown. When the degeneracy is lifted by coupling it to its image sphere, we have ranges of ‘m’ s associated with different wavelengths. Consider the case of peak ‘a’ and ‘b’ (figure 5.2). Peak ‘a’ occurs at lower wavelength and hence associated with modes, m , that are nearer to the substrate. This is because of the fact that the modes with lower values of $|m|$ have higher energy and hence lower wavelength. This makes mode ‘a’ emit at lower k values, as the electric field is located nearer to the substrate. The projection of such field onto the k -space will be near $k=0$. On the other hand peak ‘b’ contains modes away from the substrate. This makes split mode ‘b’ to emit at higher wavevectors when compared to its counterpart (see figure 5.6 (c)).

Also modes near to the substrate (modes with lower value of lm) will be enhanced more than the modes near the equatorial plane.[195] And the modes near to the substrate project onto lower k/k_0 values. Hence for the microsphere on gold film, the majority of emission happens at lower k -values (see figure 5.6 (a)). This explains the intricate relationship between the mode numbers of the WGM and its wavevector signatures.

5.5.1 Polarization structure in bi-sphere model

For quasi TE modes of the microsphere, where the polarization of the electric field is in-planar, the polarization of the light trapped inside the sphere suffers a continual change during TIR. Hence the state of polarization (SOP) of the WGMs, for TE modes, should also preserve this cylindrical symmetry of the microsphere, thus generating cylindrical vector beams. [199] When the microspheres are strongly coupled, the modes sensitive to the coupling will split. [183] To understand the polarization states of the outcoupled radiation, it is imperative to study how the mie modes are generated. We calculated the spectra using the bisphere model as shown in figure 5.15 (b). Dipoles with different orientations were placed in between two spheres and the intensity is plotted with respect to the wavelength of the oscillating dipole.

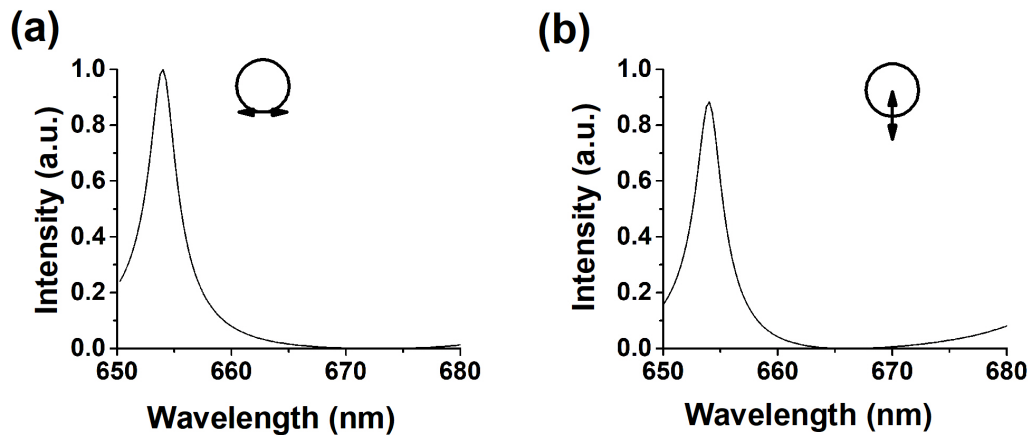


FIGURE 5.16: Calculated near field electric field spectra by exciting an individual microsphere using dipoles oriented along (a) x and (y) axes respectively as shown in the insets.

Due to coupling with the second microsphere, once degenerate mode now splits into two different modes (see figure 5.16). Polarization degeneracy in excitation is lifted and the mode ‘a’ and ‘b’ are excited using different input polarizations, which are orthogonal (see figure 5.15 (c) - (e)). Both the modes will suffer continuous TIR along the periphery of the sphere. As the input polarization of the excited modes are

orthogonal, the outcoupled radiation will also preserve this orthogonality. Since the system is cylindrically symmetric, the polarization of the modes which outcouple after suffering TIR along the periphery of the sphere will be vectorial in nature.

5.6 Extending the problem

We studied the effect of microsphere placed on metallic film on the polarization and wavevector distribution of molecular fluorescence using polarization resolved energy-momentum spectroscopy. Since the microsphere placed on metal film focuses the incoming laser to a very small area by acting as a micro-lens, one can easily enhance metal photoluminescence(PL). The enhanced metal PL will then eventually couple to the WGMs of the microsphere and gets outcoupled to specific wavevectors defined by the WGMs. One can also study the effect of the sizes of microsphere on the directionality of the outcoupled microsphere and thus probe the optical antenna property of the microsphere.

The idea of imparting vectorial polarization to spontaneous emission process like molecular fluorescence and be extended to coherent scattering processes like Raman scattering. Here, one has to carefully design the size of the microsphere to match the WGM with the Raman mode of the molecule and then analyze the polarization signatures of the outcoupled Raman signals. These studies are underway in the laboratory.

5.7 Conclusion

In summary, we have experimentally shown how a strongly coupled metallo-dielectric microsphere cavity can influence molecular fluorescence to carry exotic polarization structure in the far field regime, thus representing vectorial fluorescence emission. Using polarization and momentum resolved optical spectroscopy, we show the split modes of microresonator outcouple with azimuthal and radial polarizations respectively. This makes the system a possible generator of two vector beams with orthogonal polarization, which are distributed differently in momentum space. Given that microsphere can be deposited at desired location and shrunk in size by methods such as reactive ion etching, our studies can be extrapolated to realize active meta-atom and meta-surfaces.

Chapter 6

Conclusions and Future Directions

The work presented in this thesis mainly focused on understanding the molecular emission from different metal film based cavities. Special emphasis was on the polarization and wavevector aspect of the emission. Since wavevector analysis provides very critical information related to the antenna prospect of the structure, probing cavity with momentum space viewpoint is very illuminating. Traditionally, cavity architectures have been studied as tools to enhance molecular emission and devices paving the way to push the limits of sensing upto single molecule limit. Cavities host very complicated polarization structures which affect the coupling of molecules to the modes of the cavity and hence wavevector signatures of the outcoupled photons. Measuring Fourier plane signatures of cavity assisted molecular emission can provide a platform to integrate both cavity prospects (like enhancement and spectral modification) and antenna prospects (like directionality). Based on the nature, one can classify cavities used to modify molecular emission into three architectures. We studied all three configurations focusing on polarization and wavevector aspects of the emission. Our studies provide a sound platform to understand and extrapolate the complex polarization structures provided by the cavities and its applications.

Gap plasmon based cavity :

In chapter 3 we studied a unique example of a gap plasmon based cavity i.e, individual nanowire on dye molecule coated metallic film. The structure under study concomitantly provides an opportunity to study propagating modes of the nanowire and the enhancement of molecular emission due to the cavity. This elongated cavity supports complex polarization structure inside the cavity which affects the molecular emission characteristics like the wavevectors, intensity, and polarization. Using energy-momentum spectroscopy, we show differential wavevector distribution of

molecular fluorescence and surface enhanced Raman scattering signals from an ensemble of molecules sandwiched between nanowire and gold mirror, in the remote excitation configuration. Transverse and longitudinally polarized components of molecular emission show different wavevector signatures and the differential distribution is attributed to the strong polarization dependence of the SERS signals. We corroborate the experimental data with 3D FDTD simulations, where the molecules are modeled using xyz dipoles distributed all along the length of the cavity.

Future prospects:

As discussed in the body of the chapter, the present experimental configuration does not provide control over thickness of the molecular layer or the orientation of the molecules inside the cavity. Controlling these two parameters will be of importance as one can specifically enhance particular polarization component. This can be achieved by sandwiching layered 2D materials like transition metal dichalcogenides (TMDs) in between nanowire and metallic mirror. This experiment can also be extrapolated to study SERS emission from self assembled monolayers prepared by langmuir-blodgett method etc.

Fabry-Pérot resonance based cavity :

Chapter 4 dealt with understanding Fourier plane signatures from a vertical organic nanowire on a plasmonic film. The nanowire was grown using physical vapor deposition method on a plasmonic film. Individual nanowire was probed using evanescent excitation and the resulting outcoupled light was projected onto the Fourier plane. The choice of organic nanowire is vital as one can operate the structure in two different regimes : *active* and *passive* regimes. In active regime, the emission is mediated by Frenkel exciton-polaritons and one can probe photoluminescence from the structure. In the passive regime, the structure acts as a dielectric waveguide. Here we studied both photoluminescence and elastic scattering from an individual vertical organic nanowire. The emission pattern was doughnut shaped in both operational regimes. The experimental data was corroborated with 3D FEM based numerical simulations.

Future prospects:

Vertical organic nanowires has an immense potential to understand the energy transfer in the direction perpendicular to the substrate. DAAQ wires can be grown on different TMD materials. As the organic wires can be driven to excite Frenkel exciton-polaritons inside the structure, they form an opportunity to couple Frenkel exciton-polaritons with

wannier-mott excitons. This extrapolation can provide unique insight towards understanding molecular coupling in both strong and weak regimes. By tapering the end of the vertical wire one can probe adiabatic nanofocusing etc in the system, which is exciting.

Whispering gallery modes based cavity :

Polarization and wavevector studies of an individual microsphere on dye molecule coated gold film were reported in chapter 5. Using polarization resolved energy-momentum spectroscopy, we showed vectorial polarization signatures in molecular fluorescence coupled to the split WGMs of the structure. Usually polarization structure in WGM based resonators are studied using near field probing mechanisms. We adopt a novel far field mechanism to probe the vectorial signatures in the split WGMs. A simple bi-sphere model was utilized to explain the obtained experimental results.

Future prospects:

WGM based cavities not only provide very large Q values but also complex polarization structures. Molecular fluorescence coupled to WGMs outcouple with vectorial polarization. A straight extrapolation is to probe similar concept in Raman scattering. This will open up a new avenue in probing angular momentum in Raman scattering signals. Another possible application is to couple microsphere to TMDs. As one can produce interesting circular polarization using TMDs, [200] coupling microsphere with TMDs will give a platform to probe interaction between spin and orbit degrees of freedom in polarization.

In conclusion, we believe the work presented in this thesis, comprehensive analysis of polarization and wavevectors from metal film based cavities, will find itself very useful in understanding the cavity-molecule interaction. This area of research has potential to impact understanding fundamentals of physics and chemistry of molecules while touching application window in the day-to-day life of people at the same time.

Appendix A

Propagating modes in nanowires

Electromagnetic modes supported by subwavelength nanowires have usually been treated by considering a metallic cylinder. But the nanowires synthesized using chemical synthesis procedures have pentagonal crosssection.[127] When the size of the nanowire is of the range ($\sim 200 - 300$ nm), it is imperative to consider the accurate structure to determine the possible electromagnetic modes supported. In this section, electromagnetic modes supported by a single wedge is discussed and then will be further extrapolated to pentagonal nanowires.

A.1 Modes supported by a single wedge

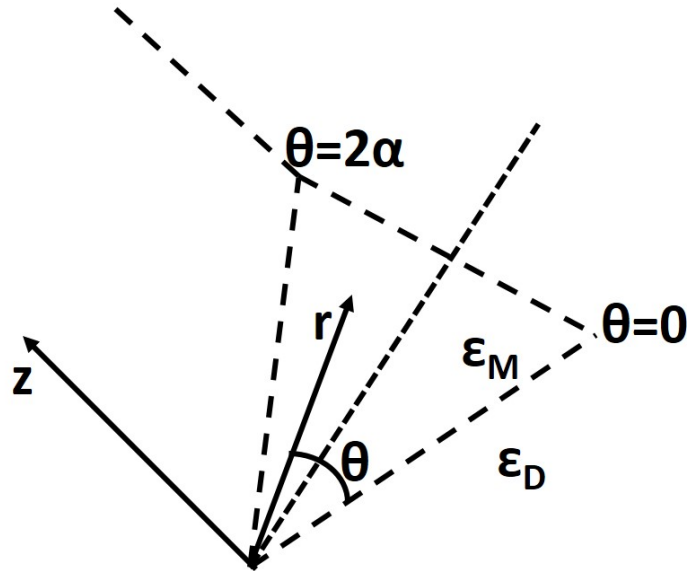


FIGURE A.1: Schematic of the metal wedge waveguide surrounded by air. Figure adapted from [201]

Let us consider an infinitely long wedge as shown in figure A.1. The analysis is done in cylindrical co=ordinates (r, θ, z) . In cylindrical co-ordinates the radial solution of the wave equation is given by the modified Bessel function of the second order, denoted

by K . Using this set of solutions, one can write the solution at each media (metal and dielectric) as,[201]

$$F(r, \theta) = \int dv f_v K_{iv}(qr) \exp(-v\theta) \quad (\text{A.1})$$

where q is the radial momentum, v is the order of K function, f_v are the expansion coefficients which define the v -spectrum of the solution.

The symmetry of the structure allows two kinds of modes : even and odd modes about the symmetry axis ($\theta = \alpha$). Solving for tangential components, the boundary conditions on the interface $\theta = 0$ are ($r > 0$)

$$\begin{cases} (i) \tilde{E}_M = \tilde{E}_D & (iii) \partial_\theta \tilde{E}_M = -f_1 \partial_\theta \tilde{E}_D - f_2 r \partial_r \tilde{H}_D \\ (ii) \tilde{H}_M = \tilde{H}_D & (iv) \partial_\theta \tilde{H}_M - f_3 r \partial_r \tilde{E}_D + f_4 \partial_\theta \tilde{H}_D \end{cases} \quad (\text{A.2})$$

where,

- $\sim$ denotes fields at interfaces.
- M,D denotes fields in metal and dielectric respectively.
- f_i s are expansion coefficients

The f_i s are given by

$$f_1 = \frac{\epsilon_D q_M^2}{|\epsilon_M| q_D^2}; f_2 = \frac{\omega \mu \beta (|\epsilon_M|) + \epsilon_D}{q_D^2 \epsilon_M}; f_3 = \frac{\omega \epsilon_0 \beta (|\epsilon_M|) + \epsilon_D}{q_D^2}; f_4 = \frac{q_M^2}{q_D^2} \quad (\text{A.3})$$

where ϵ_M and ϵ_D are dielectric permittivities of metal and the surrounding dielectric respectively, β is the modal propagation constant.

Out of the four symmetries, we provide solutions having E(even)-H(odd) symmetry here. The solution takes the form, [201]

$$E_z^e = \exp(i\beta z) \begin{cases} \int dv \{a_v K_{iv}(q_M r) \cosh(v(\theta - \alpha))\}, \text{ for } \theta \in [\theta, 2\alpha] \\ \int dv \{b_v K_{iv}(q_D r) \cosh(v(\theta - \alpha - \pi))\}, \text{ for } \theta \in [2\alpha, 2\pi] \end{cases} \quad (\text{A.4})$$

Using orthogonality of K -functions and characteristics of K integral, we can approximate the v -spectrum integral as discrete series given by, [201]

$$\sum_v a_v \cosh(v\alpha) G(v, s; \frac{q_M}{q_D}) = b_s \cosh(s(\alpha + \pi)) \frac{\pi^2}{2s \sinh(\pi s)} \quad (\text{A.5a})$$

$$\sum_v c_v \sinh(v\alpha) G(v, s; \frac{q_M}{q_D}) = d_s \sin(s(\alpha + \pi)) \frac{\pi^2}{2s \sinh(\pi s)} \quad (\text{A.5b})$$

$$\sum_v a_v \sinh(v\alpha) G(v, s; \frac{q_M}{q_D}) = -f_1 b_s \sinh(s(\alpha+\pi)) \frac{\pi^2}{2\sinh(\pi s)} - f_2 \sum_v d_v \sinh(v(\alpha+\pi)) H(v, s) \quad (\text{A.5c})$$

$$\sum_v c_v \cosh(v\alpha) G(v, s; \frac{q_M}{q_D}) = -f_3 \sum_v b_v \cosh(v(\alpha+\pi)) H(v, s) + f_4 d_s \cosh(s(\alpha+\pi)) \frac{\pi^2}{2\sinh(\pi s)} - \quad (\text{A.5d})$$

Equations for G and H are given as below,

$$G(\psi_1, \psi_2; \tau) = \frac{\pi^2 \cos(\psi_1, \ln(\tau))}{2\psi_1 \sinh(\pi\psi_1)} \delta(\psi_1 - \psi_2) + \frac{\pi^2}{16} [(\cosh(\pi\psi_1)) - \cosh(\pi\psi_2)]^{-1} g(\psi_1, \psi_2, \tau) \quad (\text{A.6})$$

$$g(\psi_1, \psi_2; \tau) = [\tau^2 - 1] \tau^{-i\psi_1} {}_2F_1[1 - i\frac{\psi_1 + \psi_2}{2}, 1 - \frac{i\psi_1 - \psi_2}{2}; 2; 1 - \tau^2] \quad (\text{A.7})$$

$$H(\psi_1, \psi_2) = \frac{\pi^2}{2} [\cosh(\pi\psi_1) - \cosh(\pi\psi_2)]^{-1} \quad (\text{A.8})$$

$$G(\psi, \psi, \tau) = H(\psi, \psi) = 0 \quad (\text{A.9})$$

The solution to this set of equations is self-consistent for vanishing determinant and results in the dispersion relation, which provides understanding of modes for a single wedge waveguide.

A.2 Modes in pentagonal wires

The previous section offered solutions to allowed modes in a single wedge waveguide. Now, a wire with pentagonal crosssection has such five corners, which will satisfy the argument provided in the last section, with proper weights. Hence a pentatwin wire supports five modes arising due to coupling of corner modes. Figure A.2 shows the modes supported by a pentagonal crosssection placed in homogeneous medium.[129] This can be calculated either using numerical analysis by solving the wave equation to find the modes or by semi-analytic approach outlined in the previous section. Interestingly the modes follow D_5h symmetry.

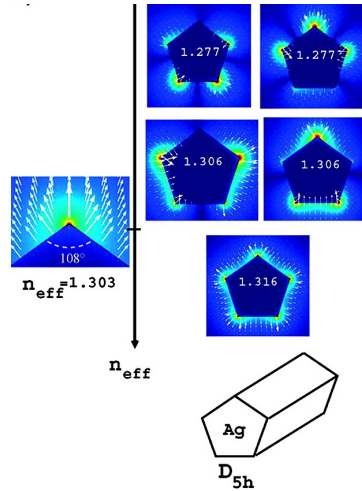


FIGURE A.2: Electric field intensity profile for different modes supported by a silver nanowire of pentagonal cross-section. Nanowire diameter is 200 nm. Figure reproduced with permission from [129]

When the same nanowire is placed on a dielectric substrate, the degeneracy of the modes gets lifted and there will be sufficient change in the propagation lengths of the modes.[129] The propagation lengths and the mode indices strongly depend on the refractive index of the substrate. Also the modes excited in any nanowire strongly depends on the diameter of the nanowire.[128]

A.3 Calculation of modes in FPN cavity

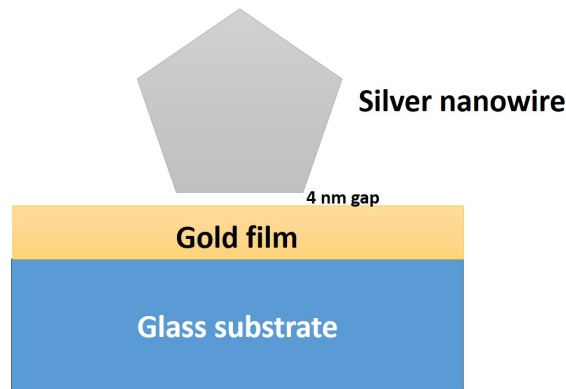


FIGURE A.3: Schematic of the simulation geometry used to calculate modes in the FPN geometry

As outlined in the previous section, the allowed modes in any geometry can be calculated using numerical simulation methodologies. We used COMSOL multiphysics 5.2, an FEM based numerical solver, to calculate the supported electromagnetic modes

in the FPN geometry (see figure A.3). The system was modeled as silver nanowire of diameter 400 nm placed over a 170 nm thick gold film. The distance between the bottom-plane of the silver nanowire and the gold plate was 4 nm. The simulation wavelength was kept at 633 nm. The simulation area was discretized using free triangular mesh of size 1 nm to ensure accuracy. The simulation area was terminated using perfectly matched layers to avoid any spurious reflections from the boundaries. The modes were identified using the mode analysis solver.

Appendix B

Brief discussion on exciton-polaritons

Exciton is a bound state of electron and hole. In the present case such excitons are created due to the external illumination. When certain conditions meet, illumination frequency equals the absorption maximum of the material, strong coupling of photons and excitons can occur and results in a strong coupled quasi-particle called exciton-polariton. Even though it is a quantum mechanical phenomenon, certain understanding can be obtained by treating the question classically.

Consider a material with complex refractive index ($\tilde{n}(\omega)$) illuminated by light of frequency ω . By solving Maxwell's equations one can calculate the electric field inside the material with wavevector k given by

$$k^2 = \tilde{n}^2(\omega)k_v^2 \quad (\text{B.1})$$

where k_v is the wavenumber in vacuum. Since $\tilde{n}^2(\omega) = \epsilon(\omega)$, dielectric permittivity of the material and $k_v^2 = (\frac{\omega}{\lambda})^2$, we can rewrite the above equation as

$$\frac{c^2 k^2}{\omega^2} = \epsilon(\omega) \quad (\text{B.2})$$

The dielectric permittivity of an absorbing material can be derived by considering coupled oscillator model[202] and can be written as

$$\epsilon(\omega) = \epsilon_b \left(1 + \frac{f}{\omega_0^2 - \omega^2 - i\omega\gamma} \right) \quad (\text{B.3})$$

where ϵ_b is the permittivity of the background matrix, f is the oscillator strength and γ is the damping constant. Using equation B.3 in B.2, we can write

$$\frac{c^2 k^2}{\omega^2} = \epsilon_b \left(1 + \frac{f}{\omega_0^2 - \omega^2 - i\omega\gamma} \right) \quad (\text{B.4})$$

This is an implicit representation of dispersion relation for polaritons. This discussion can be extrapolated study exciton-polaritons in semiconductors.

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