Plasmonic Resonances for Spectroscopy Applications using 3D Finite-Difference Time-Domain Models

Dissertation

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Abstract

Tuning plasmonic extinction resonances of sub-wavelength scale structures is essential to achieve maximum sensitivity and accuracy. These resonances can be controlled with careful design of nanoparticle geometries and incident wave attributes. In the first part of this dissertation, plasmonically enhanced effects on hexagonal-arrays of metal nanoparticles, metal-hole arrays (micro-mesh), and linear-arrays of metal nanorings are analyzed using three-dimensional Finite-Difference Time-Domain (3D-FDTD) [1, 2, 3] simulations. The effect of particle size, lattice spacing, and lack of monodispersity of a self-assembled, hexagonal array layer of silver (Ag) nanoparticles on the extinction resonance is investigated to help determine optimal design specifications for efficient organic solar power harvesting [4]. The enhancement of transmission resonances using plasmonic thin metal films with arrays of holes [5] which enable recording of scatter-free infrared (IR) transmission spectra of individual particles is also explored. This method is quantitative, non-destructive and helps in better understanding the interaction of light with sub-wavelength particles. Next, plasmonically enhanced effects on linear arrays of gold (Au) rings are studied. Simulations employing 3D-FDTD can be used to determine the set of geometrical parameters to attain localized surface plasmon resonance (LSPR). The shifts in resonances due to changes in the effective dielectric of the structure are investigated, which is useful in sensing applications.
Computational models enrich experimental studies. In the second part of this dissertation, the effect of particle size, shape and orientation on the IR spectra is investigated using 3D-FDTD and Mie-Bruggeman models [6]. This computational analysis is extended to include clusters of particles of mixed composition. The prediction of extinction and absorption spectra of single particles of mixed composition [7] helps in interpreting their physical properties and predict chemical composition. The chemical composition of respirable particles is of great interest from health, atmospheric, and environmental perspectives. Different environments may pose different hazards and spectroscopic challenges [8, 9, 10]. Common mineral components of airborne and atmospheric dust samples have strong IR transitions with wavelengths that match particle size, giving rise to interesting lineshape distortions. These models enable the determination of volume fractions of components in individual particles that are mixtures of many materials, as are the dust particles inhaled into people’s lungs.
This dissertation is dedicated to my advisors, my family, and my dear friends.
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Chapter 1: Introduction

There is much recent interest in the optical properties of metal nanoparticles due to their potential applications, such as in sensors [23, 24, 25], nano-antennas [26], and for energy transport in sub-wavelength structures [27, 28]. Arrays of sub-wavelength scale metal nanoparticles produce interesting localized resonances; however, the array spectra are considerably affected by coupling between nanoparticles [29]. Such metal nanoparticle arrays may be useful for enhancing the efficiency of organic solar panels [30]. Therefore, tuning the plasmonic extinction resonances of sub-wavelength scale structures is necessary to achieve maximum sensitivity and accuracy. The optical resonances of metal nanoparticles can be tuned by changing the size, shape, particle material, substrate, and coating of the metal particles. Further, nano-ring particles have an extra degree of freedom (DoF) in the geometry, and can be tuned by changing radial thickness, outer diameter, or height [31].

Computational models further augment experimental studies. Simulations using the three-dimensional Finite-Difference Time-Domain (3D FDTD) method [1, 2, 3] can be used to analyze plasmonically enhanced effects on arrays of metal nanoparticles and nanorings. Maxwell’s equations [32, 33, 34, 35, 36] are fundamental physical equations that govern classical electromagnetic interactions, subject to environmental and material constraints. 3D FDTD simulations are done with small finite differences
\( \Delta x, \Delta y, \Delta z, \Delta t \) in place of the infinitesimal differential elements \( dx, dy, dz, dt \). By using progressively smaller finite differences, the simulations become more accurate, converging to classically exact solutions of Maxwell’s differential equations as they approach zero. Most FDTD electromagnetic simulations use a variation of the Yee scheme [12], because it uses clever leap-frog techniques that avoid numerical instabilities and spurious modes. Basically, the electric and magnetic field components are calculated on different, interwoven spatial grids (see Figure 1.1), at different, alternating time steps. This allows the electric field to be calculated completely and independently before it is used to calculate the magnetic field, and vice-versa. The electric field at one particular time and spatial grid is used to calculate the magnetic field at a later time on a different spatial grid. The newly calculated magnetic field is then used to calculate electric field at the next time step, and so on. Computational modeling using the 3D FDTD technique is used throughout this work. The utilized software was FDTD Solutions from Lumerical Solutions Inc. (Vancouver, BC, www.lumerical.com), together with custom scripts developed to model certain complex geometries. All simulations were performed on a HP Z420 Workstation with a Microsoft Windows 7 Professional 64-bit operating system, an Intel(R) Xeon(R) CPU E5-1603 0 @ 2.80 GHz Processor, and 64-GB RAM. Examples of 3D FDTD simulation setups used in this dissertation are shown in Figure 1.2.
Figure 1.1: The Yee grid [12, 13]

Figure 1.2: Schematic examples of 3D FDTD simulations [6]
Surface plasmons (SPs) [37] are oscillations of charge density that exist at the interface between two materials having dielectric constants of opposite signs. At resonant frequencies, they interact strongly with light waves forming Surface Plasmon Polaritons (SPPs), i.e. mixed states of light and SPs. The dispersion relation for surface plasmons at a planar metal - dielectric interface is well described using Maxwell’s equations and the Drude model [38]. Localized surface plasmon resonances (LSPRs) [14] are collective electron charge oscillations in metallic nanoparticles that can be excited by light. At the resonance wavelength, they exhibit enhanced, highly localized field intensity at the nanoparticle indicating that the LSPR has very high sub-wavelength spatial resolution, limited only by the particle size. Schematic diagrams illustrating SPPs and LSPRs are shown in Figure 1.3. Chapter 2 [4] and Chapter 4 discuss plasmonically enhanced effects on hexagonal array of silver (Ag) nanoparticles and on gold (Au) nanorings respectively. Chapter 3 discusses enhancement of transmission resonances using plasmonic metal film with hole arrays, i.e. micro-mesh.
Applications of plasmonics for spectroscopy have been previously developed and described in [8, 9, 10, 15, 16]. The nickel (Ni) micro-mesh acts like a sensor with 5 µm holes to trap individual particles (see Figure 1.4) and prevent scattering. The mesh helps to create SPPs and funnel the light through the trapped particles, rather than scattering it. One of the biggest applications involves placing inhalable dust particles
into holes of the plasmonic metal mesh in order to record scatter-free IR absorption spectra of sub-wavelength size particles (see Figure 1.5). This work has particular potential for public health. Particles between 3 to 5 \( \mu \text{m} \) are among the largest able to make it down people’s airways and get deep into the lungs. Particles of size \( \sim 4 \) \( \mu \text{m} \) may be better correlated with local environmental hazards as they do not travel in air as far as smaller nanoparticles.

Figure 1.4: Scanning electron microscope (SEM) image of airborne dust particle trapped in a hole of plasmonic Ni mesh (left) [6] and a schematic example of 3D FDTD simulation of the experiment (right).
Figure 1.5: FTIR imaging microscope spectra of 5 µm diameter polystyrene sphere on a ZnSe window (top) and within a hole of metal micromesh (bottom). Dominant scattering effects are diminished by plasmonic mesh [6].

When a beam of light traverses a medium, it experiences attenuation due to energy loss. This attenuation is called extinction, which is absorption plus scattering [39, 40]. When a single isolated particle interacts with light, it results in independent elastic scattering (i.e., energy is conserved, but direction of propagation is modified). Particles much smaller than the wavelength of scattered light are well approximated by the Rayleigh scattering model [41], where the intensity of scattered radiation increases rapidly as the ratio of particle size to wavelength increases and is identical in the forward, reverse directions. The Rayleigh scattering model breaks down when the particle size becomes larger than approximately 10% of the wavelength of the incident radiation. In case of particles with dimensions greater than this, Mie’s scattering
model [42] can be used to find the intensity of the scattered radiation which is given by the summation of an infinite series of terms. Mie scattering is larger in the forward direction than in the reverse direction, and increases with increased particle size. Chapter 5 [6] discusses the spectral challenges of individual sub-wavelength scale particles, including effects of shape and orientation on the IR spectral lineshapes. Chapter 6 explores the prediction of spectra of oriented crystal microparticles with anisotropic permittivities, taking into account the effects of angular spread in various experimental setups. Chapter 7 [7, 9] discusses applications of plamonics in the mid-IR, elucidating novel ways to study and characterize dust from different environments. Chapter 8 presents a summary and outlook.
Chapter 2: Tuning Plasmonic Resonances of Hexagonal Array of Metal Nanoparticles

2.1 Background

The optical properties of gold and silver nanoparticles have attracted much interest in recent years due to their potential applications in biosensors [23, 24, 25], as nano-antennas for light signal router applications [26] and for energy transport in sub-wavelength structures [27, 28], to name just a few. The localized electric field enhancement around nanoparticles interacting with incoming light also leads to a number of surface enhanced Raman spectroscopy (SERS) applications [43, 44, 45, 46]. Numerous experimental and theoretical studies have recently been carried out to explore the potential use of nanoparticle array structures for improved nano-sensing capabilities [47, 48, 49, 50, 51, 52].

An array of 4 nm Ag nanoparticles is particularly interesting [30, 53, 54] because the lattice parameter is about 100 times smaller than a probing visible wavelength. The extinction spectrum of the array has similarities to the extinction spectrum of an isolated nanoparticle. Such resonances are attributed to localized surface plasmon resonances (LSPRs), however the array spectra are considerably affected by coupling between nanoparticles [29]. LSPRs are electron charge oscillations in metallic nanoparticles that are excited by light and at the resonance wavelength, they exhibit
enhanced, highly localized field intensity at the nanoparticle surface. Among other properties, an LSPR enables very high sub-wavelength spatial resolution as limited by the particle size, shape, and relation to neighboring particles. This work discusses plasmonically enhanced effects on hexagonal arrays of metal nanoparticles with approximately 4 nm Ag nanoparticles. There has also been work on square lattice arrays [28]. Such arrays may be useful for enhancing the efficiency of organic solar panels.

The optical absorption spectra of metal nanoparticles are dominated by LSPRs and can be tuned by changing the size, shape, particle material, substrate and coating of the metal particles. Previously, various approaches to implementing a controlled surface plasmon-active Ag film onto organic solar cells have been introduced as random Ag nano-hole films or periodic Ag nano-cavity array [55, 56, 57, 58]. In particular, enhanced optical absorption for polymerfullerene bulk hetero-junction photovoltaic (PV) devices, mainly due to the localized surface plasmon-enhanced photo generation of excitons through the usage of plasmon-active Ag nanospheres, has been demonstrated by Yoon et al [30]. While electron-beam-lithographically-prepared structures have been used to study the influence of electromagnetic interactions between the particles on extinction spectra, the effect of (inevitable) disorder due to fabrication imperfections remains an important and relatively unexplored issue [29]. Schatz and coworkers [53] investigated the effect of disorder for a two dimensional array with 30 nm particles and found that the interactions between particles are partially cancelled by disorder and blue-shifts in the observed plasmon resonances. Schatz and coworkers also studied extinction spectra of silver nanoparticles in 1D and 2D arrays as a function of particle size and inter particle distance and found that arrays
of spherical silver particles are in some cases capable of generating extremely narrow plasmon resonances due to interaction between the localized plasmons in the particles and photonic states associated with the array. Stronger coupling between particles red-shifts the plasmon peak, widens the resonance, and increases its intensity [52].

2.2 Methodology

Numerical methods, and especially the 3D finite-difference time-domain (3D FDTD) method, are instrumental for the computation of surface plasmon resonances in complex geometrical configurations, enabling the inclusion of full interaction mechanisms between particles [54]. The FDTD method discretizes the entire problem volume using hexahedral cells and then solves the coupled Maxwell’s curl equations in a marching-on-time fashion [12, 59]. In this work, plasmonically enhanced effects on a self-assembled layer of silver nanoparticles are studied by means of 3D FDTD simulations and compared against experimentally measured extinction spectra. The utilized software was FDTD Solutions 8.5.4 from Lumerical Solutions Inc. (Vancouver, BC, www.lumerical.com), along with custom scripts to model a polydisperse system.

A self-assembled layer of silver nanoparticles (Figure 2.1, left) was simulated by using 4 nm diameter and 6 nm lattice spacing. The extinction resonance is obtained at a wavelength of 465 nm, which is greater than 100 times the particle diameter. The FDTD grid utilized for the hexagonal array unit cell with Ag nanoparticles is shown schematically in Figure 2.1 (middle). An electromagnetic plane-wave light source (linearly polarized along the $x$-direction) having an effective bandwidth between wavelengths 300 nm to 800 nm is directed along the $z$-axis and is incident on the unit cell, which is embedded on a quartz substrate of thickness 4 nm. A detector
of size 6 nm × 10.3923 nm is positioned above the unit cell at a distance of approximately 45 nm to measure the intensity of light transmitted. The overall 3D FDTD simulation domain is of size 6 nm × 10.3923 nm × 150 nm. The FDTD algorithm includes automatic non-uniform meshing, implements periodic boundary conditions in the x- and y-direction, and utilizes the perfectly matched layer (PML) [60, 61, 62] absorbing boundary condition in the z-direction. The calculation time span was set to 300 fs, with a step size (dt) of 0.00038 fs, for a total of about 789,000 time steps per simulation. Each individual simulation and associated calculations required up to 25 minutes on the same system. Figure 2.1 (right) shows the simulated extinction spectra (4 nm diameter, 6 nm lattice parameter, and no other adjustable parameters) compared against the experimentally measured spectra.

Figure 2.1: Transmission electron microscopy (TEM) image of experimental self-assembled Ag nanospheres with a scale bar of 5 nm (left) (courtesy of Prof. Paul R. Berger), 3D FDTD setup of hexagonal array unit cell (center), and preliminary results comparing experimental extinction spectra and FDTD results (right) [4]
2.3 Effect of Particle Size and Lattice Parameter

Numerous prior experiments [29, 52] have shown that the optical spectra of arrays and aggregates are influenced by particle shape, size, interactions between neighboring particles, and polarization of the incident light. When the inter-particle distance is comparable to or less than the particle size, the interactions between particles play a significant role in the optical response. Initially the effects of particle radius and periodic lattice spacing on the extinction resonance of hexagonal array of Ag nanoparticles were examined. For this purpose, the original periodic lattice (center to center) spacing was held constant while varying the particle radii in steps of 0.25 nm, starting with a radius of 1 nm (where the nearest neighbors are well apart from each other) to a radius of 2.25 nm (where they are nearly touching). The resulting extinction resonances are shown in Figure 2.2a. At small particle sizes, the extinction resonance is small as much light is transmitted between particles to the detector. However as the particle size gets larger, the extinction peak becomes more prominent, due to absorption and increased scattering of light by the particle. When the particles nearly touch each other, electromagnetic coupling between adjacent nanoparticles starts distorting the resonance lineshapes. There is also an observable shift in resonance peaks to higher wavelengths with increasing particle size. Next, the original particle radius of 2 nm was maintained at a constant value while the periodic lattice (center to center) spacing was varied in steps of 0.5 nm, starting with a spacing of 10 nm (where the nearest neighbors are well apart from each other) to a spacing of 5.5 nm (where they are nearly touching). The resulting extinction resonances are shown in Figure 2.2b. As expected at large spacing, the extinction resonance is relatively small since most light goes between particles to the detector. As the center-to-center spacing is
decreased, the particles get closer and the extinction peak becomes more prominent. When the particles nearly touch each other, electromagnetic coupling between adjacent nanoparticles distorts the resonance lineshapes. Once again, there is a noticeable shift in resonance peaks to higher wavelengths with decreasing lattice spacing.

![Extinction spectra of hexagonal array of Ag nanoparticles.](image)

Figure 2.2: Extinction spectra of hexagonal array of Ag nanoparticles. (a) Constant lattice spacing (6 nm), varying radius (red circles in Fig. 2.5). (b) Constant radius (2 nm), varying lattice spacing (green circles in Fig. 2.5) [4]

### 2.4 Polydispersity

In practice, non-ideal fabrication processes result in arrays that exhibit distributions in both lattice spacing and radii, as visible in Figure 2.1 (TEM image on the
left). The effects of such variations in radii and lattice spacing on resonances can be studied by assuming a Gaussian probability distribution function for such parameters. Using the software package ImageJ, the TEM image (left of Figure 2.1) was analyzed and a binary image was created to produce a distinct contrast between the Ag nanospheres and the quartz background, as shown in Figure 2.3. ImageJ and its Java source code are in the public domain and are freely available from the National Institutes of Health (http://imagej.nih.gov/ij/).

![Binary image of experimental self assembled hex array of Ag nanospheres and their center points](image)

**Figure 2.3:** Binary image of experimental self assembled hex array of Ag nanospheres and their center points [4]

Using a scaling factor of 20.557 pixels/nm calculated from the binary image (Figure 2.3), plots of the individual particle radii ($R$) versus the corresponding particle-center-to-particle-center ($L$) values were generated (see Figure 2.4), showing Gaussian
distributions of these properties and a slight (smaller than the distribution widths) correlation between radii and lattice parameter.

Figure 2.4: Plot showing correlation between radii and lattice spacing. Experimental data points are shown as red dots, and blue circles represent points chosen for 3D FDTD simulations. Tilt of the grid lines implies correlation between $R$ and $L$.

A grid of radii and lattice parameters was chosen (see Figure 2.5, black dots) to match the range of experimental variations in Figure 2.3. The tilt of the grid lines indicates the observed correlation between radius and lattice parameter as reflected in the experimental data. 3D FDTD simulations were performed at the radii and lattice spacings of the black dots in Figure 2.5 in order to understand the impact of
the experimental distributions in radii and lattice spacing, i.e. to ascertain the effects of a lack of monodispersity in a practical fabrication process on resonances.

Figure 2.5: Geometry parameters chosen for 3D FDTD simulations (small black dots); constant lattice spacing (red circles); constant particle radius (green circles); varying particle radius, varying lattice spacing (blue circles) [4]

The extinction spectra of a related set (blue circles about black dots in Figure 2.5) are presented in Figure 2.6. This set constrains the radius ($R_i$) to a value of the lattice parameter ($L_i$) by $R_i = 0.02757L_i + 2.0089$, where both $R_i$ and $L_i$ are in units of nm. This set of spectra nicely spans the observed experimental extinction spectrum region.
2.5 Fitting Extinction Spectra of Uniform Lattices Over Range of Size and Lattice Parameters

The 3D FDTD extinction spectra \( E_j \) from a grid of \( R_i, L_i \) values (black dots in Figure 2.5) were fitted to a Lorentzian lineshape using the following equation:

\[
E_j = \frac{H}{1 + \left(\frac{\lambda_j - P}{w}\right)^2} + c \quad (2.1)
\]

In the above equation, \( j \) is an index for wavelength, \( \lambda_j \) is the wavelength, \( H \) is the peak height or intensity, \( P \) is the peak position, \( w \) is the half-width-at-half-max, and \( c \) is an offset parameter. An example of such a fit is shown in Figure 2.7.
Figure 2.7: Example of 3D FDTD model extinction spectra (in blue) fitted to a Lorentzian lineshape (in green). The best fit parameters were $H = 0.354 \pm 0.010$, $w = 33.3 \pm 2.0$, $P = 464.72 \pm 0.10$, and $c = 0.00 \pm 0.00$ [4].

Fits were also performed versus wavenumber, i.e. the reciprocal of wavelength which is proportional to energy where a Lorentzian lineshape is expected to be more appropriate, however the Lorentzian wavelength fits were better in all cases examined. Fits were obtained for the extinction spectra of all of the black dots in Figure 2.5 and the results have been presented in Table 2.1.
Table 2.1: The peak positions ($P$), peak heights ($H$), and peak widths ($W$) as full-widths-at-half-maximum for various values of nanoparticle radius ($R$) and nanoparticle array lattice parameter ($L$)

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The narrowest resonance ($W = 58.0286$ nm) was observed at $L = 7.4$ nm, and $R = 2.102$ nm. The fitted extinction lineshapes were then used to generate 3D scatter plots (blue symbols in Figure 2.8) for various radii ($R_i$) and lattice parameters ($L_i$) versus the extinction peak positions $P_i$ (top of Figure 2.8), peak heights $H_i$ (middle...
of Figure 2.8), and peak full-width-at-half-max $W_i$ ($2w_i$, bottom of Figure 2.8), where $i$ is an index over the FDTD data points (black symbols) in Figure 2.5.

![Surface plots: R vs. L vs. peak position (P, top), peak height (H, center), and FWHM (W, bottom)](image)

Figure 2.8: Surface plots: R vs. L vs. peak position (P, top), peak height (H, center), and FWHM (W, bottom) [4]

The following multiple linear regression equations give the surface fits in Figure 2.8:

$$P_i = 534.7R_i - 82.05L_iR_i + 6.341L_i^2 + 2.166L_i^2R_i$$  \hspace{1cm} (2.2)
\[ H_i = 1.233R_i - 0.2427L_iR_i - 0.01648L_i^2 + 0.02010L_i^2R_i \]  \hspace{1cm} (2.3)

\[ W_i = 96.52R_i - 18.04L_iR_i + 0.8457L_i^2 + 0.8100L_i^2R_i \]  \hspace{1cm} (2.4)

In the above equations, \( R_i, L_i, P_i \) and \( W_i \) are in units of nm and \( H_i \) is unitless (extinction). The standard deviations of the fits are 2.8 nm, 0.045, and 4.7 nm for \( P_i, H_i, \) and \( W_i \), respectively. The variance-covariance matrix shows that there are correlations between the independent variables, but this particular choice of independent variables has less correlation between variables than all others that were tried. Equations (2.2 - 2.4) allow one to predict the position, height, and width of the extinction resonance for hexagonal Ag nanoparticle arrays with \( 2.047 \text{ nm} \leq R_i \leq 2.46 \text{ nm} \) and \( 5.4 \text{ nm} \leq L_i \leq 8.29 \text{ nm} \). The surfaces are not reliable outside of these ranges.

Coupling effects are smallest when \( L \) is large and \( R \) is small, i.e. the right-hand side of the plots in Figure 2.8. All of the surfaces of Figure 2.8 increase to the left-hand side. When \( L \) is small and \( R \) is big, there is strong coupling that correlates with red-shifted peaks, more intense peaks, and wider peaks. The peak widths, \( W \) (or FWHM) relate inversely to the lifetimes of resonances, so a particular application might vary \( L \) and \( R \) to obtain the narrowest resonance and most intense peak for a desired wavelength. Narrower resonances work better for solar panel design as strong interaction of nanoparticles with light provides efficient absorption in the active layer and increases overall efficiency of the solar cell [63, 64]. These surface plots provide an excellent physical insight to help determine specifications for optimal nanoparticle radii and lattice spacing to increase absorption in solar cells. Trends can be extracted from the fits of equations (2.2 - 2.4). Consider the specific example of \( R = 2.201 \text{ nm} \), and \( L = 6.956 \text{ nm} \). The linear change in peak position with radius dominates
with $\frac{\partial P}{\partial R} = 68.8$ and $\frac{\partial P}{\partial L} = -26.1$ in units of nm of wavelength shift per nm of nanoparticle radius or lattice parameter, respectively. Likewise, the linear trends in widths dominate and are $\frac{\partial W}{\partial R} = 10.2$ and $\frac{\partial W}{\partial L} = -3.1$ in units of nm of width per nm of nanoparticle radius or lattice parameter, respectively. However, changes in peak height with either $R$ or $L$ are more complicated and not dominated by linear terms. Both change sign over the range considered, so specific values of $R$ and $L$ must be considered.

2.6 Effect of Polydispersity on Extinction Spectra

If one tries to match the experimental extinction spectrum by varying $L$ and $R$ of a homogeneous array, the predicted spectra are always narrower (see Figure 2.1, right). For nanoparticles of this small size, it is known that the permittivity can change from the bulk value as a function of particle radius [65]. However, any practical fabrication process will suffer from polydispersity, i.e. a distribution in particle sizes. It is clear from the TEM image (Figure 2.1, left) that there is a distribution in particle size and lattice spacing due to the commercial non-ideal fabrication process. To address the lack of monodispersity, additional 3D FDTD simulations were performed using a larger, non-uniform hexagonal array unit cell (Figure 2.9, top).
Figure 2.9: 3D FDTD setup (top) of hexagonal array of Ag nanoparticles with a larger, non-uniform unit cell [4]; and a comparison (bottom) of extinction spectra (E): experiment (red curve), uniform periodic hexagonal array model (blue curve), and non-uniform hexagonal array model (green curve).

While the earlier simulation involved two nanoparticles per cell, this simulation involved 36 particles per cell, and required ~2 hours on the same system. The simulation started with the positions of nanoparticles in the experimental image (Figure 2.3), to which were added variations in radius and spacing between particles from
random Gaussian deviates and distribution input values of $2.0 \pm 0.177$ nm for the mean and standard deviation of particle radius, and $5.95 \pm 0.119$ nm for the mean and standard deviation of lattice parameter. The new pattern of Ag nanoparticles (Figure 2.9, top) arising from the assumed distributions was embedded in a host substrate having an average dielectric index of 1.55. Note that in the original experiment, the self-assembled Ag nanoparticles were formed between the indium-tin oxide (ITO) coated glass substrate and poly (3,4-ethylenedioxythiophene) poly (styrene sulfonate) (PEDOT:PSS) along with a photoactive layer of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) blend film [30]. The extinction spectrum results are shown in Figure 2.9 (bottom) where the 36 particle pattern with variations is compared to that of a 2 particle homogeneous array, and the original experiment. The extinction spectra obtained using the homogeneous array is narrower and has additional higher order modes that arise due to the symmetry of the periodic hexagonal array. The 36 particle pattern with variations better emulates the lineshape of the original experimental extinction spectrum, both in its smoothness and width.

### 2.7 Conclusion

The 3D FDTD method captures the spectral behavior of hexagonal arrays of small (4 nm) Ag nanoparticles that are about 100 times smaller than the probing wavelength. The resulting extinction spectra resemble the spectra of isolated Ag nanoparticles, except that there are shifts and increases of width and intensity due to coupling between particles in the lattice. At first, the results from uniform arrays
at varying radii and lattice parameter were compared to the experimental extinction spectrum of a self-assembled hexagonal array of Ag nanoparticles with an unavoidable distribution of sizes and lattice parameters. The simulated spectra were always narrower and more structured, so a polydisperse system was modeled with a distribution of radii and lattice parameters. Polydispersity is clearly capable of explaining the breadth and smoothness of the experimental spectrum which unfortunately obscures the ability to look at other effects, such as change of the permittivity of small nanoparticles from bulk.
Chapter 3: Enhancing Transmission Resonances Using Plasmonic Metal Hole Arrays (Micro-Mesh)

3.1 Background and Introduction

In 1902, Wood [66] observed dark and bright bands in the light reflected from periodic metallic diffraction gratings. The dark bands were explained by Lord Rayleigh [67], however the bright bands remained unexplained and were referred to as Wood’s anomaly. Strong [68] showed that the angular position of reflection minima also depends on material properties, suggesting that these effects cannot solely be due to geometrical parameters. It was not until Fano explained the presence of bright bands in his seminal paper [69], by recognizing the presence of bound surface electromagnetic waves propagating along the interface of metal-dielectric between the diffraction gratings. Subsequently, these waves are now known as Fano modes. Fano recognized the similarity of these bound electromagnetic waves to the radiation by antennas near the surface of a conducting body that are now called as Sommerfeld-Zenneck waves. Although, the field of plasmonics was pioneered in the early and mid-20th century, the ability of plasmonic metal bi-gratings demonstrating Extraordinary Optical Transmission (EOT) has spurred interest very recently [70]. In EOT, transmission
peaks are observed through metal films with periodic hole arrays (>100%, when normalized to the open area of grating). Since then EOT has been demonstrated in various range of frequencies including the mid-IR [5, 71].

Figure 3.1 shows scanning electron microscope (SEM) images of Ni mesh obtained from Precision Eforming LLC (www.precisioneforming.com). The mesh is a square lattice bi-grating with a 12.7 μm lattice parameter, 5 μm square holes, and ∼2 μm thick.

![SEM images of plasmonic Ni mesh](image)

Figure 3.1: SEM images of plasmonic Ni mesh with lattice parameter $L$ of 12.7 μm, square hole width $d$ of 5 μm, and thickness of 2 μm [15].

One of the important applications of plasmonic mesh is its ability to enhance IR spectra of trapped particles. As shown previously in Chapter 1, Figure 1.5 (top) shows 5 μm polystyrene microparticle placed on ZnSe experiencing strong Mie scattering effects. A broad scattering feature can be noticed with a maximum near the size of the particle. When the particle is placed in plasmonic Ni mesh hole (12.6 μm square lattice, 5.5 μm square holes, ∼2 μm thick), the dominant effects of scattering are suppressed significantly as shown in Figure 1.5 (bottom), and the vibrations are
now the largest features. Both spectra in Figure 1.5 were recorded under the same conditions (18.75 \( \mu \text{m} \times 18.75 \mu \text{m} \) microscope window, 512 scans, 4 cm\(^{-1}\) resolution) using FTIR Spotlight 300 imaging microscope [6].

To better understand plasmonic transmission resonances of micro-mesh, consider the diffraction pattern shown in Figure 3.2 when the mesh is illuminated with laser light. The number of diffraction spots that can be observed decreases as the wavelength of light incident on the mesh increases. Similarly, the angle with which a diffraction spot exits the mesh also increases with longer wavelengths. Transmission resonances arise at wavelengths in which a specific diffraction spot is no longer transmitted. Instead, it propagates along the surface of the mesh as a surface plasmon polariton (SPP). Such a mixed state can interact with the mesh holes, coupling back out as light. The plasmonic resonances are labeled by the \((i,j)\) values which identify the corresponding diffraction spots.

![Figure 3.2: Schematic of diffraction spots showing how the spacing between diffraction spots increases as the wavelength increases. At some specific wavelength, a spot will no longer be transmitted. Instead it propagates parallel to the surface of the mesh as an evanescent wave [16].](image)
Schematic defining angles of rotation for dispersion experiments, with light incident on the mesh along the z-axis is shown in Figure 3.3. Simulations and experiments discussed in this chapter corresponds to the Γ-X space i.e. varying $\theta$ (rotation about $y$-axis), while keeping $\phi$ (rotation about z-axis) equal to 0.

Figure 3.3: Schematic defining angles of rotation for dispersion experiments, with light incident on the mesh along the z-axis.
3.2 SPPs and Cavities

One of the early issues in mesh dispersion was that mesh resonances were pushed far away from the light line. This could be due to strong cavity coupling with the width of the hole along the mesh surface. The edges of square mesh holes can act like etalons along the surface of the mesh, i.e. the SPPs are reflected or transmitted. In other words, the observations are complicated because SPPs interact with cavities.

The SPP dispersion curves for gratings in two dimensions is

\[
\tilde{\nu}_{SPP,i,j} = \frac{1}{2\pi n_{\text{eff}}} \sqrt{\left( k_x + i\frac{2\pi}{L} \right)^2 + \left( k_y + j\frac{2\pi}{L} \right)^2}
\]

where \( L \) is the lattice parameter, wavevector \( k_x = 2\pi\tilde{\nu}\sin\theta\cos\phi \), wavevector \( k_y = 2\pi\tilde{\nu}\sin\theta\sin\phi \), \( \theta \) is the tilt angle of mesh from the perpendicular incident direction of light (see Figure 3.3), \( \phi \) is rotation about the incident light direction (zero in this case, see Figure 3.3), \( i \) and \( j \) are the Bragg indices identifying a particular SPP, and \( n_{\text{eff}} \) is the real part of a smooth metal SPP \( \sqrt{\left( \epsilon_m\epsilon_d \right) / \left( \epsilon_m + \epsilon_d \right)} \) in which \( \epsilon_m = \epsilon_m' + i\epsilon_m'' \) is the complex permittivity of the metal and \( \epsilon_d \) is the permittivity of the dielectric. In the \( \Gamma\)-\( X \) geometry, \( k_y = 0 \), and \( k_x = 2\pi\tilde{\nu}\sin\theta \).

A dispersion equation has been previously derived [72] for the position of fringe associated with an IR parallel plate cavity (i.e. each hole in the mesh) as the incident angle is changed

\[
\tilde{\nu}_{\text{CAV}} = \frac{1}{2\pi} \left( \frac{n_b}{n_2} \right) \sqrt{\left( m\pi / n_b d \right)^2 + k_x^2}
\]

where \( n_2 \) is the refractive index of the dielectric in the cavity, \( n_b \) is the background refractive index, \( m \) is the mode of the cavity, and \( d \) is the thickness of the cavity.
The dispersion curves for cavities from equation (3.2) are modified for the origins, \( r, s \) of different holes in two dimensions giving

\[
\tilde{\nu}_\text{CAV},r,s = \frac{1}{2\pi} \left( \frac{n_b}{n_2} \right) \sqrt{\left( \frac{m\pi}{n_b d} \right)^2 + \left( k_x + r \frac{2\pi}{L} \right)^2 + \left( k_y + s \frac{2\pi}{L} \right)^2}
\] (3.3)

In order to better understand the splittings of transmission resonances, calculations were performed at fixed values of the reduced wavevector

\[
k_x' = k_x(\text{reduced}) = \frac{k_x}{2\pi/L}
\] (3.4)

in the \( \Gamma-X \) geometry of mesh.

Figure 3.4 shows the experimental dispersion data of mesh with \( L=12.7 \ \mu\text{m}, \ d=5 \ \mu\text{m}, \ \text{and thickness of 2} \ \mu\text{m in} \ \Gamma-X \ \text{space (i.e. with} \ k_y=0), \ \text{with polarizer set at} \ 0^\circ \ \text{and} \ 90^\circ \ \text{respectively. Details of the experiment is provided in [73]. The mesh assembly was placed inside the Spotlight 400 FTIR benchtop spectrometer having liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detectors. Dispersion curves for SPP and cavity modes are defined by equations (3.1) and (3.2) respectively. It appears that the experimentally measured peak positions are not following the SPP (black) or cavity (magenta) curves, although they are certainly related.}
Figure 3.4: Γ-X dispersion diagram with experimental transmission on Ni mesh with 5.0 µm square holes, $L=12.7$ µm, thickness of 2 µm. Experimental results are shown as blue symbols for 0° (p-like) polarized light, and green symbols for 90° (s-like) polarized light. SPP modes are plotted as black lines and cavity modes as magenta lines.

Computational 3D FDTD results can be used to interpret and enhance experimental plasmonic work on micro-mesh. As shown in Figure 3.5, the mesh was modeled as a 2 µm film of Ni (Palik) material, perforated by a square pattern of square holes of size 5 µm, and a lattice parameter ($L$) of 12.7 µm. The simulation cell was 12.7 µm $\times$ 12.7 µm $\times$ 70 µm. The simulation region had absorbing (PML) boundary conditions (BCs) at the ends, periodic BCs along the sides parallel to the electric field, and Bloch BCs along the sides perpendicular to the electric field. The Bloch BCs were used to simulate the effects of a non-zero momentum component intersecting those boundaries, which allowed the indirect calculation of the effect of light interacting with the
mesh at non-perpendicular angles. The source was a pulse of light with broad band of frequencies (400 cm\(^{-1}\) to 1200 cm\(^{-1}\)) propagating along the z-axis and it was placed -30 \(\mu\)m from the center of the simulation cell. The detector was positioned at +30 \(\mu\)m at the other end of the simulation cell. The utilized software was FDTD Solutions 8.12.527 from Lumerical Solutions, Inc. (Vancouver, BC, www.lumerical.com).

Figure 3.5: 3D FDTD simulation setup with a unit cell of the mesh at the center of the simulation region which was 12.7 \(\mu\)m \(\times\) 12.7 \(\mu\)m \(\times\) 70 \(\mu\)m. Periodic boundary conditions simulate the periodicity of micro-mesh. In a simple simulation, a pulse of light with broad band of frequencies (400 cm\(^{-1}\) to 1200 cm\(^{-1}\)) is directed along the z-axis. In full simulations, light is effectively directed towards the mesh at variable angles for different wavelengths by fixing \(k_x\) using Bloch boundary conditions. At the top, polarization of probing light is 0°. At the bottom, polarization of probing light is 90°.
The calculation time span was set to 10,000 fs, with a step size \((dt)\) of 0.0851 fs, for a total of about 117,500 time steps per simulation. Transmission spectra were calculated at reduced (dimensionless) wavevector values of 0 to 0.5 in steps of 0.025 producing 21 different spectra. Each individual fixed \(k_x\) simulation with Bloch boundary conditions and associated calculations required about 3 hours on the same system.

Transmission spectra versus reduced wavevector calculated using 3D FDTD simulations are shown at the top of Figure 3.6 for mesh with hole size \(d=5.0\ \mu m\). Two different polarizations were calculated for the mesh with \(d=5.0\ \mu m\) showing very different behavior. Dispersion curves are plotted below in Figure 3.6 by plotting positions of transmission maxima. The SPP dispersion curves are in plotted black, and the cavity dispersion curves are in magenta.
Figure 3.6: 3D FDTD simulations of transmission spectra (top) of a metal mesh in Γ-X geometry. Transmission maxima were found and plotted in the form of dispersion plots at the bottom. Blue circles are for 0° (p-like) polarized light, and green circles for 90° (s-like) polarized light. Black lines are SPP dispersion curves (equation (3.1) with φ=0, and k_y=0) and magenta lines are cavity dispersion curves (equation (3.3) with φ=0, and k_y=0). Results on mesh (5 µm square holes, L=12.7 µm, thickness of 2 µm)

From these results, it can be observed that cavity interactions perturb the SPPs on mesh, particularly the top of the dispersion plots. If the mesh was a one-dimensional grating, then only p-polarized SPPs (like top, left) can be observed, and nothing in the s-polarized direction (top, right). The features at top, right only show up for 2-dimensional gratings (such as mesh).
In the case of $0^\circ$ ($p$-like) polarized light, when $\theta$ is changed, the component of electric field changes at surfaces giving rise to strong dispersion. In the case of $90^\circ$ ($s$-like) polarized light, when $\theta$ is changed, the component of electric field is not changed resulting in less dispersion. The SPP$_{0,\pm1}$ states are split only when the polarization is $90^\circ$. This might be called an SPP-cavity polariton.

Figures 3.7 and 3.8 show comparison of 3D FDTD simulation results (hollow circles) with experimental results (solid circles) on mesh with 5 $\mu$m square holes, $L=12.7$ $\mu$m, thickness of 2 $\mu$m when polarization of probing light is $0^\circ$ and $90^\circ$ respectively. Notice that while the SPP curves are unable to fully model the experimental data, they do accurately predict peak positions obtained from the 3D FDTD simulations.

![Figure 3.7](image_url)

**Figure 3.7:** Comparison of 3D FDTD simulations (hollow circles) with experimental results (solid circles) on mesh with 5.0 $\mu$m square holes, $L=12.7$ $\mu$m, thickness of 2 $\mu$m when polarization of probing light is $0^\circ$ ($p$-like)
In Figure 3.7, the cavity does not affect the SPP\(_{-1,0}\) very much. Strictly speaking, SPP\(_{0,\pm 1}\) is not present in \(p\)-polarization of light for 1D gratings. However, in the case of 2D gratings (mesh), a little leaks through due to interaction between \(s\) and \(p\) polarizations of light. This results in SPP\(_{0,\pm 1}\) of very weak intensity, but there is no observable splitting. Also, there is observable evidence of interaction between cavity and SPP in the region between 900 cm\(^{-1}\) to 1100 cm\(^{-1}\) (top of dispersion plot), but it is hard to interpret.

Figure 3.8: Comparison of 3D FDTD simulations (hollow circles) with experimental results (solid circles) on mesh with 5.0 \(\mu m\) square holes, \(L=12.7\ \mu m\), thickness of 2 \(\mu m\) when polarization of probing light is 90\(^o\) (s-like)

In Figure 3.8, both experiment and 3D FDTD show splitting for SPP\(_{0,\pm 1}\). Notice how the splitting follows the shape of CAV\(_{0,0}\).
3.3 Analysis and Results

Figure 3.9 (top) shows dispersive transmission lineshapes for mesh with 4.4 $\mu$m square holes, $L=12.7 \, \mu$m, thickness of 2 $\mu$m. Figure 3.9 (bottom) shows transmission maxima for 90° polarization (s-like). SPP dispersion curves are plotted in black. Cavity dispersion curves are off the plot.
Figure 3.9: Results on mesh with 4.4 µm square holes (as compared to 5.0 µm in Figure 3.8), $L=12.7$ µm, thickness of 2 µm

Figure 3.10 (top) shows dispersive transmission lineshapes for mesh with 4.7 µm square holes, $L=12.7$ µm, thickness of 2 µm. Figure 3.10 (bottom) shows transmission maxima for 90° polarization ($s$-like). Black lines are SPP dispersion curves and magenta lines are cavity dispersion curves.
Figure 3.10: Results on mesh with 4.7 \( \mu m \) square holes, \( L=12.7 \mu m \), thickness of 2 \( \mu m \)

Figure 3.11 (top) shows dispersive transmission lineshapes for mesh with 5.0 \( \mu m \) square holes, \( L=12.7 \mu m \), thickness of 2 \( \mu m \). Figure 3.11 (bottom) shows transmission maxima for 90° polarization (s-like). Black lines are SPP dispersion curves and magenta lines are cavity dispersion curves.
Figure 3.11: Results on mesh with 5.0 µm square holes, \( L=12.7 \) µm, thickness of 2 µm.

Figure 3.12 (top) shows dispersive transmission lineshapes for mesh with 5.3 µm square holes, \( L=12.7 \) µm, thickness of 2 µm. Figure 3.12 (bottom) shows transmission maxima for 90° polarization (s-like). Black lines are SPP dispersion curves and magenta lines are cavity dispersion curves.
Figure 3.12: Results on mesh with 5.3 $\mu$m square holes, $L=12.7\,\mu$m, thickness of 2 $\mu$m

Figure 3.13 (top) shows dispersive transmission lineshapes for mesh with 5.6 $\mu$m square holes, $L=12.7\,\mu$m, thickness of 2 $\mu$m. Figure 3.13 (bottom) shows transmission maxima for 90° polarization (s-like). Black lines are SPP dispersion curves and magenta lines are cavity dispersion curves.
As seen in Figures 3.12 and 3.13, the closer CAV$_{0,0}$ gets to SPP$_{0,\pm1}$, the stronger the interaction.

The dispersion plots in Figures 3.9 - 3.13 were used to study the effects of varying hole size of micromesh on (a) splitting between transmission maxima of CAV$_{0,0}$ -

Figure 3.13: Results on mesh with 5.6 $\mu$m square holes, $L$=12.7 $\mu$m, thickness of 2 $\mu$m
SPP\(_{0,\pm1}\) mixed states obtained from the 3D FDTD simulations (i.e. 3D FDTD transmission maxima of mixed state), (b) shift between 3D FDTD transmission maxima of mixed state and SPP\(_{0,\pm1}\) dispersion curve, and (c) shift between CAV\(_{0,0}\) and SPP\(_{0,\pm1}\) dispersion curve. This analysis was done within a small domain of \(\Gamma-X\) space (800 cm\(^{-1}\) \(\leq k_x \leq 1400\) cm\(^{-1}\)) and (700 cm\(^{-1}\) \(\leq \tilde{\nu} \leq 1200\) cm\(^{-1}\)).

As the mesh hole size \((d)\) was increased from 4.4 \(\mu\)m to 5.6 \(\mu\)m, the splitting between the 3D FDTD transmission maxima of mixed state also increased, from 22 cm\(^{-1}\) to 40 cm\(^{-1}\) as shown in Table 3.1 and Figure 3.14. This is evidence that the splitting is not constant and is affected by the size of mesh hole \((d)\).

![Figure 3.14: 3D FDTD model splitting of SPP\(_{0,\pm1}\)](image)

As the mesh hole size \((d)\) was increased from 4.4 \(\mu\)m to 5.6 \(\mu\)m, the shift between 3D FDTD transmission maxima of mixed state and SPP\(_{0,\pm1}\) dispersion curve increased almost linearly, from 10 cm\(^{-1}\) to 39 cm\(^{-1}\) as shown in Table 3.1 and Figure 3.15.
As the mesh hole size \((d)\) was increased from 4.4 \(\mu\)m to 5.6 \(\mu\)m, the shift between \(\text{CAV}_{0,0}\) and \(\text{SPP}_{0,\pm1}\) curve defined by their respective analytical equations decreased from 349 cm\(^{-1}\) to 107 cm\(^{-1}\) as shown in Table 3.1 and Figure 3.16. This suggests that as \(d\) is increased, it should result in more interaction between \(\text{CAV}_{0,0}\) and \(\text{SPP}_{0,\pm1}\) modes. This result is consistent with the noticeable increase in splitting between the 3D FDTD transmission maxima of mixed state (Figure 3.14).
Table 3.1: SPP - Cavity interaction measurements

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<tr>
<td>5.0</td>
<td>34</td>
<td>20</td>
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</tr>
<tr>
<td>5.3</td>
<td>32</td>
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<td>157</td>
</tr>
<tr>
<td>5.6</td>
<td>40</td>
<td>39</td>
<td>107</td>
</tr>
</tbody>
</table>

3.4 Conclusion

Results of the 3D FDTD simulations were used to study the effects of varying hole size of micromesh on (a) splitting between transmission maxima of CAV$_{0,0}$-SPP$_{0,\pm 1}$
mixed states obtained from the 3D FDTD simulations (i.e. 3D FDTD transmission maxima of mixed state), (b) shift between 3D FDTD transmission maxima of mixed state and SPP$_{0,\pm 1}$ dispersion curve, and (c) shift between CAV$_{0,0}$ and SPP$_{0,\pm 1}$ dispersion curve. It was shown that as mesh hole size was increased, it resulted in more interaction between the SPP$_{0,\pm 1}$ and CAV$_{0,0}$ modes. This is definitive evidence that cavity affects the SPPs. The SPP is already a mixed state, so the SPP-cavity polariton is a mixture of surface plasmons, IR light at the surface, and a cavity. There are many higher order combinations to be discovered.
Chapter 4: Plasmonically Enhanced Effects on Metal Nanorings

4.1 Background

Among the wide variety of nanoparticles with diverse shapes, nanorings are of particular interest because they exhibit novel and unique properties in sensing [74], magnetic configuration [75], optical response [76] and plasmonic behavior [77]. Previous works have shown that the optical response of metallic nanoparticles depends on the size and shape of particles and surrounding dielectric background media [78, 79]. Localized surface plasmon resonances (LSPRs) due to coherent electron oscillations that are excited at metal-dielectric interfaces yield highly localized field enhancement and can provide guidance and confinement of electromagnetic waves below the diffraction limit via near-field coupling between closely spaced nanoparticles. Nanoring particles have better tunability and allow for further size reduction compared to nanospheres and nanodisks, because of the extra degree of freedom (DoF) in the geometry. LSPR in nanorings can be tuned by changing the radial thickness, the outer diameter, or the height. For example, the LSPR is shifted to longer wavelengths by increasing the diameter-to-height ratio of the nanoring. The electromagnetic coupling between the inner and outer ring surfaces plays an important role in optical plasmon resonance [31]. Simulations employing 3D FDTD can be used to determine the set of
geometrical parameters to attain LSPR, and also capture shifts in resonances due to changes in effective dielectric of the structure, which is useful in sensing applications. The software utilized for all the 3D FDTD simulations was provided by Lumerical Solutions, Inc. (Vancouver, BC, www.lumerical.com).

4.2 Plasmonic Resonances in Isolated Au Nanoring

Plasmonic resonances at optical frequencies can be studied using FDTD simulations. The setup in Figure 4.1 shows an electromagnetic plane wave light source ($y$-polarized, 235 nm × 35 nm) having wavelengths 700 nm to 2500 nm incident on a Au nanoring with outer diameter of 235 nm, inner diameter of 175 nm, and height of 35 nm embedded in SiO$_2$ host media. In this setup, light propagates along the plane of the ring. A detector of size 350 nm × 350 nm is positioned above the nanoring at a distance of 240 nm to measure the intensity of light transmitted by the nanoring perpendicular to the plane of incidence. The simulation region is of size 750 nm × 500 nm × 500 nm, includes auto conformal meshing (see Figure 4.2), and all absorbing, perfectly matched layer (PML) boundary conditions (BCs).
Figure 4.1: 3D FDTD simulation setup of isolated Au nanoring in SiO$_2$ host media
The geometrical parameters of the ring are mean radius \((r)\), thickness \((w)\), height \((h)\), and gap \((g)\) as shown in Figure 4.3.
The simulation is done for three cases: (a) full i.e. closed ring with no gap, (b) split ring with a gap of 20 nm, and (c) split ring with a gap of 20 nm plus a structure of size 90 nm × 20 nm × 35 nm. The transmission resonances are measured by the detector for each case and these are used to compute the extinction resonances shown in Figure 4.4.
Figure 4.4: Comparison of extinction resonances of Au/SiO$_2$ nanorings at optical frequencies, with $g=20$ nm for split rings

Figure 4.4 shows comparison of extinction resonances of Au/SiO$_2$ nanorings at optical frequencies. The extinction observed for closed ring has relatively higher intensity. Nanorings have two distinct modes - a forward propagating mode, and a backward propagating mode. Coupling between these two modes distorts the ideal Lorentzian-shaped spectrum, giving rise to resonance splitting [80], and this can be observed in all three cases above.

4.3 Analytical Model for Estimating Isolated Au Nanoring Resonances

In this section, a lumped parameter model for estimating Au nanorings resonances is derived for various source polarizations. This model associates various lumped
circuit parameters such as resistance \( (R) \), inductance \( (L) \), and capacitance \( (C) \) to material and geometrical parameters of the ring (such as thickness \( (w) \), mean radius \( (r) \), and height \( (h) \)). Similar expressions have been previously derived in [17, 81].

The resonant frequency of a nanoring is inversely proportional to the total inductance and capacitance [81].

\[
\omega = \frac{1}{\sqrt{LC}} = \frac{2\pi c}{\lambda} \quad (4.1)
\]

In other words, the resonant wavelength is directly proportional to the total inductance \( (L) \) and capacitance \( (C) \).

\[
\lambda \propto \sqrt{LC} \quad (4.2)
\]

### 4.3.1 Effect of Capacitance

In the case of split rings, there are two types of capacitances: the gap capacitance \( (C_g) \), and the surface capacitance \( (C_s) \). The capacitance of the ring due to the gap is a parallel-plate capacitor whereas the surface capacitance is provided by charges on the ring’s surfaces. The total capacitance is the sum of the gap and surface capacitances. Geometrical parameters determine whether or not the surface capacitance contributes much to the total capacitance. From earlier studies [81], it has been determined that if the gap is narrow, the gap capacitance dominates, but not enough to neglect the surface capacitance. As the gap widens, the gap capacitance decreases faster than the surface capacitance. For wide gaps, both capacitances contribute approximately the same amount.

The capacitance (especially for narrow gaps) is written as

\[
C_g = \varepsilon_0 \frac{hw}{g} + C_0 \quad (4.3)
\]
where \( \varepsilon_0 \) is the free-space permittivity. The first term on the right-hand side is the parallel-plate capacitor formed by the gap, and the second term is a correction factor taking into account the fringing fields.

\[
C_0 = \varepsilon_0 (h + w + g) \quad (4.4)
\]

The surface capacitance per unit height (p.u.h) is defined as

\[
C_s^{(p.u.h)} = \int_0^{\pi} \frac{\sigma(\theta) r}{V(\theta)} d\theta \quad (4.5)
\]

where \( \sigma, V, \theta, \) and \( \theta_g \) have been previously defined.

Also,

\[
V = \frac{V_0}{\pi} (\pi \theta) \quad (4.6)
\]

where \( V_0 \) is the gap voltage.

By substituting equations,

\[
C_s^{(p.u.h)} = \varepsilon_0 \int_0^{\pi} \frac{\cot \frac{\theta_g}{2}}{\pi - \theta} d\theta \quad (4.7)
\]

The above integral cannot be found analytically. However, for small \( \theta_g \), the value of \( \cot(\theta_g/2) \) is large enough to neglect \( \theta \) in the denominator. Therefore,

\[
C_s^{(p.u.h)} \approx \frac{\varepsilon_0}{\pi} \int_{\theta_g}^{\pi} \frac{\theta}{2} d\theta = \frac{2\varepsilon_0}{\pi} \log \frac{4r}{g} \quad (4.8)
\]

Taking \( \theta_g = g/2r \) for small gaps, the surface capacitance of the split ring with mean radius \( r \), thickness \( w \), height \( h \), and gap size \( g \) is hence given by the expression

\[
C_s = (h + w) C_s^{(p.u.h)} \quad (4.9)
\]

Substituting for \( C_s^{(p.u.h)} \) gives,
\[ C_s = \frac{2\varepsilon_0(h + w)}{\pi} \log \frac{4r}{g} \] (4.10)

In case of full rings (i.e. closed rings with no gap), the total capacitance is equivalent to the surface capacitance \( C_s \) and the gap capacitance \( C_g \) does not exist.

### 4.3.2 Effect of Inductance

In the case of an isolated nanorings and split rings, the total inductance \( L \) is equivalent to the self inductance \( L_s \) which can be written as \[ L = \mu_0 r_m \left( \log \frac{8r_m}{h + w} - \frac{1}{2} \right) \] (4.11)

where \( \mu_0 \) the free space permeability and \( r_m = r + w/2 \)

### 4.4 Effect of Nanoring Shape on Extinction Resonances

Previously, extinction resonances of isolated circular nanorings were studied. In this section, the effect of the nanoring’s shape on its extinction resonances is analyzed using 3D FDTD simulations.

The 3D FDTD simulation setup shown in Figure 4.5 is similar to the setup previously shown in Figure 4.1, with an electromagnetic plane wave light source (y-polarized, 235 nm × 35 nm) having wavelengths 700 nm to 2500 nm incident on a square Au nanoring of size 235 nm × 235 nm, thickness of 30 nm, and height of 35 nm embedded in SiO\(_2\) host media. As before, light propagates along the plane of the ring. A detector of size 350 nm × 350 nm is positioned above the nanoring at a distance of 240 nm to measure the intensity of light transmitted by the nanoring.
perpendicular to the plane of incidence. The simulation region is of size $750 \text{ nm} \times 500 \text{ nm} \times 500 \text{ nm}$, includes auto conformal meshing, and all absorbing (PML) BCs.

Figure 4.5: 3D FDTD simulation setup of isolated square Au nanoring in SiO$_2$ host media

The simulation is again done for three cases: (a) full i.e. closed ring with no gap, (b) split ring with a gap of 20 nm, and (c) split ring with a gap of 20 nm plus a structure of size $90 \text{ nm} \times 20 \text{ nm} \times 35 \text{ nm}$. The transmission resonances are measured
by the detector for each case and these are used to compute the extinction resonances shown in Figure 4.6.

![Figure 4.6: Comparison of extinction resonances of square Au/SiO$_2$ nanorings at optical frequencies, with $g=20$ nm for split rings](image)

A comparison of extinction resonances of square Au/SiO$_2$ nanorings at optical frequencies is presented in Figure 4.6. These are similar to the results obtained for circular rings. However, there are additional broad modes present at higher frequencies (i.e. smaller wavelengths). These can be attributed to energy losses at the sharp corners of square rings [82].

### 4.5 Plasmonic Effects in Arrays of Au Nanorings

The study on isolated nanorings can be further extended to arrays of Au nanorings. In this section, the effects of inter-element coupling are studied using 3D
FDTD simulations for periodically-arranged (uniform) versus randomly-distributed (non-uniform) dispersions of nanorings. The resulting shift and behavior of the resonant peaks are investigated.

Figures 4.7, 4.8, and 4.9 show 3D FDTD simulation setup for two, three, and $3 \times 3$ array of uniformly spaced Au nanorings in SiO$_2$ host media. The electromagnetic plane wave light source ($y$-polarized, 235 nm $\times$ 35 nm) having wavelengths 700 nm to 2500 nm is incident on the Au nanoring array. Each nanoring has outer diameter of 150 nm, thickness of 41.5 nm, and height of 50 nm embedded in SiO$_2$ host media. The center-to-center spacing between adjacent nanorings is 225 nm. As before, light propagates along the plane of the ring. A detector positioned above the nanoring array at a distance of 240 nm measures the intensity of light transmitted perpendicular to the plane of incidence. The simulation region includes auto conformal meshing, and all absorbing (PML) BCs.

In Figure 4.7, the simulation region is of size $750 \text{ nm} \times 500 \text{ nm} \times 500 \text{ nm}$, and the detector is of size $375 \text{ nm} \times 375 \text{ nm}$. In Figure 4.8, the simulation region is of size $975 \text{ nm} \times 500 \text{ nm} \times 500 \text{ nm}$, and the detector is of size $600 \text{ nm} \times 375 \text{ nm}$. In Figure 4.9, the simulation region is of size $975 \text{ nm} \times 750 \text{ nm} \times 500 \text{ nm}$, and the detector is of size $600 \text{ nm} \times 600 \text{ nm}$.
Figure 4.7: 3D FDTD simulation setup of two Au nanorings in SiO$_2$ host media
Figure 4.8: 3D FDTD simulation setup of three uniformly spaced Au nanorings in SiO$_2$ host media
In Figure 4.10, comparison of extinction resonances for uniform dispersion of Au nanorings in SiO$_2$ host media is presented on increasingly larger structures. It can be observed that the number of splits in the optical resonance increases with array size. At this size relative to the wavelength of incident light, an isolated ring produces one peak with no splitting, two rings produce two similar peaks, three rings produce two unequal peaks, and a $3 \times 3$ array of rings produce three peaks due to greater mutual coupling between the rings.
Figures 4.11, and 4.12 show 3D FDTD simulation setup for three, and 3 × 3 array of non-uniformly spaced Au nanorings in SiO₂ host media. The electromagnetic plane wave light source (y-polarized, 235 nm × 35 nm) having wavelengths 700 nm to 2500 nm is incident on the Au nanoring array. Each nanoring has outer diameter of 150 nm, thickness of 41.5 nm, and height of 50 nm embedded in SiO₂ host media. As before, light propagates along the plane of the ring. A detector positioned above the nanoring array at a distance of 240 nm measures the intensity of light transmitted perpendicular to the plane of incidence. The simulation region includes auto conformal meshing, and all absorbing (PML) BCs.
In Figure 4.11, the simulation region is of size $975\ \text{nm} \times 500\ \text{nm} \times 500\ \text{nm}$, and the detector is of size $562.5\ \text{nm} \times 375\ \text{nm}$. In Figure 4.12, the simulation region is of size $975\ \text{nm} \times 750\ \text{nm} \times 500\ \text{nm}$, and the detector is of size $562.5\ \text{nm} \times 600\ \text{nm}$.

Figure 4.11: 3D FDTD simulation setup of three non-uniformly spaced Au nanorings in SiO$_2$ host media
Figure 4.12: 3D FDTD simulation setup of $3 \times 3$ array of non-uniform dispersion of Au nanorings in SiO$_2$ host media

In Figure 4.13, a comparison of extinction resonances for non-uniform dispersion of Au nanorings in SiO$_2$ host media is presented on increasingly larger structures. Similar to uniform dispersions (shown previously), it can be observed that the number of splits in the optical resonance increases (as expected) with array size. The most notable feature is in the extinction spectra of the $3 \times 3$ array of rings, with maximum intensity for the middle peak, corresponding to maximum coupling at the center ring.
Figure 4.13: Comparison of extinction resonances for non-uniform dispersion of Au nanorings in SiO$_2$ host media

Figures 4.14 and 4.15 show pairwise comparisons of extinction resonances (uniform versus non-uniform dispersion) for three and $3 \times 3$ array of Au/SiO$_2$ nanorings respectively.
Figure 4.14: Comparison of extinction resonances for three Au nanorings in SiO$_2$ host media

Outer diameter = 150 nm
Thickness (w) = 41.5 nm
Height (h) = 50 nm
Closely spaced nanorings might couple electromagnetically. Along with surface capacitance ($C_s$) and gap capacitance ($C_g$), a coupling capacitance ($C_c$) will also be present. The total inductance will be a sum of the self inductance ($L_s$) and mutual inductance ($L_m$). An analytical model for estimating Au nanorings array resonances is presented in Appendix A.

Resonance frequency can be expressed as \[ \omega_0 = \frac{1}{\sqrt{(L_s + 4L_m)(C_s + C_c + C_g)}} \] (4.12)

In case of periodic arrangement, all coupling capacitances between any two adjacent nanorings will be the same. Likewise, all mutual inductances between any two adjacent nanorings will be the same.

Figure 4.15: Comparison of extinction resonances for $3 \times 3$ array of Au nanorings in SiO$_2$ host media
On the other hand, in case of randomly-distributed rings, the coupling capacitances and mutual inductances between any two adjacent nanorings will vary depending on geometry, and lattice spacing.

4.6 Applications: Sensing

Particles trapped in nanorings change the effective dielectric of the structure, shifting the overall optical response. In this section, 3D FDTD models are used to investigate these shifts in resonances, which is useful in sensing applications.

The 3D FDTD setup in Figure 4.16 shows an electromagnetic plane wave light source (x-polarized, 1250 nm × 1250 nm) having wavelengths 50 nm to 1550 nm incident on a Au nanoring with outer diameter of 1000 nm, inner diameter of 600 nm, and height of 500 nm. The particle is a polystyrene sphere of size (diameter) 500 nm. In this setup, light propagates perpendicular to the plane of the ring. A detector of size 1250 nm × 1250 nm is positioned above the nanoring at a distance of 750 nm to measure the intensity of light transmitted by the nanoring along the plane of incidence. The simulation region is of size 1500 nm × 1500 nm × 1750 nm, includes auto conformal meshing, and all absorbing (PML) BCs.
Figure 4.16: Shift in optical response due to particle trapped in isolated Au nanoring

The 3D FDTD setup in Figure 4.17 shows an electromagnetic plane wave light source (x-polarized, 3000 nm × 3000 nm) having wavelengths 50 nm to 1550 nm incident on a hexagonal arrangement of Au nanorings, with each ring having an outer diameter of 1000 nm, inner diameter of 600 nm, and height of 500 nm. The particle is a polystyrene sphere of size (diameter) 500 nm. In this setup, light propagates perpendicular to the plane of the ring. A detector of size 3000 nm × 3000 nm is positioned above the nanorings at a distance of 750 nm to measure the intensity of light transmitted by the nanorings along the plane of incidence. The simulation region is of size 3500 nm × 3500 nm × 1750 nm, includes auto conformal meshing, and all absorbing (PML) BCs.
Figure 4.17: Shift in overall optical response due to particle trapped between Au nanorings

In Figures 4.16, 4.17 it can be observed that the inclusion of a particle within an isolated nanoring, and between adjacent nanorings respectively, shifts the transmission resonances, and also gives rise to additional optical modes. This is because the presence of particle affects the effective dielectric of the structure and it results in resonance shifts in the transmission spectrum.

The 3D FDTD setup in Figure 4.18 shows an electromagnetic plane wave light source (\(x\)-polarized) having wavelengths 50 nm to 1550 nm incident on a Au nanoring with outer diameter of 1000 nm, inner diameter of 600 nm, and height of 500 nm. The particle is a polystyrene sphere of size (diameter) 500 nm. In this setup, light propagates perpendicular to the plane of the ring. The detector is positioned above...
the nanoring at a distance of 750 nm to measure the intensity of light transmitted by the nanoring along the plane of incidence. The simulation region is of size 1250 nm × 1250 nm × 1750 nm, includes auto conformal meshing, absorbing (PML) BCs at the ends, and periodic BCs along the other sides to simulate the periodicity of an array of Au nanorings.

![FDTD setup: Au nanoring array, PERIODIC BCs (x, y)](image1)

![FDTD setup: Au nanoring + particle array, PERIODIC BCs (x, y)](image2)

Figure 4.18: Shift in overall optical response due to particles trapped in periodic array of Au nanorings

In Figure 4.18, a particle is present in every hole of a periodic nanoring array. Due to periodicity, Wood’s anomaly (characteristic of periodic subwavelength structures) can be observed at a wavelength equal to the array lattice parameter (1250 nm). As before, inclusion of particle in every hole of the array shifts resonances in the spectra due to change in effective dielectric.
4.7 Conclusion

3D FDTD simulations and analytical models were used to study plasmonic effects on isolated and arrays of Au nanorings. This provided a good understanding on how optical resonances of sub-wavelength structures can be tuned with respect to their geometries. Nanoring structures enable higher LSPR tunability due to the extra DoF in the geometry. It was shown that a change in the effective dielectric of the structure affects the overall optical response, which is beneficial in sensing applications.
Chapter 5: Spectral Challenges of Individual Wavelength-Scale Particles

5.1 Background and Introduction

Single particle techniques [83, 84, 45] such as infrared (IR) spectroscopy [85, 8, 86, 87] are of interest in many fields of science. Scatter-free infrared (IR) transmission spectra of single particles can be recorded using plasmonic Ni mesh [5], i.e. by trapping the particles in periodic holes of a thin metal film which suppresses scattering. This type of single particle IR spectroscopy [85, 8] can serve as a quantitative and non-destructive method that identifies individual particles for further study. This chapter focuses on vibrational features in spectral regions dominated by scattering, and on quantifying the amount of a particle component by the strength of such vibrational features.

3D-FDTD is a direct numerical integration of Maxwell’s equations [12], and the simulations provide a transmission spectrum which can be interpreted just like an experiment. Simulations were obtained on slabs and spheres of the same volume in order to assess the applicability of the Beer-Lambert [18, 19] law and to investigate dispersive contributions to lineshape. Then, simulations on cylinders and aggregates of spheres are used to show simple, non-Beer-Lambert behavior and then more dramatic effects when more vibrations are involved. A number of fundamental questions
are addressed, such as the effect of scattering on strong vibrational lineshapes, the validity of Beer-Lambert law, and the treatment of mixtures of components in a particle.

5.1.1 The Beer-Lambert Law

The Beer-Lambert [18, 19] law relates the absorption of light to the properties of the material through which the light is traveling. In other words, it is a linear relationship between absorbance and concentration of an absorber of electromagnetic radiation. The general Beer-Lambert law is written as:

$$A = alc$$

where $A$ is the measured absorbance, $a$ is wavelength-dependent molar extinction coefficient, $l$ is the path length, and $c$ is the sample concentration. Experimental measurements are usually made in terms of transmittance $T$, which is defined as $T = I_1 / I_o$, where $I_1$ is the light intensity after it passes through the sample and $I_o$ is the initial light intensity as shown in Figure 5.1.

![Figure 5.1: Absorption of light by a sample [18, 19, 20]](image-url)
The relation between $A$ and $T$ is given by:

$$A = -\log(T) = -\log \frac{I_1}{I_0}$$ (5.2)

In traditional spectroscopic studies with bulk samples, the vibrational integrated peak area is linearly proportional to the amount of material, i.e. this is in the scope of influence of the Beer-Lambert law. However, with condensed phase particles of wavelength size, the spectrum may change with particle orientation, and a nonlinear Mie-like theoretical model might be required to analyze vibrational lineshapes.

### 5.2 Particle Vibrations, Theoretical Models, and the Phase Problem

The position, intensity, and width of vibrational peaks are readily measured quantities that are usefully encoded in many models. Both 3D-FDTD simulations and Mie theory [42] require the complex index of refraction $m$ of the subject particle which varies with wavelength. Vibrational transitions are often added as damped harmonic oscillators (classical dispersion theory) [40] to the permittivity $\varepsilon$ of the dielectric material, whose square root is the complex index of refraction $m$:

$$m^* = \sqrt{\varepsilon} = \sqrt{\varepsilon_0 + \sum_j \frac{A_j \tilde{\nu}_0^2}{\tilde{\nu}_0^2 - \tilde{\nu}^2 - i2\Gamma_j \tilde{\nu}}}$$ (5.3)

where $j$ is an index over the vibrations, $\varepsilon_0$ is the constant complex dielectric, $A_j$ is the unitless strength of each vibration (i.e. in dielectric units), $\tilde{\nu}_{0,j}$ is the position of each vibration in wavenumbers, and $2\Gamma_j$ is the full-width-at-half-max (FWHM) of the feature in wavenumbers, i.e. $\Gamma_j$ is the half-width-at-half-max (HWHM).
5.3 3D-FDTD Simulations of Slabs and Spheres: Testing the Beer-Lambert Law

To better illustrate the single particle issues, spectral simulations were performed on a sequence of slabs and spheres of equal volumes to each of which a single vibrational feature was added. The spheres were chosen so that their diameters tune through the phonon transition wavelength region. The utilized software was FDTD Solutions 8.0.4 from Lumerical Solutions, Inc. (Vancouver, BC, www.lumerical.com). Initially, the simulation regions were 10 \( \mu m \times 10 \mu m \times 80 \mu m \) for both the slabs and spheres (as shown in Figure 5.2). Since the spheres do not share the symmetry of the cell, a larger cell of 20 \( \mu m \times 20 \mu m \times 80 \mu m \) was employed for the spheres (Figure 5.3) in order to reduce possible boundary effects. Unlike the slabs, small changes in a spherical particle’s simulation cell can be expected to change spectral lineshape with the detector geometry. Simulation parameters included auto non-uniform meshing and all absorbing, perfectly matched layer (PML), boundary conditions. The source was a plane wave pulse of light with broad band of frequencies (2600 cm\(^{-1}\) to 3200 cm\(^{-1}\)) propagating parallel to the \(z\)-axis (left to right) with dimensions of 10 \( \mu m \times 10 \mu m \) and it was placed -40 \( \mu m \) from the slab which was centered. The detector was the same size and positioned at the end of the simulation cell. The extinction spectrum without the vibration was subtracted from the identical simulation with the vibration \((\varepsilon_0 = 2.3+i0.0, A = 0.005, \nu_0 = 2917.0 \text{ cm}^{-1}, \Gamma = 5.0 \text{ cm}^{-1})\) in each trace in Figures 5.2 and 5.3. The slabs of Figure 5.2 are all 10 \( \mu m \times 10 \mu m \) having thicknesses of 0.10, 0.30, 0.50, 0.70, 0.90, 1.00, 1.50, 2.00, 2.50, and 3.00 \( \mu m \). Each sphere of Figure 5.3 has the same volume as a corresponding slab in Figure 5.2. The sphere radii are 1.34, 1.93, 2.29, 2.56, 2.78, 2.88, 3.30, 3.63, 3.91, and 4.51 \( \mu m \).
Figure 5.2: Plot of the extinction without vibration subtracted from extinction with vibration (in units of $10^{-7}$ cm$^2$) for slab pathlengths, $l$, of 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.5, 2.0, 2.5, and 3.0 µm. Results calculated using 3D-FDTD simulations. Schematic of the simulation is provided at top [6].

The phase shift ($\phi$), intensity ($S/\Gamma$), position ($\nu_0$), and HWHM ($\Gamma$) can be determined by fitting the extinction lineshapes in Figure 5.2 and Figure 5.3 to the following absorption-dispersion lineshape [88]

$$E(\tilde{\nu}) = \frac{S}{\Gamma} \left[ \cos \phi - \frac{\tilde{\nu} - \tilde{\nu}_0}{\Gamma} \sin \phi \right] + C$$  \hspace{1cm} (5.4)

where $C$ is a constant added for better fits with non-flat baselines.
Figure 5.3: Plot of the extinction without vibration subtracted from extinction with vibration (in units of $10^{-7}$ cm$^2$) for sphere radii, of 1.34, 1.93, 2.29, 2.56, 2.78, 2.88, 3.30, 3.63, 3.91, and 4.15 µm. Results calculated using 3D-FDTD simulations. Schematic of the simulation is provided at top [6].

All of the lineshapes in Figures 5.2 and 5.3 were fit to equation (5.4) yielding the data in Tables 5.1 and 5.2. An example fitting program is presented in Appendix B. The following notation is used to represent the error: 0.2039(6) is 0.2039±0.0006. The rest can be described in a similar way.
Table 5.1: Slab fit parameters according to equation (5.4) of the spectra in Figure 5.2. The dielectric input parameters \([A = 0.005, \text{HWHM} = 5.0 \text{ cm}^{-1}, \text{and } \nu_0 = 2917.0 \text{cm}^{-1}]\) were accurately recovered.

<table>
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<th>Volume(µm³)</th>
<th>S/Γ(cm)</th>
<th>φ(radians)</th>
<th>Γ(cm⁻¹)</th>
<th>ν₀(cm⁻¹)</th>
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<td>2917.18(3)</td>
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<td>0.074(5)</td>
<td>5.33(3)</td>
<td>2917.84(2)</td>
</tr>
<tr>
<td>300.0</td>
<td>2.313(21)</td>
<td>-0.024(5)</td>
<td>4.98(4)</td>
<td>2917.55(4)</td>
</tr>
</tbody>
</table>

Table 5.2: Sphere fit parameters according to equation (5.4) of the spectra in Figure 5.3. The dielectric input parameters \([A = 0.005, \text{HWHM} = 5.0 \text{ cm}^{-1}, \text{and } \nu_0 = 2917.0 \text{cm}^{-1}]\) were accurately recovered.

<table>
<thead>
<tr>
<th>Volume(µm³)</th>
<th>S/Γ(cm)</th>
<th>φ(radians)</th>
<th>Γ(cm⁻¹)</th>
<th>ν₀(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.0864(1)</td>
<td>0.213(15)</td>
<td>9.7(2)</td>
<td>2916.0(2)</td>
</tr>
<tr>
<td>30.0</td>
<td>0.192(3)</td>
<td>1.217(16)</td>
<td>15.5(3)</td>
<td>2917.7(4)</td>
</tr>
<tr>
<td>50.0</td>
<td>0.277(7)</td>
<td>1.42(3)</td>
<td>16.9(8)</td>
<td>2915.3(8)</td>
</tr>
<tr>
<td>70.0</td>
<td>0.289(9)</td>
<td>2.20(4)</td>
<td>17.0(9)</td>
<td>2920.7(9)</td>
</tr>
<tr>
<td>90.0</td>
<td>0.463(24)</td>
<td>2.18(4)</td>
<td>24.7(12)</td>
<td>2915.9(12)</td>
</tr>
<tr>
<td>100.0</td>
<td>0.489(19)</td>
<td>2.64(6)</td>
<td>24.8(17)</td>
<td>2918.9(17)</td>
</tr>
<tr>
<td>150.0</td>
<td>0.70(3)</td>
<td>3.75(7)</td>
<td>28.0(8)</td>
<td>2930(4)</td>
</tr>
<tr>
<td>200.0</td>
<td>0.78(3)</td>
<td>4.47(8)</td>
<td>28.5(21)</td>
<td>2936(4)</td>
</tr>
<tr>
<td>250.0</td>
<td>0.62(4)</td>
<td>5.03(9)</td>
<td>28.3(31)</td>
<td>2932.7(28)</td>
</tr>
<tr>
<td>300.0</td>
<td>0.85(4)</td>
<td>5.51(7)</td>
<td>20.9(18)</td>
<td>2938.2(17)</td>
</tr>
</tbody>
</table>
The slab lineshapes follow a pattern related to the Beer-Lambert law where absorbance is related to the molar extinction coefficient of the sample \(a\), which changes with wavelength), the path length of light through the solution \(l\), and the molar concentration of the solute \(c\). For purposes of comparing to particles, the slab line strengths will also be proportional to slab volume within the simulation cell. Absorption dominates, linewidths are assumed to be constant and line strengths increase with the thickness (or volume) of the slab. These are the predominant features of the slab results of Figure 5.2, although subtle hints of scattering are evident upon close examination of the tables.

The spheres of Figure 5.3 show dramatic changes in lineshape and phase \([\phi\ of\ equation\ (5.4)]\) and they have mixtures of absorbance and dispersion contributions. The question is whether the spheres, after correcting for phase, are still following a Beer-Lambert like trend. A plot of the intensity \((S/\Gamma)\) versus volume is given in Figure 5.4. The spheres diverge significantly from the Beer-Lambert law trend at larger volumes. In fact, the phased Lorentzian lineshape model of equation (5.4) becomes inadequate for spheres whose diameters are similar to the strong phonon transition wavelength.
5.4 Orientation Effects Due to Anisotropy

5.4.1 Cylindrical Rods

The above preliminary study on the distortion of spectral lineshapes by homogeneous, isotropic spheres can be further extended to include more complex shapes such as cylindrical rods. This study will also enable understanding orientation effects on the spectral lineshapes of sub-wavelength scale particles. 3D FDTD simulations were performed on a sequence of cylinders, having equal volumes as the corresponding sizes of slabs and spheres, and to each of which a single vibrational feature was added. The cylinder radii are 1.34, 1.93, 2.29, 2.56, 2.78, 2.88, 3.30, 3.63, 3.91, and 4.51 µm. The cylinder lengths (i.e. heights) are 1.77, 2.56, 3.03, 3.40, 3.71, 3.84, 4.38, 4.84.
4.83, 5.21, and 5.54 µm. Simulation region and parameters are the same as previously described for spheres. Each Figures 5.5, 5.6, and 5.7 show plots of extinction spectra for cylinder oriented along the $z$, $x$, and $y$-directions respectively.

Figure 5.5: Plot of the extinction without vibration subtracted from extinction with vibration (in units of $10^{-7}$ cm$^2$) for cylinder oriented along the $z$-direction. Results calculated using 3D-FDTD simulations. Schematic of simulation is provided at top.
Figure 5.6: Plot of the extinction without vibration subtracted from extinction with vibration (in units of $10^{-7}$ cm$^2$) for cylinder oriented along the $x$-direction. Results calculated using 3D-FDTD simulations. Schematic of simulation is provided at top.
Figure 5.7: Plot of the extinction without vibration subtracted from extinction with vibration (in units of $10^{-7} \text{ cm}^2$) for cylinder oriented along the $y$-direction. Results calculated using 3D-FDTD simulations. Schematic of simulation is provided at top.

It can be observed that phasing effects are stronger in Figures 5.6 and 5.7, when compared to Figure 5.5. This is because the cylinder’s extinction lineshapes are affected by its orientation relative to the light source. Also, notice that light is incident on the cylinder’s curved surface in Figures 5.6 and 5.7, whereas in Figure 5.5, light is incident on the cylinder’s flat surface (base). All of the lineshapes in Figures 5.5, 5.6 and 5.7 were fit to equation (5.4) yielding the data in Tables 5.3, 5.4 and 5.5.
Table 5.3: Cylinder fit parameters according to equation (5.4) of the spectra in Figure 5.5. The dielectric input parameters \(A = 0.005, \text{HWHM} = 5.0 \text{ cm}^{-1}, \text{and } \nu_0 = 2917.0 \text{cm}^{-1}\) were accurately recovered.

<table>
<thead>
<tr>
<th>Volume((\mu\text{m}^3))</th>
<th>(S/\Gamma(\text{cm}))</th>
<th>(\phi(\text{radians}))</th>
<th>(\Gamma(\text{cm}^{-1}))</th>
<th>(\nu_0(\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.108(14)</td>
<td>-0.29(14)</td>
<td>7.8(15)</td>
<td>2918.5(15)</td>
</tr>
<tr>
<td>30.0</td>
<td>0.265(21)</td>
<td>0.050(8)</td>
<td>10.7(12)</td>
<td>2917.6(12)</td>
</tr>
<tr>
<td>50.0</td>
<td>0.354(7)</td>
<td>0.23(2)</td>
<td>9.9(3)</td>
<td>2916.7(3)</td>
</tr>
<tr>
<td>70.0</td>
<td>0.465(6)</td>
<td>0.42(14)</td>
<td>12.1(2)</td>
<td>2916.0(2)</td>
</tr>
<tr>
<td>90.0</td>
<td>0.544(8)</td>
<td>0.64(17)</td>
<td>12.7(3)</td>
<td>2916.1(3)</td>
</tr>
<tr>
<td>100.0</td>
<td>0.58(11)</td>
<td>0.70(2)</td>
<td>12.8(3)</td>
<td>2915.7(3)</td>
</tr>
<tr>
<td>150.0</td>
<td>0.78(24)</td>
<td>-0.028(5)</td>
<td>13.7(6)</td>
<td>2911.4(6)</td>
</tr>
<tr>
<td>200.0</td>
<td>0.86(30)</td>
<td>1.11(4)</td>
<td>16.9(9)</td>
<td>2911.6(9)</td>
</tr>
<tr>
<td>250.0</td>
<td>0.65(27)</td>
<td>1.30(5)</td>
<td>18(1)</td>
<td>2914(1)</td>
</tr>
<tr>
<td>300.0</td>
<td>0.55(39)</td>
<td>1.79(8)</td>
<td>19(2)</td>
<td>2922(2)</td>
</tr>
</tbody>
</table>

Table 5.4: Cylinder fit parameters according to equation (5.4) of the spectra in Figure 5.6. The dielectric input parameters \(A = 0.005, \text{HWHM} = 5.0 \text{ cm}^{-1}, \text{and } \nu_0 = 2917.0 \text{cm}^{-1}\) were accurately recovered.

<table>
<thead>
<tr>
<th>Volume((\mu\text{m}^3))</th>
<th>(S/\Gamma(\text{cm}))</th>
<th>(\phi(\text{radians}))</th>
<th>(\Gamma(\text{cm}^{-1}))</th>
<th>(\nu_0(\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.131(2)</td>
<td>-0.23(17)</td>
<td>9.8(2)</td>
<td>2916.8(2)</td>
</tr>
<tr>
<td>30.0</td>
<td>0.251(3)</td>
<td>0.57(13)</td>
<td>13.4(2)</td>
<td>2917.6(2)</td>
</tr>
<tr>
<td>50.0</td>
<td>0.340(7)</td>
<td>0.97(2)</td>
<td>14.7(4)</td>
<td>2917.0(4)</td>
</tr>
<tr>
<td>70.0</td>
<td>0.431(9)</td>
<td>1.27(2)</td>
<td>17.5(5)</td>
<td>2916.3(5)</td>
</tr>
<tr>
<td>90.0</td>
<td>0.49(14)</td>
<td>1.62(3)</td>
<td>18.9(8)</td>
<td>2916.6(9)</td>
</tr>
<tr>
<td>100.0</td>
<td>0.54(2)</td>
<td>1.75(5)</td>
<td>19(1)</td>
<td>2916(1)</td>
</tr>
<tr>
<td>150.0</td>
<td>0.68(3)</td>
<td>3.12(5)</td>
<td>27(2)</td>
<td>2926(2)</td>
</tr>
<tr>
<td>200.0</td>
<td>0.59(5)</td>
<td>4.1(11)</td>
<td>27(4)</td>
<td>2918(4)</td>
</tr>
<tr>
<td>250.0</td>
<td>0.61(4)</td>
<td>5.19(9)</td>
<td>24(3)</td>
<td>2927(3)</td>
</tr>
<tr>
<td>300.0</td>
<td>0.72(4)</td>
<td>5.59(6)</td>
<td>23(2)</td>
<td>2923(2)</td>
</tr>
</tbody>
</table>
Table 5.5: Cylinder fit parameters according to equation (5.4) of the spectra in Figure 5.7. The dielectric input parameters \([A = 0.005, \text{HWHM} = 5.0 \, \text{cm}^{-1}, \text{and } \nu_0 = 2917.0 \, \text{cm}^{-1}]\) were accurately recovered.

<table>
<thead>
<tr>
<th>Volume((\mu m^3))</th>
<th>S/(\Gamma)(cm)</th>
<th>(\phi)(radians)</th>
<th>(\Gamma)(cm(^{-1}))</th>
<th>(\nu_0)(cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.134(2)</td>
<td>-0.30(17)</td>
<td>9.8(2)</td>
<td>2916.7(2)</td>
</tr>
<tr>
<td>30.0</td>
<td>0.261(3)</td>
<td>0.58(14)</td>
<td>12.9(2)</td>
<td>2917.7(2)</td>
</tr>
<tr>
<td>50.0</td>
<td>0.346(7)</td>
<td>1.03(2)</td>
<td>15.4(5)</td>
<td>2917.0(5)</td>
</tr>
<tr>
<td>70.0</td>
<td>0.43(12)</td>
<td>1.20(3)</td>
<td>17.9(7)</td>
<td>2915.0(8)</td>
</tr>
<tr>
<td>90.0</td>
<td>0.48(15)</td>
<td>1.79(4)</td>
<td>19.5(9)</td>
<td>2917(1)</td>
</tr>
<tr>
<td>100.0</td>
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<td>1.94(5)</td>
<td>20(1)</td>
<td>2918(1)</td>
</tr>
<tr>
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<td>0.64(2)</td>
<td>3.20(4)</td>
<td>28(2)</td>
<td>2926(2)</td>
</tr>
<tr>
<td>200.0</td>
<td>0.62(5)</td>
<td>4.3(11)</td>
<td>24(3)</td>
<td>2927(3)</td>
</tr>
<tr>
<td>250.0</td>
<td>0.63(5)</td>
<td>5.22(9)</td>
<td>24(3)</td>
<td>2928(3)</td>
</tr>
<tr>
<td>300.0</td>
<td>0.67(3)</td>
<td>5.55(6)</td>
<td>25(2)</td>
<td>2922(2)</td>
</tr>
</tbody>
</table>

Plot of the intensity \((S/\Gamma)\) versus volume for cylinder oriented along the \(x\), \(y\), and \(z\)-directions is given in Figure 5.8. It can be observed that the cylinders also diverge significantly from the Beer-Lambert law trend at larger volumes.
Figure 5.8: Plot of the intensity, $S/\Gamma$ versus volume for cylinder oriented along $x$ (red circles), $y$ (green circles), and $z$ (blue circles) directions as determined by fitting the lineshapes in Figures 5.5, 5.6 and 5.7 compared against results of slab (black circles).

5.4.2 Homogeneous Clusters

3D FDTD simulations were performed on a sequence of homogeneous cluster of 13 spheres. The total volume of each cluster is equal to the volumes of the corresponding sizes of slabs, spheres, and cylinders discussed previously. To each of these clusters, a single vibrational feature was added. Simulation region and parameters are the same as previously described for spheres and cylinders. Figure 5.9 shows plots of extinction spectra for homogeneous cluster of 13 spheres.
Figure 5.9: Plot of the extinction without vibration subtracted from extinction with vibration (in units of $10^{-7}$ cm$^2$) for homogeneous cluster of 13 spheres. Results calculated using 3D-FDTD simulations. Schematic of the simulation is provided at top.

All of the lineshapes in Figure 5.9 were fit to equation (5.4) yielding the data in Table 5.6.
Table 5.6: Homogeneous cluster fit parameters according to equation (5.4) of the spectra in Figure 5.9. The dielectric input parameters \( A = 0.005, \text{HWHM} = 5.0 \text{ cm}^{-1}, \) and \( \nu_0 = 2917.0 \text{ cm}^{-1} \) were accurately recovered.

<table>
<thead>
<tr>
<th>Volume ((\mu m^3))</th>
<th>S/(\Gamma) (cm)</th>
<th>(\phi) (radians)</th>
<th>(\Gamma) (cm(^{-1}))</th>
<th>(\nu_0) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.107(3)</td>
<td>-0.15(3)</td>
<td>8.7(3)</td>
<td>2917.7(3)</td>
</tr>
<tr>
<td>30.0</td>
<td>0.209(1)</td>
<td>0.246(9)</td>
<td>9.7(13)</td>
<td>2917.2(1)</td>
</tr>
<tr>
<td>50.0</td>
<td>0.344(5)</td>
<td>0.57(15)</td>
<td>12.3(2)</td>
<td>2916.2(2)</td>
</tr>
<tr>
<td>70.0</td>
<td>0.435(8)</td>
<td>0.89(21)</td>
<td>14.7(4)</td>
<td>2915.6(4)</td>
</tr>
<tr>
<td>90.0</td>
<td>0.50(14)</td>
<td>1.26(34)</td>
<td>17.8(7)</td>
<td>2915.3(8)</td>
</tr>
<tr>
<td>100.0</td>
<td>0.52(2)</td>
<td>1.56(48)</td>
<td>18(1)</td>
<td>2917(1)</td>
</tr>
<tr>
<td>150.0</td>
<td>0.58(3)</td>
<td>1.90(6)</td>
<td>21(17)</td>
<td>2917(2)</td>
</tr>
<tr>
<td>200.0</td>
<td>0.79(3)</td>
<td>3.11(54)</td>
<td>29(2)</td>
<td>2926(2)</td>
</tr>
<tr>
<td>250.0</td>
<td>0.60(4)</td>
<td>3.79(9)</td>
<td>31(4)</td>
<td>2923(3)</td>
</tr>
<tr>
<td>300.0</td>
<td>0.47(3)</td>
<td>4.47(9)</td>
<td>28(3)</td>
<td>2933(3)</td>
</tr>
</tbody>
</table>

A plot of the intensity \((S/\Gamma)\) versus volume for homogeneous cluster of 13 spheres is given in Figure 5.10. When compared against the results of homogeneous spheres (from Figure 5.4), it can be noticed that the trends are quite similar, except at larger volumes. This confirms that at smaller sizes, particles or clusters can often be treated as homogeneous isotropic spheres or can be approximated in such a way that Mie’s theory is applicable [89].
5.5 The Case of Mixed Media Clusters

5.5.1 Inhomogeneous Clusters

In nature, particles often exist as inhomogeneous clusters consisting of several kinds of elements. Such mixed media clusters are of interest especially in studies that involve sub-wavelength particles such as dust from different environments. The study on slabs and spheres can also be extended to better understand the interaction of light with mixed media clusters as shown in Figure 5.11 and Figure 5.13. The total volume of each sphere (in Figure 5.11) and cluster (in Figure 5.13) is equal to the volumes of the corresponding sizes of slabs, spheres, cylinders, and homogeneous clusters discussed previously. Simulation region and parameters are the same as
previously described for spheres, cylinders, and homogeneous clusters. The extinction spectrum without the vibration was subtracted from the identical simulation with the vibration ($\varepsilon_0 = 2.3+i0.0, A = 0.005, \nu_{01} = 2850.0\text{cm}^{-1}, \nu_{02} = 3010.0\text{cm}^{-1}, \Gamma = 5.0\text{ cm}^{-1}$) in each trace in Figures 5.11 and 5.13.

Figure 5.11: Plot of the extinction without vibration subtracted from extinction with vibration (in units of $10^{-7}\text{ cm}^2$) for a sphere with a 50-50 mix of two phonon vibrations, and having radii of 1.34, 1.93, 2.29, 2.56, 2.78, 2.88, 3.30, 3.63, 3.91, and 4.15 $\mu$m. Results calculated using 3D-FDTD simulations. Schematic of the simulation is provided at top.

All of the lineshapes in Figure 5.11 were fit to equation (5.4) yielding the data in Table 5.7.
Table 5.7: Sphere fit parameters according to equation (5.4) of the spectra in Figure 5.11. The dielectric input parameters \([A = 0.005, \text{HWHM} = 5.0 \text{ cm}^{-1}, \nu_{01} = 2850.0 \text{ cm}^{-1}, \text{ and } \nu_{02} = 3010.0 \text{ cm}^{-1}\) were accurately recovered.

<table>
<thead>
<tr>
<th>Volume((\mu\text{m}^3))</th>
<th>(S/(\Gamma))(_1)(cm)</th>
<th>(\phi_1)(radians)</th>
<th>(\Gamma_1)(cm(^{-1}))</th>
<th>(\nu_{01})(cm(^{-1}))</th>
<th>(S/(\Gamma))(_2)(cm)</th>
<th>(\phi_2)(radians)</th>
<th>(\Gamma_2)(cm(^{-1}))</th>
<th>(\nu_{02})(cm(^{-1}))</th>
</tr>
</thead>
<tbody>
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<td>0.037</td>
<td>0.080</td>
<td>16.268</td>
<td>3003.890</td>
</tr>
<tr>
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<td>0.921</td>
<td>17.436</td>
<td>2846.213</td>
<td>0.085</td>
<td>1.055</td>
<td>17.804</td>
<td>3000.815</td>
</tr>
<tr>
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<td>0.145</td>
<td>1.535</td>
<td>20.046</td>
<td>3003.193</td>
</tr>
<tr>
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<td>2843.942</td>
<td>0.126</td>
<td>1.667</td>
<td>27.709</td>
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</tr>
<tr>
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<td>2859.722</td>
<td>0.249</td>
<td>2.586</td>
<td>24.299</td>
<td>3006.329</td>
</tr>
<tr>
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<td>2.283</td>
<td>22.868</td>
<td>2844.179</td>
<td>0.219</td>
<td>2.548</td>
<td>21.269</td>
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</tr>
<tr>
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<td>25.649</td>
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<td>0.320</td>
<td>3.553</td>
<td>22.276</td>
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</tr>
<tr>
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<td>20.005</td>
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<td>0.424</td>
<td>4.763</td>
<td>30.643</td>
<td>3015.246</td>
</tr>
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<td>30.779</td>
<td>2852.698</td>
<td>0.396</td>
<td>4.535</td>
<td>34.324</td>
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</tr>
<tr>
<td>300.0</td>
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<td>28.466</td>
<td>2843.740</td>
<td>0.393</td>
<td>5.213</td>
<td>21.183</td>
<td>2995.374</td>
</tr>
</tbody>
</table>
Figure 5.12: Plot of the intensity, $S/\Gamma$ versus volume for a sphere with a 50-50 mix of two phonon vibrations as determined by fitting the lineshapes in Figure 5.11. One phonon vibration is at 2850 cm$^{-1}$ (green circles), other is at 3010 cm$^{-1}$ (blue circles).
Figure 5.13: Plot of the extinction without vibration subtracted from extinction with vibration (in units of $10^{-7}$ cm$^2$) for an inhomogeneous cluster of 13 spheres, with $\sim$50-50 mix of two phonon vibrations. Results calculated using 3D-FDTD simulations. Schematic of the simulation is provided at top.

All of the lineshapes in Figure 5.13 were fit to equation (5.4) yielding the data in Table 5.8.
Table 5.8: Inhomogeneous cluster fit parameters according to equation (5.4) of the spectra in Figure 5.13. The dielectric input parameters \([A = 0.005, \text{HWHM} = 5.0 \text{ cm}^{-1}, \nu_{01} = 2850.0 \text{cm}^{-1}, \text{ and } \nu_{02} = 3010.0 \text{cm}^{-1}]\) were accurately recovered.

<table>
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<th>Volume(µm³)</th>
<th>((S/\Gamma)_1(\text{cm}))</th>
<th>(\phi_1(\text{radians}))</th>
<th>(\Gamma_1(\text{cm}^{-1}))</th>
<th>(\nu_{01}(\text{cm}^{-1}))</th>
<th>((S/\Gamma)_2(\text{cm}))</th>
<th>(\phi_2(\text{radians}))</th>
<th>(\Gamma_2(\text{cm}^{-1}))</th>
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<td>2964.476</td>
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</table>
Figure 5.14: Plot of the intensity, $S/\Gamma$ versus volume for an inhomogeneous cluster with ~50-50 mix of two phonon vibrations as determined by fitting the lineshapes in Figure 5.13. One phonon vibration is at 2850 cm$^{-1}$ (green circles), other is at 3010 cm$^{-1}$ (blue circles).

### 5.5.2 Mie-Bruggeman Model Fits

Typical individual dust particles have two or more components, so a model for mixtures has been developed [10] that combines Mie theory with the Bruggeman mixture theory in order to model the average spectrum of particles of mixed composition. The Bruggeman relation provides a constraint between the effective permittivity ($\varepsilon_{\text{eff}}$) of a mixture and the permittivities ($\varepsilon_i$) and volume fractions ($f_i$) of each component in the mixture

$$\sum_i f_i \frac{\varepsilon_i - 2\varepsilon_{\text{eff}}}{\varepsilon_i + 2\varepsilon_{\text{eff}}} = 0 \quad (5.5)$$

It is difficult to analytically solve for the effective dielectric of particles that have many components, so an iterative numerical approach was used with an initial guess.
\[ \varepsilon_{\text{eff}} = \sum_{i} f_i \varepsilon_i \]  

(5.6)

where each \( \varepsilon_i \) is determined by fitting the spectrum and \( f_i \) is determined manually by looking at comparison plots. Rearranging equation 5.5 gives the iterative formula for the permittivity of the mixture

\[ \varepsilon_{\text{eff},k} = \frac{\sum_{i=0}^{n-1} f_i \varepsilon_i}{\sum_{i=0}^{n-1} f_i \varepsilon_i + 2\varepsilon_{\text{eff},k-1}} \]  

(5.7)

Convergence is usually observed in \(<10 \) iterations. The input of \( \varepsilon_{\text{eff}} \) for a certain mixture of components and a specific radius for the particle enables the prediction of an IR absorption spectra by standard Mie formulas. The predicted spectrum is compared to the FDTD model response for a particle of given size, and the volume fractions are varied until good agreement is obtained. A Fortran program was written that performed an unweighted, nonlinear least squares fit using a parameter grid search method [90] that adjusted the volume fractions and particle radius until reasonable fits were obtained as shown in Figure 5.15. The program was somewhat nonstandard because at each grid step of a fitted variable, the program renormalized the volume fractions so that they always added up to 1.
Figure 5.15: Mie-Bruggeman fit of FDTD absorption spectra for an inhomogeneous cluster with ∼50-50 mix of two phonon vibrations, and having effective radii of ∼1.34 µm. Red trace is the FDTD model spectra, and the blue trace is the Mie-Bruggeman model fit.

The Mie-Bruggeman model estimated the effective particle radius as 1.158 µm, with mixture volume percentages of 53.36% phonon vibration at 2850 cm\(^{-1}\) and 46.64% phonon vibration at 3010 cm\(^{-1}\). The value of the estimated standard deviation of the fit was 0.00176 in absorbance units. Standard deviation and error estimation is described in detail in [10].

5.6 Conclusion

Wavelength-scale particles have their own unique set of spectroscopic challenges. At small sizes relative to the wavelength, particles exhibit Beer-Lambert-like behavior. As the particle size increases to about the wavelength of incident light, this behavior starts to diverge from Beer-Lambert as shown with 3D FDTD simulations. It was observed that spectral lineshapes of wavelength scale particles can be distorted by
phase, saturation, and orientation. Further, the Mie-Bruggeman model was tested by fitting absorption spectrum obtained from 3D FDTD simulations, and it reasonably predicted actual volume fractions of a mixed composition particle.
Chapter 6: Applications: Oriented Crystal Microparticles with Anisotropic Permittivities

3D FDTD simulations can be used to study spectral distortions of single particles similar in size to the wavelength of probing light. This is useful in predicting the IR spectra of single particles trapped in mesh holes. In this chapter, prediction of IR spectra of oriented crystal microparticles with anisotropic permittivities (quartz) is studied, taking into account the effects of angular spread on transmission widths.

6.1 Background and Introduction

This section describes experimental spectra of individual crystalline quartz particles to show simple, non-Beer-Lambert behavior and then more dramatic effects when stronger vibrations are involved. This will also illustrate some of the difficulties that will occur in ultimately treating dust particle spectra which are typically mixtures of multiple mineral components with some organics attached.

Quartz is one of the most prevalent mineral components in airborne particulate matter [8, 91, 92, 93, 94, 95], i.e. people routinely breathe it into their lungs. Breathing in too much quartz is the cause of silicosis [96] so it is important to know the distribution of quartz in ordinary airborne particulate matter as an indication of tolerable levels. IR scatter-free spectra were recorded of 15 different, single $\alpha$-quartz
particles in plasmonic metal mesh holes, as shown in Figure 6.1. Each spectrum is unique due to variation in size (range of 3-5 $\mu$m diameters) and orientation. Quartz phonons are divided into two groups (ordinary and extraordinary) due to birefringence. The groups have transition moments perpendicular to each other. There are two notable effects to be extracted from these spectra: 1) non-Beer-Lambert behavior of the normal looking pair of peaks at 777 and 799 cm$^{-1}$ and 2) intense lineshape broadening and distortion of the most intense asymmetric SiO$_4$ stretching vibrations at 1072 and 1080 cm$^{-1}$.

![Graph showing IR scatter-free spectra of 15 different, single $\alpha$-quartz particles showing variations with orientation and size][1]

Figure 6.1: IR scatter-free spectra of 15 different, single $\alpha$-quartz particles showing variations with orientation and size [6].

The band at 777 cm$^{-1}$ is extraordinary and the band at 799 cm$^{-1}$ is ordinary, i.e. a crystal orientation that is good for detecting one will be bad for the other and vice
versa. The intensities of these bands were originally measured in reflection by Spitzer and Kleinman [97]. These bands are 6 times weaker [by the $A$ parameter of equation (5.3)] than the strongest bands according to Spitzer’s work. These two peaks in all 15 individual spectra were fit to Gaussian lineshapes with a nonlinear least squares fitting routine and a representative fit is shown in Figure 6.2. A plot of the fitted peak widths versus peak intensity is presented in Figure 6.3.

Figure 6.2: Nonlinear least square fits of the extraordinary and ordinary peaks at 777 and 799 cm$^{-1}$ [6].
Figure 6.3: Nonlinear least square fitted values of peak width (full-width-at-half-maximum, FWHM) versus peak intensity for 15 α-quartz particles. Beer-Lambert behavior would give rise to a flat trend with constant width. Characteristic quartz bands at 777 cm\(^{-1}\) (A\(^2\) symmetry, extraordinary, blue) and 799 cm\(^{-1}\) (E symmetry, ordinary, green) show systematic increases in band width with increases in absorption, i.e. non-Beer-Lambert behavior [6].

If these peaks of medium strength were obeying the Beer-Lambert relation, then the peak widths would remain constant, but there is clearly a trend that more intense peaks are also broader. This non-Beer-Lambert behavior is problematic enough (a factor of two increase in band width and a less than linear rise in intensity with an increase in volume), but it is a subtle effect when compared to the behavior of a stronger transition. Basically, these lineshape effects are manifest when the cross section attributed to the vibration (as calculated with Mie theory) becomes comparable to the physical cross section of the particle.
The lineshape effects are much more dramatic for the peaks at 1072 (E symmetry, ordinary) or 1080 cm\(^{-1}\) (A2 symmetry, extraordinary) which are the strongest phonons for quartz \([A=0.67\) of equation (5.3) by reflection\] \([97]\). As is evident in Figure 6.1, the bands in this region extend over a range of 400 cm\(^{-1}\), they are curiously flattened, not six times stronger than the bands at 777 and 799 cm\(^{-1}\), and there appear to be more peaks than there are fundamentals.

6.2 Modeling Spectra of Quartz Particle Trapped in Micro-Mesh

3D FDTD simulation setup of a 5 µm spherical quartz particle trapped in plasmonic mesh hole is shown in Figure 6.4. The quartz particle has anisotropic dielectric permittivity, with its optic axis (c-axis) oriented along the x-axis. The real and imaginary indices of refraction for quartz were obtained from the HITRAN (HIgh-resolution TRANsmission molecular absorption) database at www.cfa.harvard.edu, and were tabulated by E. P. Shettle of the Naval Research Laboratory.

At the center of the simulation region is a unit cell of the mesh modeled as a 2 µm film of Ni (Palik) material, perforated by a square hole of size 5 µm, and a lattice parameter \((L)\) of 12.7 µm. The simulation cell is 12.7 µm × 12.7 µm × 70 µm. The simulation region has absorbing (PML) boundary conditions (BCs) at the ends, periodic BCs along the sides parallel to the electric field (to simulate periodicity of micro-mesh), and Bloch BCs along the sides perpendicular to the electric field. The Bloch BCs are used to simulate effects of non-zero momentum components intersecting those boundaries, which allows indirect calculations of the effect of light interacting with the mesh at non-perpendicular angles. A pulse of light with broad
band of frequencies (700 cm$^{-1}$ to 1500 cm$^{-1}$), and having polarization of 0° is effectively directed along the z-axis towards the mesh at variable angles for different wavelengths by fixing wavevector ($k_x$) using Bloch boundary conditions. The source is placed -30 µm from the center of the simulation cell, and the detector is positioned at +30 µm at the other end of the simulation cell. The utilized software was FDTD Solutions 8.7.3 from Lumerical Solutions, Inc. (Vancouver, BC, www.lumerical.com).

The calculation time span was set to 10,000 fs, with a step size ($dt$) of 0.0851 fs, for a total of about 117,500 time steps per simulation. Transmission spectra were calculated at reduced (dimensionless) wavevector values of 0 to 0.25, and 0.25 to 0.5, in steps of 0.025 producing 21 different spectra in total. Each individual fixed $k_x$ simulation of quartz particle trapped in mesh hole, with Bloch boundary conditions required about 3 hours. Additionally, each background (empty mesh) fixed $k_x$ simulation required ∼3 hours on the same system, resulting in a total of ∼6 hours for each fixed $k_x$ calculation.

Figure 6.4: 3D FDTD simulation setup of quartz particle trapped in mesh hole

Figures 6.5 and 6.6 show 3D FDTD simulated scatter-free extinction spectra of 5 µm quartz particle for reduced wavevector ($k_x'$) ranging from 0 to 0.25 (i.e. for
angle ($\theta$) ranging from 0° to 16.37° typical of the angular spread in a FTIR benchtop spectrometer), and for $k_x \gamma$ ranging from 0.25 to 0.5 (i.e. for angle ($\theta$) ranging from 16.37° to 34.32° typical of the angular spread in a FTIR microscope) respectively.

Figure 6.5: Plot of scatter-free extinction spectra of quartz particle for reduced wavevector ($k_x \gamma$) ranging from 0 to 0.25 i.e. for angle ($\theta$) ranging from 0° to 16.37° typical of the angular spread in a FTIR benchtop spectrometer. Results calculated using 3D FDTD simulations.
Figure 6.6: Plot of scatter-free extinction spectra of quartz particle for reduced wavevector \((k_x')\) ranging from 0.25 to 0.5 i.e. for angle \((\theta)\) ranging from 16.37\(^o\) to 34.32\(^o\) typical of the angular spread in a FTIR microscope. Results calculated using 3D FDTD simulations.

The experimental spectrum is simulated by weighting the intensity at every frequency point \(\tilde{\nu}\) in each calculated single \(k_x\) spectrum with a Gaussian weighting function

\[
N(\tilde{\nu}, k_x, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left( -\frac{1}{2} \left( \frac{\theta}{\sigma} \right)^2 \right)
\]

where, \(\theta = \sin^{-1}[k_x/(\tilde{\nu} L)]\)

In the above equation, \(\theta\) is the angle of incident light as measured from the z-axis in the zx plane and is determined indirectly by choosing \(\tilde{\nu}\) and \(k_x\). The adjustable
parameter $\sigma$ represents the first standard deviation in the spread of angles of the Gaussian beam at the sample in the experimental spectrometer. Intensities at each frequency point in a particular fixed $k_x$ spectrum were also multiplied by the zero-order grating function $G_{0,0}(\tilde{\nu},k_x)$, which represents the fraction of transmitted light that scatters into the (0,0) diffraction spot (see Figures 6.7, 6.8).

Figure 6.7: Grating functions calculated for each fixed $k_x$ transmission spectrum for FTIR benchtop spectrometer.
Figure 6.8: Grating functions calculated for each fixed $k_x$ transmission spectrum for FTIR microscope.

The simulated spectrum $E'(\tilde{\nu})$ was calculated by choosing a particular value of $\sigma$ and then adding up contributions from each fixed $k_x$ spectrum $E(\tilde{\nu}, k_x)$ as weighted by angular intensity $N$ and the zero-order grating function $G_{0,0}$

$$E'(\tilde{\nu}_i) = \sum_i E(\tilde{\nu}_i, k_{xj}) N(\tilde{\nu}_i, k_{xj}, \sigma) G_{0,0}(\tilde{\nu}_i, k_{xj})$$

(6.2)

where $j$ is an index over the fixed $k_x$ spectra and $i$ is an index over the wavenumber steps within each individual spectrum. The beam spread $\sigma$ is the only adjustable parameter in this weighting calculation.
Further details of the above averaging strategy for simulation is provided in [98].

Figures 6.9 and 6.10 show the averaged simulated scatter-free extinction spectra of quartz particle using FTIR benchtop spectrometer (representing $\sigma$ value of 3.0°), and FTIR microscope (representing $\sigma$ value of 10.0°) respectively for the range of 700 cm$^{-1}$ to 1500 cm$^{-1}$.

Figure 6.9: Best fit 3D FDTD simulation of scatter-free extinction spectra of quartz particle with angular spread of 0° to 16.37° and $\sigma=3.0^\circ$. 
Other miscellaneous results on quartz particle trapped in micro-mesh, including effects of particle size, shape, and polarization of probing light, were produced using 3D FDTD simulations. These results are listed in Appendix C.

6.3 Conclusion

From Figures 6.9 and 6.10, it is evident that the experimental IR spectra of single quartz particles are difficult to reproduce. This difficulty is attributed to various factors. Firstly, quartz is anisotropic, resulting in different spectra at different orientations relative to the direction of probing light. Secondly, the experimental IR
scatter-free spectra of individual quartz particles were recorded using the FTIR imaging microscope, whose Cassegrain optical system is quite complex to simulate. This illustrates some of the difficulties that will occur in studying dust particle spectra which are typically mixtures of multiple mineral and organic components.
Chapter 7: Applications in Mid-IR: Dust From Different Environments

7.1 Background and Introduction

A distribution of different sizes of particulate matter that can be inhaled deeply into the respiratory system is shown in Figure 7.1. Such particulate matter has the potential to damage cells in the lung’s airway passages and impair the respiratory system’s ability to fight infections. Airborne particles of $\sim$3-5 $\mu$m diameter are among the largest globular particles that get past the filtering of the nose and throat, making it into the lungs.

Typical urban concentration of airborne particulate matter is $\sim$30 $\mu$g/m$^3$. A rise of just 10 $\mu$g/m$^3$ from such typical values has been correlated with a rise of 0.25% in all-cause human mortality rates [92] and a rise of $\sim$0.75% in respiratory-related mortality rate. It has also been correlated with stroke, therefore breathing of particulate matter could affect the cardio-vascular system [99]. It is thought that particulate matter rose to as much as 14000 $\mu$g/m$^3$ during the great London smog disaster [94] in 1952, in which at least 4000 people were killed as a result. The US Environmental Protection Agency (EPA) regulates particulate matter with a national ambient air quality standard, with an annual mean of 15 $\mu$g/m$^3$ and a 24-hour mean of 35 $\mu$g/m$^3$ for particulate matter smaller than 2.5 $\mu$m (PM 2.5). The standard for
particulate matter smaller than 10 µm is a 24-hour average of 150 µg/m³. Respirable dust particles in the 3-5 µm range fall between fine and coarse designations, and are under increased scrutiny by the EPA. Since larger particles are not likely to travel as far as smaller ones, the chemical identity of larger particles may be more reflective of the local environment. There are many known diseases associated with long-term exposure to specific dusts [92, 94, 100], such as silicosis (from silica dust), asbestosis or mesothelioma (from asbestos), and black lung disease (from coal dust). Therefore the chemical characterization of respirable dust particles is important.

A method to record scatter-free IR spectra of individual dust particles of ∼4 µm size by trapping the particles in the holes of a metal plasmonic mesh has been previously developed [8, 9, 85] as shown in Figure 7.2. Many single particle spectra of pure materials known to be in dust samples have also been measured [101]. The dust collection technique is shown in Figure 7.3.
Figure 7.2: SEM images of plasmonic Ni mesh with a lattice parameter of 12.7 µm, a square hole width of ∼5 µm, and a thickness of ∼2 µm. When air is pumped through the mesh, dust particles of a specific size are trapped in the mesh holes as shown on the right-hand side. Scatter-free IR absorption spectra can be recorded of individual particles trapped in this manner because IR light runs along the metal surface rather than going directly through the holes [9].

Figure 7.3: Dust collection
Permittivities versus wavelength were extracted for the components of a dust sample and a Mie-Bruggeman model was developed that predicts the extinction or absorption spectra of any desired mixture of the calibrating components. It can predict as a function of composition and particle size, but averages over shape and orientation effects [102]. Previously, the Mie-Bruggeman method has given good results for the average single particle IR spectra of dust samples from laboratory air (from room 0055 of Evans Lab at the Ohio State University, Columbus), a home air filter, the 9/11/2001 World Trade Center event, and the International Space Station [9]. Dust libraries comprising collections of individual particle spectra from each of these environments is shown in Figure 7.4.

![Figure 7.4: Dust library. Collections of individual dust particle spectra from laboratory air, a house filter, the World Trade Center 9/11/2001 event, and the International Space Station. Each collection comprises of approximately 60 spectra of single particles. Also in the library are single particle IR spectra of pure materials found in respirable dust samples. [9]](image)

7.2 Predicting IR Spectra of Atmospheric Dust Samples of Mixed Composition Particles

With the advent of infrared (IR) LIDAR on a global scale [103, 104], the importance of dust in weather prediction [105, 106], and the effects of particulate matter
on human health [107, 92] motivate the development of IR spectral models that can deal with the complexities of atmospheric dust samples [108, 109].

A Mie-Bruggeman model (see Figure 7.5) is used to predict the shape and orientation-averaged infrared extinction and absorption spectra of a Saharan dust sample [110, 111, 112, 113] of mixed composition and size. The common minerals of atmospheric dust samples have strong infrared transitions which match the particle size and probing wavelengths giving rise to strong lineshape distortions [6]. These distortions may need to be considered for quantitative analysis of infrared spectra measurements of atmospheric dust samples. The quantitative analysis of IR spectral measurements of atmospheric dust samples may need to consider these distortions in order to choose the best wavelengths for future studies.

Figure 7.5: The Mie-Bruggeman model for predicting the IR spectra of particles with mixed components such as atmospheric dust. A mixed composition particle is illustrated at the top left consisting of components with known permittivities ($\varepsilon_i$). The model numerically predicts (top right equations) the effective permittivity ($\varepsilon_{eff}$) of the mixture, then predicts the IR spectrum of the mixture from a Mie theory approach. Volume fractions are varied iteratively to fit the sample being modeled [7].
The Mie-Bruggeman model identifies primary issues associated with extracting quantitative information from IR spectra of atmospheric dust mixture samples. The calibration components currently include calcite, dolomite, gypsum, illite, kaolinite, montmorillonite, quartz, yeast, polyethylene, humic acid/salt, and hydrated alumina, but new components can be added to improve the model provided that a set of single particle spectra can be recorded of the additional component. The use of the Mie-Bruggeman model is illustrated in this work by modeling a Saharan dust sample with a mineral composition from the literature [114] and a particle size distribution that was measured upon transport across the Atlantic Ocean [22] (see Figure 7.6). Some organics were added to the mixture to illustrate this feature of the model.

Figure 7.6: Long-range transport of North African (Saharan) dust

Given the permittivities ($\varepsilon_i$) and volume fractions ($f_i$) of each component as indexed with $i$, an effective permittivity is predicted for the mixture ($\varepsilon_{eff}$) which is
used to predict a Mie spectrum [40] of the mixture assuming some particle diameter, i.e. this is a shape and orientation averaged prediction for a sample. The prediction is compared to a dust sample spectrum of interest and the volume fractions and particle diameter are changed in a gridded nonlinear least squares fashion to improve the agreement. The volume fractions of the components are good if all of the important components in the sample are part of the calibration, likewise there will be systematic errors if important components are not in the calibration list. To illustrate use of the model, it is applied to some data from the literature on Saharan dust as it crosses the ocean.

7.3 Analysis and Results

Mineral compositions of field samples from the south central Saharan Desert by empirical mineralogy have been previously reported [114] as 9% dolomite, 31% illite, 16% kaolinite, 34% montmorillonite, 1% amorphous silica, and 9% feldspar. Organics were added [8] at approximately the 10% level in the form of yeast and polyethylene to give volume fractions of 0% calcite, 8.2% dolomite, 0% gypsum, 28.2% illite, 14.6% kaolinite, 30.9% montmorillonite, 9.1% quartz (feldspar was changed to quartz since feldspar is not yet in the calibration), 4.6% yeast, 4.6% polyethylene, 0% humic acid/salt, and 0% hydrated alumina for illustration of Mie-Bruggeman spectral modeling. After obtaining a permittivity for the mixture, IR spectra were calculated with a Mie program in MATLAB based on seminal work [40] at sizes from 0.5 to 15 microns diameters with incremental steps of 0.5 microns.

In order to investigate the effect of a particle size distribution on the IR spectrum, the published volume distribution versus particle size of Saharan dust as measured
at Izana, Tenerife, Canary Islands by Maring et al. [22] was digitized (see Figure 7.7) and interpolated at each of the particle diameters from 0.5 to 15 microns diameters with incremental steps of 0.5 microns to provide weights.

Figure 7.7: Peak height normalized dust aerosol volume size distributions from the free troposphere at Izana, Canary Islands (solid line) and from the marine boundary layer at Puerto Rico (dashed line) [22].

This distribution was not log normal due to loss of larger particles upon transport across the ocean, had multiple maxima, and was most intense in the 3-10 microns size regime (Figure 7.9). The normalized weighted sum over the Maring et al particle size distribution is presented as a black trace in Figure 7.9.

The IR absorption spectra of these Mie mixed-composition particles are shown in Figure 7.8 and Figure 7.13. The spectral intensities in cross section units were normalized by the particle volume. If there were no particle effects, i.e. in a Beer’s Law
limit, all of these spectra would be the same. Many common minerals, like the clays in Saharan dust, have strong vibrational transitions at approximately 1000 cm$^{-1}$ which is similar to the particle size and probing wavelength, so one can expect strong lineshape distortions [6]. To better see the lineshape distortions with particle diameter, the results in Figure 7.8 have been rotated and zoomed in Figure 7.9 to better observe the particle size lineshape distortions. The largest particles at 15 microns diameter give a broad and flattened profile at approximately 1000 cm$^{-1}$ which is the particle analog of the thickness saturation of films, while particles of approximately 5 µm diameter give the most intensity due to well-known Mie resonance effects. From this, it is evident that the strongest vibrational peak in the IR absorption spectrum can change dramatically with size.

Figure 7.8: Effect of particle diameter on the IR absorption spectra of particles of mixed composition characteristic of Saharan dust (Izana, Canary Islands). The black trace is the weighted average over the size [7].
Figure 7.9: Rotated and zoomed view of the effect of particle diameter on the IR absorbance spectrum of a characteristic Saharan dust mixture [7]. The black trace is the weighted average of these spectra based on the weights of the inset distribution as measured at Canary Islands [22].

Most atmospheric dust work involves the measurement of extinction spectra which are dominated by scattering effects. The IR extinction spectra of the Mie mixed-composition particles at Izana, Canary Islands is shown in Figure 7.10, and rotated, zoomed in Figure 7.11. Figure 7.12 compares the weighted average absorption and extinction spectra for the Saharan dust mixture and size distribution under consideration. The two spectra are on the same relative scale. There are many dispersive contributions in the extinction spectrum which will change dramatically with changes in the particle size distribution.
Figure 7.10: Effect of particle diameter on the IR extinction spectra of particles of mixed composition characteristic of Saharan dust (Canary Islands). The black trace is the weighted average over the size.
Figure 7.11: Rotated and zoomed view of the effect of particle diameter on the IR extinction spectrum of a characteristic Saharan dust mixture (Canary Islands). The black trace is the weighted average over the size.
Figure 7.12: Weighted average over the size distribution of the extinction and absorption spectra of the Saharan dust mixture under consideration (Canary Islands) [7].

If the size distribution changes with transport across the ocean, as shown by similar measurements in Puerto Rico, then the IR spectrum changes, even if the chemical composition is unchanged. To better see the lineshape distortions with particle diameter, the results in Figure 7.13 have been rotated and zoomed in Figure 7.14 to better observe the particle size lineshape distortions.
Figure 7.13: Effect of particle diameter on the IR absorption spectra of particles of mixed composition characteristic of Saharan dust (Puerto Rico). The black trace is the weighted average over the size.
Figure 7.14: Rotated and zoomed view of the effect of particle diameter on the IR absorbance spectrum of a characteristic Saharan dust mixture. The black trace is the weighted average of these spectra based on the weights of the inset distribution as measured at Puerto Rico. [22]

The IR extinction spectra of the Mie mixed-composition particles at Puerto Rico is shown in Figure 7.15, and rotated, zoomed in Figure 7.16.
Figure 7.15: Effect of particle diameter on the IR extinction spectra of particles of mixed composition characteristic of Saharan dust (Puerto Rico). The black trace is the weighted average over the size.
Figure 7.16: Rotated and zoomed view of the effect of particle diameter on the IR extinction spectrum of a characteristic Saharan dust mixture (Puerto Rico). The black trace is the weighted average over the size.

Figure 7.17 shows a comparison of particle size distributions between Canary Islands and Puerto Rico. Figures 7.18 and 7.19 compares the weighted average absorption and extinction spectra respectively for the Saharan dust mixture from the two locations under consideration.
Figure 7.17: Comparison of particle size distribution
Figure 7.18: Comparison of weighted absorption spectra
7.4 Conclusion

Due to the presence of very strong vibrational transitions in the common minerals present in atmospheric dust, the most intense IR signals that might be observed by infrared LIDAR are likely to be strongly affected by chemical composition, hence the utility of the Mie-Bruggeman model for mixed composition particles. Users can vary the composition and, in the context of a particular size distribution, predict the spectral response.
Chapter 8: Summary and Outlook

Photonic systems at subwavelength-scales are limited on their ability to control and focus electromagnetic waves. One of the important application of plasmonic systems is their ability to control light in a volume substantially smaller than the wavelength of probing light. Such control is made possible by carefully designing nanoparticle geometries and incident wave attributes. In this study, spectroscopic applications of plasmonic systems were explored using 3D FDTD simulations.

Chapter 1 provided an introduction to plasmonics, 3D FDTD simulations, and outlined some of the spectroscopic applications which were discussed in-depth in the following chapters.

In Chapter 2, the effects of particle size, lattice spacing, and lack of monodispersity of hexagonal arrays of Ag nanoparticles on the extinction resonance were investigated to help determine optimal design specifications for efficient organic solar power harvesting. The spectral behavior of hexagonal arrays of small (∼4 nm) Ag nanoparticles that are ∼100 times smaller than the probing wavelength was captured using the 3D FDTD method. The resulting extinction spectra resembled spectra of isolated Ag nanoparticles, except that there were shifts, increases in widths and intensities due to coupling between particles in the lattice. Results from uniform, periodic arrays (at varying radii and lattice parameter) were compared to the experimental extinction
spectrum of self-assembled hexagonal array of Ag nanoparticles with an unavoidable distribution of sizes and lattice parameters. The simulated spectra were always narrower and more structured, so a non-uniform, polydisperse system was modeled with a distribution of radii and lattice parameters. It was observed that polydispersity better explained the breadth and smoothness of the experimental spectrum.

In Chapter 3, transmission resonances of plasmonic micromesh were investigated. Simulations were performed using the 3D FDTD method. Transmission maxima for 0° and 90° polarizations of probing light were modeled with the SPP and cavity dispersion equations. The transmission maxima were compared to experimentally obtained results and it was found that although SPP curves were unable to fully model experimental data, they accurately predict peak positions obtained from 3D FDTD simulations. Strong cavity coupling with the widths of holes along the mesh surface were investigated. Results of the 3D FDTD simulations were used to study the effects of varying hole size of micromesh on (a) splitting between transmission maxima of CAV$_{0,0}$-SPP$_{0,\pm1}$ mixed states obtained from the 3D FDTD simulations (i.e. 3D FDTD transmission maxima of mixed state), (b) shift between 3D FDTD transmission maxima of mixed state and SPP$_{0,\pm1}$ dispersion curve, and (c) shift between CAV$_{0,0}$ and SPP$_{0,\pm1}$ dispersion curve. It was shown that as mesh hole size was increased, it resulted in more interaction between the SPP$_{0,\pm1}$ and CAV$_{0,0}$ modes. Hence it is concluded that cavity interactions perturb SPPs on plasmonic mesh, particularly at higher frequencies (i.e. top of dispersion plots).

In Chapter 4, plasmonic effects on isolated and arrays of Au nanorings were investigated both analytically, and using 3D FDTD simulations. This provided a great insight on how optical resonances can be controlled and tuned with respect to their
geometries. Nanoring structures allow higher LSPR tunability due to the extra DoF in the geometry, that facilitates interaction between the nanoring walls. It was also observed that a change in effective dielectric of the structure shifts the overall optical response, which is useful in sensing applications.

In Chapter 5, it was observed that wavelength-scale particles have their own unique set of spectroscopic challenges. At small sizes relative to the wavelength, particles exhibited Beer-Lambert-like behavior. However, with increase in particle size to about the wavelength of incident light, this behavior began to diverge from Beer-Lambert as shown with 3D FDTD simulations. It was observed that spectral lineshapes of wavelength scale particles can be distorted by phase, saturation, and orientation. Further, the Mie-Bruggeman model was tested by fitting absorption spectrum obtained from 3D FDTD simulations. Although more work is needed, the Mie-Bruggeman method reasonably predicted actual volume fractions of a mixed composition particle.

In Chapter 6, 3D FDTD simulations were performed to predict IR spectra of individual quartz particles trapped in holes of plasmonic Ni mesh. IR spectra of quartz are difficult to reproduce, not only because quartz is anisotropic, but also due to the fact that the Cassegrain optical system of FTIR microscope is quite complex to simulate. To reproduce such experimental spectra, the effects of angular spread on transmission widths were taking into account, and simulated by weighting the intensity at every frequency point in each calculated spectrum.

In Chapter 7, an application for the Mie-Bruggeman model was discussed. Due to the presence of very strong vibrational transitions in common minerals of atmospheric dust, the most intense IR signals are likely to be strongly affected by chemical
composition. It was shown that the Mie-Bruggeman model could be used to identify chemical composition of mixed particles. This model can predict shape and orientation-averaged extinction or absorption spectra of any desired mixture. This information will help not only climate studies, but also have implications for health studies associated with inhaling particulate matter from different environments.

The 3D FDTD simulations employed here based on Yee’s scheme are computationally intensive. In addition, consideration of a large number of different particles scenarios as done in this dissertation, involving mixed media cluster compositions, relative orientations of anisotropic particles, non-periodically trapped particles in a mesh and so on, can be very time-consuming. High-performance distributed computing resources, if available, can help accelerate the simulations. In addition, algorithm improvements can be done in the Yee’s scheme to reduce the computation cost. Of these, three improvements in particular can be applied in the future to the scenarios considered in this dissertation: (1) The use of FDTD subgridding techniques [115, 116, 117, 118] aimed at adaptively reducing the grid cell size in the regions where fine geometrical features are present to lessen the overall number of grid points necessary for a given numerical accuracy, (2) the use of unconditionally stable FDTD schemes [119, 120, 121, 122, 123] to overcome the Courant stability condition and allow for larger time steps, and (3) the use of Finite-Element Time-Domain (FETD) techniques [124, 125, 126, 127, 128] to provide higher flexibility in capturing particle geometries.
Appendix A: Analytical Model for Estimating Au Nanorings Array Resonances

In this section, an analytical model for estimating array resonances of Au nanorings is presented. Similar expressions have been previously derived by Elhawil et al [11].

To calculate the mutual inductance ($L_m$) between rings, Lyle’s method [129] is used. This method suggests that two circles of wire with rectangular cross section can be replaced by circular filaments, as shown in Figure A.1(a). The distance between the filaments called equivalent depth ($\delta$) (see Figure A.1(c)) can be obtained as

$$\delta = 2\sqrt{\frac{w^2 - t^2}{12}}$$  \hspace{1cm} (A.1)
To calculate mutual inductance between two filaments with parallel axes, the mutual inductance between filaments placed in a coaxial position ($M_0$) is first computed, as shown in Figure A.1(b). Then as described in [130, 131], this value is multiplied by a factor $F$ as follows

$$M = M_0 F$$  \hspace{1cm} (A.2)
in which the factor $F$ depends on the ratio of $2a/l$, where $l$ is the distance between the centers (lattice constant) and $a$ is the radius of the filament. The values of $F$ are given in [129] for different values of $2a/l$. The filaments 1 and 3 have the same radius, which is equal to $a_1 = a_3 = r + \delta/2$, and the radii of filaments 2 and 4 are $a_2 = a_4 = r - \delta/2$.

For filaments of unequal radii (1 and 4, 2 and 3), the value $F$ is approximately the average of corresponding values of their factors. Maxwell’s formula for $M_0$ is given by [129, 130, 131]

$$M_0 = \mu_0 \sqrt{a_1 a_2} \left( \left( \frac{2}{k} - k \right) E_1 - \frac{2}{k} E_2 \right)$$  \hspace{1cm} (A.3)

where $a_1$ and $a_2$ are the radii of the two filaments, $E_1$ and $E_2$ are the complete elliptic integrals of the first and second kind, respectively, to modulus $k$, where

$$k = \frac{2 \sqrt{a_1 a_2}}{\sqrt{(a_1 + a_2)^2 + l^2}}$$  \hspace{1cm} (A.4)

The total mutual inductance between the rings is the mean of the four inductances $M_{13}$, $M_{14}$, $M_{23}$, and $M_{24}$, where $M_{13}$ is the mutual inductance of filaments 1 and 3 etc.
Further, the total capacitance of the ring also includes coupling capacitance ($C_c$). The coupling capacitance is estimated using the rectangular sub-domain modeling method. This method was presented in [132]. As shown in Figure A.2, the ring is divided into rectangles and the coupling capacitance between the rings is considered by calculating the capacitance between the matched rectangles at each side of the ring. The final derived expression of the coupling capacitance of this circuit becomes

$$C_c = \frac{1}{2 \varepsilon_{r_{v1}}} + \frac{2}{2 \varepsilon_{r_{v2}}}$$  \hspace{1cm} (A.5)

where, $C_{r1} = C_1 + 2C_2$ and $C_{r2} = 2C_3 + 2C_4$. The derived expression for the capacitance between two parallel plates on a substrate is given in [133, 134].

$$C = \frac{\varepsilon_m L}{2} \left[ \frac{K(k_0')}{K(k_0)} + \varepsilon_r \frac{K(k_1')}{K(k_1)} \right]$$  \hspace{1cm} (A.6)
where $K(k'_{0}), K(k_{0}), K(k'_{1}),$ and $K(k_{1})$ are the complete elliptic integrals of the first kind with $k'_{0} = \sqrt{1 - k_{0}^2}$ and $k'_{1} = \sqrt{1 - k_{1}^2}$. $k_{0}$ and $k_{1}$ are obtained from Table A.1.

<table>
<thead>
<tr>
<th>Capacitance</th>
<th>$l$</th>
<th>$W_s$</th>
<th>$W_l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_g$</td>
<td>$w$</td>
<td>$g$</td>
<td>$r_{i-g/2}$</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$2r_i$</td>
<td>$1-2r_0$</td>
<td>$w$</td>
</tr>
<tr>
<td>$C_2, C_3$</td>
<td>$w$</td>
<td>$1-2r_0+2w$</td>
<td>$r_i$</td>
</tr>
<tr>
<td>$C_4$</td>
<td>$r_{i-g/2}$</td>
<td>$1-2r_0$</td>
<td>$w$</td>
</tr>
</tbody>
</table>

$$k_0 = \frac{W_s}{2W_l + W_s} \quad (A.7)$$

$$k_1 = \frac{\tanh(\pi W_s/4h)}{\tanh(\pi(2W_l + W_s)/4h)} \quad (A.8)$$

where $W_s$ is the spacing between the plates, $W_l$ is the width of the plates, and $l$ is the length of the plates. Table A.1 lists expressions of $W_s$ and $W_l$ for each capacitance.
Appendix B: Example MATLAB Program for Fitting Lineshapes to Equation (5.4)

%% Written by A. Luthra, and A. Ravi

clear all; clc; close all;
Data=xlsread('DATASET.xlsx');
Ext=Data(:,2:end);
nudata=Data(:,1);
[r c]=size(Ext);

%% model parameters
A=0.2; %S/Gamma
B=0.1; %phi
C=2917; %nu0
D=10; %Gamma
E=0.0; %constant
%Abs-Disp = A*(cos(B)-((Nu-C)/D)*sin(B))/(1+((Nu-C)/D)^2)+E

for i=1:c
  %% data
  Edata=[Ext(:,i)];

  %% optimized fitting
  options=optimset('Display','iter','TolFun',1e-25,'TolX',1e-25,'TolCon',1e-25,'FinDiffRelStep',1e-25,'MaxIter',10000);
  alpha0=[A B C D E];
  Emodel=@(alpha,nudata)myfunFDTD(alpha,nudata);
  [alpha,R,J,CovB,MSE,ErrorModelInfo]=nlinfit(nudata,Edata,Emodel,alpha0,options);
  A=alpha(1);
  B=alpha(2);
  C=alpha(3);
D = alpha(4);
E = alpha(5);
Optimized(:,i) = [A; B; C; D; E];

%% nlparci: Confidence Interval
ci = nlparci(alpha, R, 'Jacobian', J);
lowerbound = ci(:,1);
upperbound = ci(:,2);
Err1(i,:) = alpha' - lowerbound;
Err2(i,:) = alpha' - upperbound;
Emodel = A.*(cos(B) - ((ndata - C)./D).*sin(B))./(1 + ((ndata - C)./D).^2) + E;
plot(nudata, Ext(:,i), 'r')
hold on
plot(nudata, Emodel, 'b')
end
Appendix C: Other Miscellaneous Results on Quartz Particle Trapped in Micro-Mesh

IR experimental spectra of individual crystalline quartz particles are difficult to reproduce, not only due to their anisotropic permittivities, but also due to the complexity of experimental optical systems. Nevertheless, quartz is one of the most prevalent mineral components in airborne particulate matter [8, 91, 92, 93, 94, 95], i.e. people routinely inhale it into their lungs. Therefore it is important to know the distribution of quartz in ordinary airborne particulate matter as an indication of tolerable levels.

Plasmonic mesh makes it possible to record scatter-free IR spectra of different, individual quartz particles by trapping them in mesh holes. 3D FDTD simulation models enrich such experimental studies. In this section, miscellaneous 3D FDTD results on quartz particle trapped in mesh hole are listed.
Figure C.1: Scatter-free averaged spectra (dotted line) plotted against quartz spectra at perpendicular incidence, $k_x = 0$ for various particle sizes. Results calculated using 3D FDTD simulations.
Figure C.2: Effect of source polarization on scatter-free spectra of quartz particle at perpendicular incidence, $k_x = 0$ calculated using 3D FDTD simulations.
From Figures C.1, C.2, and C.3, it is evident that there are many factors that affect the spectra of oriented crystal microparticles with anisotropic permittivities.
Appendix D: List of Abbreviations and Nomenclature

1D.......... one-dimensional
2D.......... two-dimensional
3D.......... three-dimensional
Ag.......... silver
Au.......... gold
BC.......... boundary condition
DoF.......... degree of freedom
EOT.......... extraordinary optical transmission
EPA.......... Environmental Protection Agency
fs.......... femtosecond
FDTD.......... Finite-Difference Time-Domain
FETD.......... Finite-Element Time-Domain
FTIR.......... Fourier transform infrared
FWHM.......... full-widths-at-half-maximum
HWHM.......... half-widths-at-half-maximum
ITO........ indium-tin oxide

IR.......... infrared

LIDAR....... LIght Detection And Ranging

LSPR........ localized surface plasmon resonance

MCT.......... mercury cadmium telluride

Ni.......... nickel

nm......... nanometer

PM.......... particulate matter

P3HT........ poly(3-hexylthiophene)

PCBM........ [6,6]-phenyl C61 butyric acid methyl ester

PEDOT:PSS... poly (3,4-ethylenedioxythiophene) poly (styrene sulfonate)

PML......... perfectly matched layer

PV.......... photovoltaic

SEM.......... scanning electron microscope

SERS........ surface enhanced Raman spectroscopy

SiO₂... silicon dioxide

SP.......... surface plasmon

SPP......... surface plasmon polariton

TEM......... transmission electron microscopy

ZnSe........ zinc selenide
Bibliography


