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Subradiant, Superradiant and Fano Resonances in Dimer and Ring/Disk Nanocavities

by

Heidar Sobhani Khakestar

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APPROVED, THESIS COMMITTEE:

Peter J. Nordlander, Chair
Professor of Physics and Astronomy
Professor of Electrical and Computer Engineering

Naomi J. Halas
Stanley C. Moore Professor of Electrical and Computer Engineering
Professor of Chemistry

Daniel Mittleman
Professor of Electrical and Computer Engineering

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ABSTRACT

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Subradiant and superradiant plasmon modes in ring/disk nanocavities and dimers are investigated theoretically and experimentally. The subradiance is obtained through an overall reduction of the total dipole moment of the hybridized mode due to antisymmetric coupling of the dipole moments of the parent plasmons. We observe the appearance of Fano resonances in the optical response of plasmonic nanocavities due to the coherent coupling between their superradiant and subradiant plasmon modes due to structural symmetry breaking. Both subradiant modes and Fano resonances exhibit substantial reductions in linewidth compared to the parent plasmon resonances, opening up possibilities in optical and near IR sensing via plasmon lineshape design. Four reduced-symmetry nanostructures studied via Plasmon Hybridization and FDTD (Finite Difference Time Domain), a dolmen-style slab arrangement, a ring/disk dimer, a ring/disk cavity and a colloid dimer, clearly exhibit the strong polarization and geometry dependence expected for this behavior at the individual nanostructure level, confirmed by experimental result in each case, multiple Fano resonances occur as structure size is increased.
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Chapter 1: Introduction

Localized plasmon resonances in small metallic nanostructures have attracted large interest in the scientific community for over a century, because of their strong interaction with visible light [1,2]. Initially, studies focused mainly on colloidal particles but more recently, along with the development of the field of nanoplasmics, more insight and control has been gained on localized plasmon resonances in well-controlled structures fabricated using top-down nanotechnology [3,4]. It is well-known that the electromagnetic field in the vicinity of a nanoparticle is enhanced at the plasmon resonance. This enhanced near field can be used to increase the sensitivity of various spectroscopic techniques, such as Raman scattering or infrared absorption spectroscopy [5-7]. Moreover, the scattering and absorption cross sections of nanoparticles are enhanced at the plasmon resonance, which can be used to increase the efficiency of solar cells [8], or possibly cure cancer utilizing thermal effects [9]. As the spectral position of the plasmon resonance depends on the refractive index of the medium surrounding the nanoparticle, nanoplasmic structures can also be utilized as highly integrated optical sensors [10].

All the above-mentioned applications use the fact that the plasmon resonance depends directly on the morphology and size of the nanoparticle. Various geometries have been proposed and fabricated to match the requirements of the application, ranging from spheres [1,11], rods [11] or rings [12,13] to more complex structures such as
nanoeggs or nanostars [14,15]. Control over the spectral position of the plasmon resonance in such single nanostructures is generally very good. However, control over the line shape of the resonance has not yet received as much attention, although many applications would benefit from for example nanostructures with sharp plasmon resonances – i.e. a higher quality factor. For instance, Sherry and coworkers have introduced the concept of a figure of merit (FOM) to characterize the sensitivity of a plasmonic sensor [16]: this FOM is inversely proportional to the width of the resonance. Another example is the “(lasing) spaser” [17]: the production of a coherent output of surface plasmons or photons in plasmonic nanocavities, which will also require a high quality factor.

The main decay channels contributing to the linewidth of a plasmon resonance are: non-radiative decay of the coherent electron oscillations in internal channels (inter-/intra-band transitions of the electrons, interaction with phonons etc...), and radiative decay [18,19]. For small particles (diameter < \( \lambda_{\text{res}} \)), non-radiative processes are dominating [11,19]. For larger particles (diameter > \( \lambda_{\text{res}} \)), radiative damping dominates [20]. To manipulate the radiative damping, one can exploit the concept of plasmon hybridization [21] to study coherent coupling between closely spaced nanostructures. For example, it has been predicted theoretically that concentric ring/disk cavities (CRDC) will exhibit sub and superradiant modes due to hybridization of the fundamental dipolar modes of the two constituents [22] and that Fano resonances can arise due to the interaction with higher order modes, when the structural symmetry is broken [23]. Coherent effects in plasmonic nanocavities and particularly Fano resonances have recently received a large
amount of attention [23–32]. The Fano resonance can evolve into a classical analogue of electromagnetically induced transparency (EIT) when the energy levels of the interacting resonances coincide [30,33,34].

In this thesis we focus on sub- and superradiant plasmonic modes, as well as Fano resonances, in different structures as a dolmen-style slab arrangement, a ring/disk dimer, a ring/disk cavity and a colloid dimer. Using confocal spectroscopy of single cavities, we experimentally demonstrate that a CRDC exhibits both subradiant and superradiant dipolar modes, as suggested by earlier simulations [22]. Moreover, by displacing the disk from the center of the ring in a non-concentric ring/disk cavity (NCRDC) or using Ring Near Disk Cavities (RNDC) or using colloid dimer we observe the coherent interaction between the bright dipolar resonance of one particle and the dark multipolar resonances of the other nanoparticle, which generates Fano resonances. We also comment on the sensing capacities of these CRDC structure. At the end we look at the transverse excitation of colloid nanoparticle and explore the directional properties of dimer structures. The experimental results and finite-difference time-domain (FDTD) simulations have a very good agreement, which shed light on the nature of the underlying resonances.
Chapter 2: Subradiant and Superradiant

2.1 Introduction

In this chapter we focus on a first experimental characterization of sub- and superradiant plasmonic modes in ring/disk nanocavities. We also comment on the sensing capacities of these structures. The subradiance is obtained through an overall reduction of the total dipole moment of the hybridized mode due to antisymmetric coupling of the dipole moments of the parent plasmons. We use plasmon hybridization to highlight how the sub- and superradiant dipolar modes arise from the associated parent plasmon modes.

2.2 Subradiant and Superradiant in CRDC

Figure 2.1 presents a hybridization diagram outlining how the sub- and superradiant dipolar modes arise from the associated parent plasmon modes in a CRDC of dimensions $D_{\text{out}} = 250 \text{ nm}$, $D_{\text{in}} = 100 \text{ nm}$, $D_{\text{disk}} = 75 \text{ nm}$ and thickness 50 nm. Figure 2.1a shows the experimentally measured extinction and Figure 2.1b the corresponding curves obtained via FDTD. The extinction of the ring alone (black curve) exhibits a peak in the near-infrared, corresponding to a dipolar mode, as shown by the charge plot in the inset. If a disk with a diameter $D_{\text{disk}}$ slightly smaller than $D_{\text{in}}$ is inserted at the center of the ring, its dipolar mode (red curve) hybridizes with the dipolar ring modes as indicated by the dotted lines, giving rise to the observed extinction spectrum of a CRDC (blue curves).
Figure 2.1: Hybridization diagram for a concentric ring/disk cavity (CRDC). a. Experimental extinction measurements of single structures, a disk (red), CRDC (blue) and ring (black). $D_{\text{out}} = 250$ nm, $D_{\text{in}} = 100$ nm, $D_{\text{disk}} = 75$ nm. The insets show scanning electron microscopy (SEM) images of the structures, with a scale bar of 100 nm. b. Simulated extinction curves for the structures of panel a., for $D_{\text{out}} = 250$ nm, $D_{\text{in}} = 100$ nm, $D_{\text{disk}} = 92$ nm and a thickness of 60 nm. The insets show the charge densities for the respective resonances, blue (resp. red) indicating negative (resp. positive) charges.

The dipolar mode at higher energies exhibits an increased linewidth and has acquired a superradiant character due to a parallel coupling between the dipolar modes of the parent disk and ring plasmons. Conversely, in the low energy mode, an anti-parallel orientation of the parent dipole moments leads to a reduced net dipole moment. This subradiant character is reflected in the spectrally sharper linewidth with smaller radiative losses. This interpretation is well supported by the surface charge plots at the associated resonance energies, depicted in the insets.

To experimentally obtain the true resonance linewidth, problems induced by chromatic aberrations at low energies had to be circumvented. We therefore performed
separate measurements, employing illumination by short wavelength intervals at a time (not shown). These measurements show experimental full width at half maximum linewidths of $680 \pm 50$ meV for the ring dipole, and $330 \pm 50$ meV for the subradiant mode of a CRDC with an estimated gap of 6 nm. For these device parameters, simulations have indicated linewidths of $350 \pm 10$ meV for the ring and $130 \pm 10$ meV for the CRDC. One will note that in this study, the simulated linewidths are systematically lower than the experimental linewidths. We attribute this to the fact that in the simulations, the dielectric constant used to simulate the gold is a bulk dielectric constant. The fabricated structures present a high surface over volume ratio, which deviates from a bulk approximation. Moreover, the walls of the structures are rough, because of the fabrication process used here. This can be observed on the SEM images presented in this report. Those two effects contribute to the increase of the losses in the structures, leading to linewidths larger in the experiment than in the simulations.

This concentric arrangement allows for a formidable control over the plasmon resonance position and width of the structure. Indeed, as it is the case for any plasmonic resonator, one can select the spectral position of the resonances by changing its dimensions. This is illustrated on Figure 2.2: panel a (resp. b) presents the experimental extinction cross sections for cavities built out of a ring with dimensions $D_{\text{out}} = 250$ nm, $D_{\text{in}} = 100$ nm (resp. $D_{\text{out}} = 220$ nm, $D_{\text{in}} = 75$ nm). The corresponding FDTD simulations are shown on panels b and d. One can observe that the 30 nm reduction in the diameter of the ring leads to a 100 nm blue-shift of the resonances. In addition to this feature common
to all plasmonic cavities, the linewidth tuning, for a specific ring, of the corresponding CRDC can be achieved by varying the gap between ring and disk. The smaller the gap, the stronger the interaction between ring and disk modes, leading also to an increase in the spectral separation of the sub- and superradiant modes.

Figure 2.2 illustrates this effect for the same ring as in Figure 2.1. In the experimental structures (SEM images shown in Figure 2.2e, f and g; measured extinction spectra in Figure 2.2a), the target gap is changed by steps of 2.5 nm. The gap obtained at the end of the fabrication process is difficult to estimate, as shown on the SEM images. In
the simulations (Figure 2.2b), the gaps are 8, 6 and 4 nm. Both measured and simulated extinctions clearly show how the subradiant mode shifts towards the red and narrows as the gap is reduced, with widths of 190±10, 140±10 and 90±10 meV for gaps of 8, 6 and 4 nm, respectively. This additional degree of freedom on the plasmon resonance can be of interest for many applications. We will discuss two of them: Surface Enhanced Raman Scattering (SERS), and sensing, in a later part of this report.

2.3 Sensing Capacity

We finish this chapter by a preliminary sensing study where the whole structure is immersed in liquid. Figure 2.3a shows how the resonance of the structure described in Figure 2.1a (blue curves) behaves in media with different refractive indexes. The experiment has been conducted by creating a small “cell” with the substrate and a second glass slide, separated by optical fibres, as sketched in panel c. Water is introduced in the cell after treating the sample in an O2 plasma cleaner (50 W, 3 min.) to improve wetting of the surface, and the spectra are acquired (blue curve in Figure 2.3b). They are then compared with the spectra for the cell filled with air (red curves). In the experiment a red-shift of 90±10 nm of the low-energy peak is observed (i.e. 510 meV RIU⁻¹), which would correspond to a FOM (Figure Of Merit) [35] of 1.6. Turning our attention to the corresponding simulations (Figure 2.3b), we observe that the expected shift should be 175 nm for a similar refractive index change (600 meV RIU⁻¹, FOM of 3, red curve to green curve).
Figure 2.3: Sensing with a CRDC. a. Experimental extinction spectra for the cavity (dimensions $D_{\text{out}} = 250$ nm, $D_{\text{in}} = 100$ nm and $D_{\text{disk}} = 75$ nm) in air (red) and water (blue). b. Simulated spectra for a similar cavity ($D_{\text{out}} = 248$ nm, $D_{\text{in}} = 100$ nm and $D_{\text{disk}} = 88$ nm). Red: in air, green: in water, with the gap completely filled and blue: in water with 3/4th of the gap filled. c. Sketches of the sensing cell: optical fibres (diameter = 200 µm) separate the sample from a capping glass coverslip.

The discrepancy can be explained by the fact that most of the sensing capabilities of the cavities lie in the gap [22,23], where the water wetting is very poor. This reduces the observed shift compared to total filling. For instance, a simulation accounting for a filling of only 3/4th of the gap height seems to reproduce very well the experimental shift (Figure 2.3b, green curve). Although higher FOMs for single nanostructures have indeed been reported in the literature (up to 5.4 for silver nanoparticles with resonances in the visible part of the spectrum [37,38]), our approach allows for radiative loss and hence FOM engineering throughout the whole near- and via scaling also the mid-IR part of the spectrum, where resonances of single nanostructures show large radiative damping due to their physical size. Further optimization of cavity fabrication should allow to create structures with higher FOMs [23].
Chapter 3: Fano resonance

3.1 Introduction

Fano interference is a physical phenomenon that takes place in atoms [44-46], metamaterials [26], and plasmonic [7,23,43,48,49] and excitonic structures [48-50]. Generally speaking, it exists when a discrete excited mode and a broad mode with similar energy interfere to result in a characteristic dip or asymmetry in the extinction spectrum. Fano resonances can occur in plasmonic nanostructures when narrow LSPR modes couple to broad LSPR modes [23,30,43,50,51]. The geometry of the structure plays a key role in whether or not a Fano resonance can occur because it strongly influences the spectral locations of all of the modes.

In this chapter we investigate Fano resonances in non-concentric gold ring-disc cavities, nanoscale dolmen-style gold slabs and gold nanoparticle dimers. Strong coupling between a broad superradiant mode with high radiation dissipation and a dark mode with low radiation loss, that are close in energy induce Fano resonance in all these structure. Interestingly, these conditions do not require a high degree of asymmetry, as would be found in heterodimers, which consist of two different particles. We will explain how both heterodimers and homodimers, which consist of two identical particles, are capable of exhibiting Fano resonances.
3.2 Fano resonance in Dolmen slabs and Ring/Disk Cavities

In structural symmetric systems, only plasmon modes of the same multipolar index \( (l) \) can interact because coupling coefficients are zero for different plasmon modes in system Hamiltonian due to system symmetry. By breaking symmetry in dolmen-style slab, ring/disk and colloid dimer all different plasmon modes can interact with each other and produce Fano resonance. Dimension parameters for dolmen-style slab and ring near disk cavity are defined in figure 3.1.

![Figure 3.1: Geometry and labeling convention for (a) dolmen-type resonators and (b) disk-near-ring resonators. Insets: SEM images of single structures, scale bar 200 nm.](image)

For the dolmen structure, the Fano interference phenomenon occurs due to the structural overlap of a bright dipolar mode of the slab monomer with an antisymmetric dark mode of the dimer [33]. The latter is set up due to counter propagating currents in the two individual slabs constituting the pair, leading to vanishing dipole moment. Results from extinction measurements of a single Au dolmen structure are presented in Figure 3.2.
Figure 3.2: Fano resonance of an individual dolmen structure with the following parameters: $L_1 = 160$ nm, $w_1 = 110$ nm, $L_2 = 135$ nm, $w_2 = 100$ nm, $S = 55$ nm, $G = 20$ nm, $H = 60$ nm. Panels (A) and (B) show experimentally and numerically obtained extinction spectra, respectively, for the particular structure shown in the SEM inset, with polarization as defined by the two arrows. Panel C shows the evolution of these two extinction spectra as the polarization direction is changed in regular steps.

For this particular structure, the dimensions of the individual slabs are $L_1 = 160$ nm, $w_1 = 110$ nm, $L_2 = 135$ nm, $w_2 = 105$ nm, $S = 40$ nm, the height (i.e. the gold thickness) $H = 60$ nm, and the spacing between the slab dimer and monomer is $G = 20$ nm. Panel A shows experimentally obtained extinction spectra for two distinct polarizations, as indicated in the inset. For the electric field vector parallel to the symmetry axis of the dimer (red curve), a broad dipolar mode of this structure is excited, due to the setup of copropagating surface currents in the individual slabs. However, for field polarization perpendicular to the dimer axis (blue curve), and hence along the direction of the long axis on the monomer, the excitation of counterpropagating currents in the slab dimer leads to the establishment of a dark quadrupolar mode. While dark for individual dimers, the presence of the monomer allows for dispersive interference between the sharp quadrupolar and broad dipolar modes. The resulting asymmetric Fano lineshape with the
central dip at about $\lambda = 750$ nm is clearly resolved. Panel B shows numerical results obtained using finite difference time domain (FDTD) modeling of extinction, and is seen to be in good agreement with our experimentally obtained results. The insets showing surface charge distributions reveal the symmetries of the associated oscillator modes. For the modeling, the dielectric response of the metal was fitted using a combination of Drude and Lorentz oscillator terms to the experimentally determined dielectric permittivity [42]. This fit has an excellent agreement with the dielectric permittivity measured by ellipsometry on the gold of our samples. Finally, in panel C we show how the experimentally obtained extinction spectra for both polarizations highlighted in panel A evolve into each other for changes of in-plane polarization direction in $10^\circ$ steps. We point out that the structure presented here is not optimized in terms of obtaining a maximum sharpness for the dip in extinction, in a context of EIT. The strength of the EIT phenomenon depend both on the spectral overlap of the sharp and broad resonances, and their coupling strength mediated by the separation between dimer and monomer. Ultimately, the sharpness of the dip is limited by the dielectric losses of the metal [27].

Analogous results for a representative RNDC configuration are presented in Figure 3.3. The geometric parameters of this particular structure are $D = 325$ nm, $d2 = 425$ nm, $T = 80$ nm, $G = 20$ nm and height $H = 30$ nm. While not as pronounced as for the dolmen presented in figure 3.2, a clear depression in extinction is observed in the spectral region around $\lambda = 1100$ nm for polarization along the dimer axis (panel A).
Figure 3.3: Fano resonance of a RNDC structure, with the following dimensions: D = 325 nm, d\textsubscript{2} = 425 nm, T = 80 nm, G = 20 nm, H = 30 nm. Apart from the following precisions, the layout of the figure is identical to Figure 3.2. A. Inset: scale bar 320 nm (disc diameter). B. Inset: charge plot for the wavelength corresponding to the dip indicated by the arrow. The experimental data show a less pronounced dip and a red shift of all the spectrum compared to the simulation, of approximately 100 nm.

An inspection of the associated surface charge distributions reveals that this depression is due to the coupling of a quadrapolar ring mode with a broad dipolar disk mode. Experimentally and computationally obtained extinction spectra are qualitatively similar. The discrepancy could be due to the fact that our illumination spot is smaller than the full spatial extend of the RNDC, leading to a direct extinction of multipolar modes and hence weakening the asymmetry of the Fano lineshape [23]. For polarization perpendicular to the dimer axis on the other hand the mutual coupling is very weak and the extinction spectrum coincides with the sum spectrum of an individual disk and ring.
Figure 3.4: Fano resonances in non-concentric ring/disk cavities (NCRDC). a. Measured extinction spectra of single cavities with various degrees of broken structural symmetry. Black: disk with $D_{\text{disk}} = 150$ nm; grey: ring with $D_{\text{out}} = 350$ nm and $D_{\text{in}} = 200$ nm; red: concentric combination of both; orange, green and blue: non-concentric arrangements with increasing offsets. b. Corresponding simulated extinction cross sections. Color code identical to panel a., but grey (resp. dotted grey): ring illuminated at grazing (resp. normal) incidence. Orange, green and blue curves are for structures with gaps of 12, 8 and -4, respectively. Spectra have been offset for clarity, the dotted lines giving their baselines. c, d, and e. SEM images of the corresponding ring (grey curves), CRDC (red curves) and NCRDC (orange curves). Scale bars: 100 nm.

Figure 3.4 shows this effect for a specific NCRDC made out of a ring with the parameters $D_{\text{out}} = 350$ nm and $D_{\text{in}} = 200$ nm and a disk of diameter $D_{\text{disk}} = 150$ nm. Figure 3.4a and b show extinction spectra obtained from measurements and simulations, respectively, with different degrees of symmetry breaking. Figure 3.4c, d, and e show representative SEM images of the ring, CRDC and NCRDC. As apparent from the
extinction spectrum obtained using oblique incidence (grey solid line in Figure 3.4b), the ring cavity exhibits a series of higher-order, dark modes at energies within the superradiant continuum, which are not directly excited at normal incidence (grey dotted line). The insets in Figure 3.4a present the charge distributions associated with those high order modes, illustrating their symmetry: the lowest wavelength peak is an octupole mode, and the peak just below 800 nm is a quadrupole mode. When the symmetry of the CRDC is broken by displacing the disk from the centre of the ring (cf. Figure 3.4e), these dark ring modes can interact with the superradiant mode. Hence a change in lineshape occurs from that of the concentric case (red curve) to a situation where dips in extinction are apparent, with a depth increasing with increasing offset of the disk from the ring center (Figure 3.4, orange and green curves). The interaction gets even stronger when the disk starts to touch the ring (blue curve). The experimental trend follows very well the simulations, apart from a slight red-shift of a few tens of nanometers. The Fano resonance represents a narrow spectral transmission band within the broad continuum with a linewidth around 150±20 meV, which is less than half of the 370±20 meV linewidth of the disk alone.

3.3 Fano resonance in Colloid Dimers.

ESEM images of the specific dimers to be discussed in this project are shown in Figure 3.5. These consist of three NP-NP dimers and three NP-NS dimers, in which the size of one particle remains the same while the size of the adjacent particle changes.
Throughout the rest of this thesis, these structures will be referred to as Dimers A-F, as indicated in Figure 3.5.

Figure 3.5. ESEM images of six individual dimers to be discussed in this thesis. Dimers are on PVP-functionalized glass. Nanoparticles are identified by facets and uniform contrast. Nanoshells are identified by nonuniform contrast due to the thin gold shell. (A-C) NP-NP dimers; (D-F) NP-NS dimers. See Table 1 for specific dimensions of particles used in FDTD simulations.

Spectroscopic analyses of each dimer were carried out using an inverted dark field microscope equipped with a polarizing filter and a spectrometer, as in a previous work by Lassiter and coworkers [37]. The incident beam consisted of s-polarized white light from a halogen lamp, and the angle of polarization parallel to the plane of the sample was adjusted by rotating the sample stage. Scattering spectra were taken with light polarized parallel and perpendicular to the dimer axis. For each angle of polarization, a second measurement was taken with the k-vector facing the opposite direction, resulting in a total of four polarized scattering spectra for each dimer.
Scattering spectra were fitted using the finite difference time domain (FDTD) method. In each simulation, the particles in each dimer were surrounded by a 2-nm dielectric layer with $\varepsilon = 2.25$, which corresponded to the MUOH passivation layer. The dimers were located on top of an infinite dielectric slab with $\varepsilon = 2.25$, where the dimer axis was parallel to the surface of the slab. The PVP adhesion layer was incorporated into the slab as also having a permittivity of $\varepsilon = 2.25$. Table 1 lists the specific dimensions of the dimers in each simulation. All particles were approximated as perfect spheres except Particle 2 in Dimer A, which was prolate. The gap size corresponds to the shortest distance between the outer surfaces of the particles at the junction region.

Table 3.1 Dimensions of Dimers A-F in FDTD simulations. See Figure 3.5 for corresponding ESEM images. The two radii given for Particle 2 in Dimer A represent its minor and major axes, respectively.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>Nanoparticle 1</th>
<th>Nanoparticle 1 Radius (nm)</th>
<th>Nanoparticle 2</th>
<th>Nanoparticle 2 Inner Radius</th>
<th>Nanoparticle 2 Outer Radius</th>
<th>Gap Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NP</td>
<td>24</td>
<td>NP</td>
<td>--</td>
<td>76, 90</td>
<td>1</td>
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<tr>
<td>B</td>
<td>NP</td>
<td>50</td>
<td>NP</td>
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<td>76</td>
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<td>C</td>
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<td>D</td>
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<td>F</td>
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<td>76</td>
<td>NS</td>
<td>66</td>
<td>84</td>
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</tbody>
</table>
The dielectric response of the metal was fitted using Lorentzian oscillator terms according to the permittivity of gold defined by Johnson and Christy [40]. The incident light beam was s-polarized with the k-vector parallel to the substrate. To accommodate for experimental error, the incident polarization angle was adjusted slightly until a proper fit was obtained. Backscattering data were collected from a cone angle of 64 degrees from normal, which corresponds to the collection angle of the dark field objective used in the experiment.

As stated above, when the incident beam is polarized parallel to the dimer axis, the plasmon modes of the constituent particles hybridize to result in a unique scattering spectrum for each dimer geometry. This is evident in Figure 3.6, which shows experimental and theoretical backscattering spectra calculated by FDTD for Dimers A-F with the incident light polarized in the longitudinal direction. The spectra are not affected by the direction of the propagation vector, k, because each system is symmetrical along dimer axis. Therefore, for simplicity, all theoretical spectra in Figure 3.6 include only one direction of propagation.
Figure 3.6. Experimental and theoretical backscattering spectra for Dimers A-F with longitudinally polarized incident light. Because the spectra for opposing k-vectors are identical due to symmetry, theoretical plots include only one direction of propagation. Dimensions for each dimer simulation are given in Table 1.

When Particle 2 is replaced with a nanoshell in Dimers D-F, the comparative spectra are strikingly similar. This indicates that the plasmon modes are primarily interacting at the outer surfaces of the particles. Two main features are identified in each spectrum: a small peak around 600 nm and a large peak between 800-1000 nm. As the size of Particle 1 increases, the large peak broadens and redshifts, while the small peak retains its location around 600 nm. The reason for this trend will be clearer with an understanding of the plasmon modes that are producing these resonances. Because the dimers have similar geometries, mode assignments in one dimer will be similar to those in the rest.
Therefore, we will focus the following discussion of plasmon hybridization on Dimer A.

The plasmon hybridization method has long been used as an intuitive tool to determine the plasmon energies of metallic nanostructures [36,38,39]. Since it has been rigorously derived only in the quasistatic limit, we must scale down the size of the structure in order to make an accurate comparison between FDTD and plasmon hybridization. Figures 3.7A and 3.7B give a series of absorption and scattering spectra, respectively, calculated by FDTD for an idealized Dimer A, in which both particles are spherical with radii of 24 nm and 76 nm and a gap size of 2 nm.

The top spectrum in each panel corresponds to the full-size structure, and in each subsequent spectrum, the entire geometry is scaled down by increments of 10%. Figure 3.7C gives absorption versus energy calculated by the plasmon hybridization method (dashed line), which shows excellent agreement with the FDTD result at a size scaling of 0.1 (solid line). Assignment of peaks is straightforward when comparing this plot with Figure 3.7D, which gives the energies of the eigenstates in Dimer A as a function of gap size calculated by the plasmon hybridization method with an azimuthal index of $m = 0$. Each eigenstate may be identified by $\Phi_n$, where the lowest eigenstate is $\Phi_1$, the next is $\Phi_2$, and so on. For convenience, the x-axis of Figure 3.7D displays the gap of the full-size structure.
The energies at this size are identical to those in the 0.1 case because the plasmon hybridization method is scale-invariant because retardation effects are not included. The lowest-energy curve ($\Phi_1$, dark blue) is the symmetric longitudinal dipole mode ($l = 1, m = 0$). This results from hybridization between the dipole of Particle 1 and the dipole of Particle 2, where the resonances of both particles are oscillating in phase with each other.
We will refer to this mode as the bonding dipole-dipole (BDD) mode. In \( \Phi_2 \) and \( \Phi_3 \), we see an exchange between the antibonding dipole-dipole (ADD) mode (green), in which the dipole resonances are oscillating out of phase, and the bonding dipole-quadrupole (BDQ) mode (red), which results from hybridization between the dipole of Particle 1 and the quadrupole of Particle 2. At large gap sizes, the BDQ mode is higher in energy than the ADD mode. However, when the gap size reduces to 5-7 nm, there is an avoided crossing between the eigenstates, where the energy curves repel each other. Although the states are fairly separated in energy, this observation indicates that they are strongly interacting. Further inspection shows that the BDQ and ADD modes exchange at small gap sizes. In Figure 3.7D, this is represented by a change in color between green and red at a gap of 5 nm in \( \Phi_2 \) and 7 nm in \( \Phi_3 \).

Similarly, \( \Phi_4 \) and \( \Phi_5 \) exchange between the antibonding dipole-quadrupole (ADQ) mode (yellow) and the bonding dipole-octupole (BDO) mode (light blue), which results from hybridization between the dipole of Particle 1 and the octupole of Particle 2. In these energy levels, the transition occurs at a gap size of about 8 nm. One should note that in this case and in that described previously for \( \Phi_2 \) and \( \Phi_3 \), the exchange does not occur exactly at the transition point but gradually over a broad range of gap sizes. At a gap of 2 nm, all energies in Figure 3.7D match very well with the peak energies in Figure 3.7C, where each mode is identified by a colored dot. The ADQ mode does not appear in the spectrum because it is a dark mode, which does not interact strongly with the incident light beam.
A detailed analysis of the eigenstates is necessary to interpret the exchange between the DQ and ADD plasmon modes. Because the modes are coupling very strongly, the Hamiltonian matrix for the system is not diagonal. Therefore, the eigenvalues of the Hamiltonian cannot be degenerate, and there is an avoided crossing between the adiabatic states, which are displayed as solid black curves in Figure 3.8A. The higher-energy state is signified by $\Phi_1$, and the lower-energy state by $\Phi_2$. Dashed red and green curves are approximate values for the diabatic states corresponding to the DQ and ADD modes, respectively.

Each adiabatic eigenvector can be represented by a linear combination of all of the diabatic eigenvectors:

$$|\Phi> = C_{\text{SDD}} |\text{SDD}> + C_{\text{ADD}} |\text{ADD}> + C_{\text{DQ}} |\text{DQ}> + \ldots,$$

where $C_{\text{SDD}}$, $C_{\text{ADD}}$, and $C_{\text{DQ}}$ are the coefficients for the eigenvectors of the SDD, ADD, and DQ modes, respectively. Figure 3.8B gives the probabilities, represented by the squares of the coefficients, of the diabatic eigenvectors for $\Phi_1$. At large gap sizes, $|C_{\text{DQ}}|^2$ is equal to 0.9996, and $|C_{\text{ADD}}|^2$ and $|C_{\text{SDD}}|^2$ are almost zero.
Figure 3.8. Avoided crossing between plasmon modes of an idealized Dimer A with radii of 24 and 76 nm and a gap size of 2 nm. (A) Solid black curves are the energy eigenvalues of the Hamiltonian the adiabatic eigenstates $\Phi_2$ and $\Phi_3$ as a function of gap size. Dashed curves are the diabatic BDQ (red) and ADD (green) states. Adiabatic eigenvectors can be represented as linear combinations of the diabatic eigenvectors: $|\Phi_2\rangle = C_{\text{BDQ}}|\text{BDQ}\rangle + C_{\text{ADD}}|\text{ADD}\rangle + C_{\text{BDI}}|\text{BDI}\rangle + ...$ (B) $|C_{\text{BDQ}}|^2$ (blue), $|C_{\text{ADD}}|^2$ (green), and $|C_{\text{BDI}}|^2$ (red) calculated by the plasmon hybridization method for $\Phi_3$. $|C_{\text{ADD}}|^2$ decreases at small gap sizes due to contributions from $|C_{\text{BDQ}}|^2$, $|C_{\text{ADD}}|^2$, and higher-order modes not shown. (C) The same coefficients in (B) calculated for $\Phi_2$, $|C_{\text{BDQ}}|^2$ decreases at small gap sizes in (C) due to contributions from $|C_{\text{ADD}}|^2$ and higher-order modes not shown.

As the particles approach each other, $\Phi_1$ gradually transitions from the DQ mode to the ADD mode with a crossover point at a gap of 7 nm. The value for $|C_{\text{BDQ}}|^2$ remains negligible at all gap sizes. At 2 nm, $|C_{\text{DQ}}|^2$ is nearly zero, and $|C_{\text{ADD}}|^2$ has a value of 7.9.
This data gives clear evidence that the peak at 2.65 eV in Figure 3.7C corresponds to the ADD mode. The sum of these probabilities does not equal 1.0 because contributions from other terms in the linear combination are not shown.

Probabilities of the diabatic eigenvectors for $\Phi_2$ are given in Figure 3.8C. At large separations, $|C_{ADD}|^2$ dominates with a value of 0.9996, and $|C_{DQ}|^2$ is almost zero. With decreasing gap size, the modes begin to mix, such that $|C_{ADD}|^2$ decreases and $|C_{DQ}|^2$ increases. Unlike the case in $\Phi_1$, $|C_{SDD}|^2$ also becomes larger because the SDD mode experiences significant coupling with the DQ mode. At about 5 nm, all three modes intersect, and the SDD mode begins to suppress the DQ mode as the particles continue to become closer together. At 2 nm, $|C_{DQ}|^2$ is clearly greater than $|C_{ADD}|^2$. Therefore, considering the avoided crossing of the adiabatic curves and the charge distributions of Dimer A to be discussed below, we can assign the peak at 2.58 eV in Figure 3.7C to the DQ mode.

Interestingly, $|C_{SDD}|^2$ has a significant contribution that is greater than both $|C_{DQ}|^2$ and $|C_{ADD}|^2$ at a gap size of 2 nm. The remaining 50% of the probability is attributable to other higher-order modes not shown. This observation illustrates the true implications of non-spherical symmetry in plasmonic systems, that each energy level is in fact a broad mixture of many different hybridized modes. For the sake of this discussion, however, we will assign $\Phi_2$ to the DQ mode at small gap sizes and explore how it interacts with the lowest-energy curve in Figure 3.7D, which corresponds to the SDD mode.
An understanding of the mode assignments in Figure 3.7C allows us to better interpret their relative peak amplitudes. In the quasistatic limit, the peak amplitudes are determined by the strength of which each mode couples to the incident light beam. One would expect the SDD mode to have the highest intensity. However, the ADD mode is the most intense, followed by the DQ mode and finally the SDD mode. Although the ADD mode is primarily a combination of the dipole modes of Particles 1 and 2, it also contains significant contributions from higher-order modes of Particle 2, which enhance the strength of the overall dipole moment of the dimer. These contributions are included in the remaining 20% of the eigenstate probabilities in Figure 3.8B. Likewise, about 50% of the probabilities for the DQ peak are attributable to higher-order modes (Figure 3.8C).

In previous works, dipole activity has been attributed to mixtures with dipole modes \((l = 1)\). However, Dimer A is asymmetric in that it contains a small particle adjacent to large particle. At small gap sizes, the dipole mode in the small particle induces a localized charge in the large particle. The overall charge distribution in the large particle is then altered such that it is no longer dipolar. Therefore, higher-order modes in the large particle couple more strongly to the dipole mode in the small particle. We believe that this effect influences the drastic changes in the diabatic eigenstate probabilities shown in Figures 3.8B and 3.8C. Also, it means that contributions from higher-order hybridized modes in a given eigenstate actually increase the net dipole moment of the entire structure, allowing it to couple more strongly to the incident light beam. This is evident in the peak amplitudes of the DQ and ADD modes, which are higher than that for the
SDD mode in Figure 3.7C.

As the size of the dimer increases, retardation causes all of the modes to shift to lower energies. The dashed red and blue lines in Figures 3.7A and 3.7B represent the spectral locations of the DQ and SDD modes, respectively. The DQ mode redshifts more than the SDD mode because it couples more strongly to incident light, as described above. In the full-size structure, the DQ mode sufficiently overlaps with the SDD mode to produce a Fano resonance, which is indicated by a dip in the scattering spectrum. The discussion below will further explore this resonance and give a comprehensive view of the origins of the DQ and SDD modes.

As mentioned earlier, the DQ and SDD modes are hybridizations between plasmon resonances in the constituent particles. Figure 3.9 illustrates this concept according to the extinction spectrum of the full-size dimer geometry. Panels A and C show that the dipole resonances of Particles 1 and 2 are at 2.61 and 2.35 eV, respectively, and the quadrupole resonance of Particle 2 is at 2.63 eV. When the particles are brought together to form a dimer with a gap of 2 nm (Figure 3.9B), their plasmon modes hybridize and redshift in energy. The dipole resonances form the SDD mode (blue), and the dipole of Particle 1 and the quadrupole of Particle 2 form the DQ mode (red). According to Figure 3.8C, the DQ and SDD modes couple very strongly to each other in the quasistatic limit. In the full-size structure (Figure 3.9B), retardation has caused the modes to overlap in energy, allowing them to couple to an even greater extent to produce a Fano resonance.
Figure 3.9. Plasmon hybridization diagram for an idealized Dimer A, including extinction spectra of (A) a NP with a radius of 26 nm, (C) a NP with a radius of 76 nm, and (B) a dimer consisting of each of the particles in (A) and (C). (A) and (C) were calculated with Mie Theory using unpolarized incident light and the Drude model for the permittivity of gold. (B) was calculated by FDTD using longitudinally polarized light and the permittivity of gold defined by Johnson and Christy.42 Blue lines correspond to the BDD mode. Red lines correspond to the BDQ mode. (i-iii) Surface charge plot distributions of positive (red) and negative (blue) charge intensities calculated by the finite element method. The plot in (i) predominantly exhibits the BDD mode but also contains small, localized charge regions within the junction that are not visible in this figure.
Evidence of the Fano resonance is revealed in surface charge plots at 2.44, 2.28, and 2.09 eV, indicated by (i), (ii), and (iii), respectively, in Figure 3.9. The charge distributions at the two peaks, located at 2.44 and 2.09 eV, clearly indicate the SDD mode. However, in the dip at 2.28 eV, Particle 1 exhibits a dipolar pattern while Particle 2 exhibits a quadrupolar pattern. This charge distribution corresponds to the DQ mode, proving that the DQ mode is narrow in comparison to the SDD mode and that the two modes are interacting to produce a Fano resonance. This observation suggests that in the full-size structure, the SDD mode couples more strongly to light than the DQ mode because it is very broad due to radiative damping. However, this is not the case in the quasistatic limit, where the DQ mode has higher intensity and redshifts more than the SDD mode as the size of the structure increases. We speculate, then, that with progressively larger geometries, retardation and mixing of higher- and lower-order modes in the constituent particles change the relative dipole activity of the DQ and SDD resonances.

With accurate identification of plasmon modes in Dimer A, similar mode assignments can be made for other dimers. The plasmon hybridization schemes in Dimers B and C are comparable to the scheme in Dimer A, except as the size of Particle 1 increases, the SDD mode redshifts and the DQ mode retains its location (Figure 3.6). This occurs due to changes in the amount of coupling between the modes of the individual particles. The progressively larger cross-section of Particle 1 results in a larger dipole moment, allowing stronger coupling between the dipole modes of the constituent
particles and weaker coupling between the dipole of Particle 1 and the quadrupole of Particle 2. Weaker coupling between modes should result in a blueshift, but we do not see this in the DQ mode because it is balanced by the redshift of the dipole mode of Particle 1 due to the particle's larger size.

A similar argument can be made when comparing the backscattering spectra of Dimers A-C to those of Dimers D-F (Figure 3.6). These spectra are virtually the same not only because plasmon coupling primarily occurs at the surfaces of the particles, but also, when Particle 2 is replaced by a NS, plasmon coupling weakens due to the differences in potential energies of the two particles. This should cause a blueshift in the DQ and SDD modes, but we do not see a blueshift because is balanced by a redshift in the initially lower energy of the NS resonance. As a result, the DQ and SDD modes in Dimers D-F have nearly the same energy as those in Dimers A-C, respectively.

Because the plasmon hybridization schemes in all of the dimers are similar, all of them contain a Fano resonance similar to that described for Dimer A. According to surface charge plots of each dimer, both peaks in the backscattering spectra correspond to the SDD mode, and the dip corresponds to the DQ mode. However, when the size of Particle 1 increases and the SDD mode redshifts, the modes experience less overlap, and the Fano resonance weakens. Replacing the NP in Dimers A-C with a NS in Dimers D-F does not adversely affect the Fano resonance because the plasmon energies of the corresponding structures are nearly the same.
Dimer C is unique in that it is a homodimer with a Fano resonance, while the rest of the structures are heterodimers. Varying degrees of asymmetry, then, are not always necessary to produce a plasmonic Fano resonance. Here, Fano resonances are possible simply because modes with different angular momenta, $l$, in the constituent particles are capable of hybridizing due to the non-spherical symmetry of the system. The particles do not need to have different sizes in order for this to occur. Therefore, other plasmonic homodimers consisting of spherical particles are expected to exhibit Fano resonances as long as the DQ and SDD modes sufficiently overlap in energy. Lassiter and coworkers described plasmon hybridization in NS homodimers [37]. Although these NSs were slightly smaller than those used in this study, the spectrum for longitudinal excitation of the strongly interacting dimer was strikingly similar to the spectra for Dimers C and F in Figure 3.6. We postulate, then, that the NS homodimers analyzed by Lassiter and coworkers also contained Fano resonances.

As mentioned above, incident polarization in the longitudinal direction has been of large interest in plasmonic dimers due to the large intensity of the electric field in the junction region and the strong coupling of plasmon modes [41]. Transverse polarization has received less attention because field enhancement and plasmon coupling are weaker. In the case of NP-NS heterodimers, however, polarization in the transverse direction presents a very interesting asymmetry in the scattering properties, depending on the direction of propagation of incident light. The following discussion will explain the causes of this asymmetry in dimers already presented in this study.
Chapter 4: Directional excitation of Dimer

4.1 Introduction

Transverse polarization has received less attention because field enhancement and plasmon coupling are weaker. In the case of NP-NS heterodimers, however, polarization in the transverse direction presents a very interesting asymmetry in the scattering properties, depending on the direction of propagation of incident light. The following discussion will explain the causes of this asymmetry in dimers already studied in the previous chapter.

4.2 Transverse Excitation

Experimental and theoretical backscattering spectra of Dimers A-F with transversely polarized incident light are shown in Figure 4.1. Conditions for all spectra are the same as those in Figure 3.6, except the angle of polarization is now perpendicular to the dimer axis with the k-vector parallel to the dimer axis. Dimers A-C have similar spectra with a peak around 600 nm. This feature for Dimer A is slightly redder and broader than for Dimers B and C because Particle 2 in Dimer A is prolate with a larger radius in the transverse direction.
Dimers D-F have spectra that are redder than those for Dimers A-C due to the initially lower energy of the NS resonance. Also, they have noticeably different spectra as the size of Particle 1 increases, particularly when the k-vector hits Particle 1 first (green curves). These data may be clearly understood by examining Dimer F, which has the most prominent change in backscattering when the direction of the k-vector is reversed.

![Diagram of experimental and theoretical backscattering spectra](image)

**Figure 4.1.** Experimental and theoretical backscattering spectra calculated by FDTD for Dimers A-F with transversely polarized incident light. The theoretical spectrum for Dimer C includes only one direction of propagation because spectrum for the opposite direction is identical due to symmetry. The theoretical spectra for opposing k-vectors in Dimers A and D are nearly identical.

With transverse polarization, plasmon coupling is relatively weak. Therefore, the hybridized modes undergo little splitting, such that their energies are nearly the same as those of the constituent particles. In Dimer F, the higher-energy mode is closer to the
dipole resonance of the NP, and the lower-energy mode is closer to the dipole resonance of the NS (Figure 4.2A). These modes are the symmetric and antisymmetric transverse dipole resonances \((l = 1, m = \pm 1)\), respectively. The difference in energy between these modes allows for easy distinguishability in the backscattering spectra of the dimer. The solid curves in Figure 4.2B are the same as the theoretical spectra for Dimer F in Figure 4.1. The dashed curves are for the NP only (green) and the NS only (yellow), obtained under the same simulation conditions as the dimer spectra.

![Diagram](image)

**Figure 4.2.** (A) Schematic plasmon hybridization diagram of Dimer F. (B) Theoretical backscattering spectra of a NP with a radius of 75 nm (dashed green), a NS with an inner radius of 66 nm and an outer radius of 84 nm (dashed yellow), Dimer F with transversely polarized incident light hitting the NP first (solid green), and Dimer F with transversely polarized incident light hitting the NS first (solid yellow). (C, D) Electric field enhancement plots of Dimer F with transversely polarized incident light hitting the NP first (C) and the NS first (D) at \(\lambda = 571\) and 675 nm, respectively. (E) Scattering distribution of Dimer F with transversely polarized incident light hitting the NP first (green) and the NS first (yellow). The blue shaded region is the cone angle used for data collection. Both plots in (E) were taken at \(\lambda = 675\) nm. All calculations were performed by FDTD.

When the \(k\)-vector first encounters the NS (solid yellow curve), the antisymmetric mode has a much higher intensity than the symmetric mode, which appears as a shoulder.
However, when the k-vector travels in the opposite direction, encountering the NP first (solid green curve), both modes decrease in intensity, and the symmetric mode is more easily identified. This mode is broader than the antisymmetric mode because it undergoes more radiative damping due to its surface charge distribution.

The backscattering spectra of the dimer are different for each direction of excitation because the hybridized modes are very close in energy to the dipole resonances of the constituent particles. In concordance with the plasmon hybridization model, electric field maps plainly show that the NP resonance dominates the symmetric mode (Figure 4.2C), and the NS resonance dominates the antisymmetric mode (Figure 4.2D). Therefore, depending on which particle is excited first, the scattering properties of the dimer will be most characteristic of the corresponding hybridized mode. This explains why the symmetric mode is more identifiable in Figure 4.2B when the k-vector first passes through the NP.

The shape of the scattering pattern is also different for each direction of excitation. Figure 4.1E gives the scattering distribution of the dimer when the k-vector hits the NS first (yellow) and the NP first (green) at an incident wavelength of 675 nm. Only half of the distribution is shown because the remaining half includes the glass substrate. The shaded region between 26 and 154 degrees represents the backscattering cone angle used to collect experimental and theoretical data. Since the cone angle encompasses a larger portion of the yellow pattern than the green pattern, more light is
collected from the yellow pattern, and the yellow backscattering spectrum in Figure 4.2B has a higher intensity than the green spectrum. This observation is an excellent example of how the scattering distribution of a nanostructure can affect the collection of data.

The scattering properties of the dimer are primarily determined by the sizes of the scattering cross-sections of each constituent particle. In Dimer F, Particle 2, the NS, has a larger scattering cross section than Particle 1, the NP (Figure 4.2B). In any dimer, if the scattering cross-section of one particle is significantly larger than that of the adjacent particle, then the former particle will dominate the scattering properties of the dimer regardless of the direction of the k-vector when it propagates along the dimer axis. As described earlier, Dimer F has the most noticeable difference in backscattering spectra (Figure 4.1). Dimer E, however, only has a slight difference, and Dimer D has virtually no difference at all. In the lattermost case, the NS dominates the scattering properties of the dimer, such that the backscattering spectra are more characteristic of the antisymmetric mode than the symmetric mode. The scattering cross-section of Particle 1 is greatly reduced because Particle 1 contains far less electrons in Dimer D than in Dimers E or F. The intensities of the peaks experience no change regardless of the direction of excitation because the shape of the scattering pattern is the same, allowing an equal amount of light to be collected for data analysis. Dimer E has a slight difference in spectra because the scattering cross-section of Particle 1 is large enough to have an effect on the overall scattering properties of the dimer. This effect is even greater in Dimer F, where the scattering cross-section of Particle 1 is even larger.
Dimers A, B and C exhibit similar backscattering spectra for both directions of transverse excitation (Figure 4.1). Because Particle 2 is a NP instead of a NS, the dipole energies of the constituent particles are very close together. Therefore, the symmetric and antisymmetric dimer modes have a much smaller difference in energy, such that they cannot be distinguished in the backscattering spectra. When the size of Particle 1 changes, however, the overall scattering distribution may change its shape, altering the amount of scattered light detected within the backscattering cone angle. Dimer A shows virtually no change in the backscattering spectra for both directions of excitation. This scenario is analogous to that for Dimer D, where Particle 1 is so small that it does not strongly affect the scattering properties. In the theoretical spectra for Dimer B (Figure 4.1), we see a slight difference in backscattering. As in Dimer E, Particle 1 is large enough to affect the scattering distribution, and in accordance with the backscattering cone angle, the peak intensity decreases when the k-vector hits Particle 1 first. Dimer C gives identical spectra for both directions of excitation because it is symmetrical. For this reason, only one theoretical spectrum for Dimer C is displayed in Figure 4.1.

One should note that variations in the scattering properties of these structures, particularly Dimers E and F, are only possible when the k-vector is parallel to dimer axis. If the k-vector were perpendicular to the dimer axis with transverse polarization, then both directions of excitation should result in the same scattering properties due to symmetry.
Chapter 5: Summary

The work presented here provides a deeper understanding of the interactions between plasmons of neighboring metallic particles, one of the most fundamental structures in nanophotonics. Polarization-dependent analyses of individual dimers reveal a wide range of interesting physical properties. Longitudinally polarized incident light produces Fano resonances in heterodimers and homodimers, proving that large degrees of asymmetry are not required to induce a plasmonic Fano resonance. Because the system lacks spherical symmetry, each energy level represents a mixture of hybridized modes, and at varying gap sizes, the mixing of these modes drastically changes. In Dimer A, an exchange happens between the antisymmetric dipole-dipole mode and the dipole-quadrupole mode, even though the energy curves representing these modes are significantly spaced apart. With transversely polarized incident light, heterodimers exhibit directional excitation, where the overall scattering properties are determined by the direction of the k-vector. These dually functional structures can therefore be considered nanophotonic diodes that can exhibit Fano resonances.

We also report experimental demonstrations of hybridized subradiant, superradiant, and Fano-type modes in ring/disk plasmonic nanocavities. For the subradiant mode, the linewidth is reduced by more than a factor of two compared to the parent ring and disk modes. By breaking the symmetry of the structure narrow Fano resonances are induced. Our investigations show that radiative lifetime tuning of hybridized nanocavity
modes is a promising path for the development of plasmonic substrates for chemical and biosensing, and of efficient SERS substrates.
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