Pitch-dependent resonances and near-field coupling in infrared nanoantenna arrays

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Abstract: We investigate coupling in arrays of nanoparticles resonating as half-wave antennas on both silicon and sapphire, and find a universal behavior when scaled by antenna length and substrate index. Three distinct coupling regimes are identified and characterized by rigorous finite-difference time domain simulations. As interparticle pitch is reduced below the oft-described radiative to evanescent transition, resonances blue shift and narrow and exhibit an asymmetric band consistent with a Fano lineshape. Upon further pitch reduction, a transition to a third regime, termed here as near-field coupling, is observed in which the resonance shifts red, becomes more symmetric, and broadens dramatically. This latter regime occurs when the extension of the resonant mode beyond the physical antenna end overlaps that of its neighbor. Simulations identify a clear rearrangement of field intensity accompanying this regime, illustrating that longitudinal modal fields localize in the air gap rather than in the higher index substrate at a pitch consistent with the experimentally observed transition.

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### 1. Introduction

Plasmonic nano- and microstructures have impacted molecular spectroscopy [1, 2], photo-chemistry [3–5], and sensing [6] through the spectral overlap of plasmonic resonances with a given optical response such as surface-enhanced Raman scattering (SERS), absorption, scattering, or fluorescence. While the resonant behavior of individual plasmonic antennas is of widespread interest [7–10], many studies have arranged resonators in periodic arrays to improve signals in fundamental research [11–14], and to explore applications for high-sensitivity sensing [15–17], frequency-selective surfaces for molecular spectroscopy [18, 19], enhanced and directional fluorescence [20], photocurrent generation [21], and even information transfer [13].

Previously, two extensively-studied pitch-dependent coupling regimes among nanoantennas in periodic arrays have been reported [12, 15, 22, 23]. The radiative regime occurs when the array pitch is large enough that light at the antenna resonance-wavelength diffracts above (or below) the substrate. Here, the polarizability of an individual array element is only slightly modified through electric-dipole coupling with other array elements. The transition from this regime to the so-called evanescent regime occurs when the pitch

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becomes small enough that the resonant wavelength diffracts in-plane, creating modes propagating through the structure but evanescently decaying normal to the substrate [12]. As array pitch is reduced, this transition first occurs for diffractive modes in air, and then in the substrate [23]. The present report is concerned with the substrate transition, which occurs when the array lattice constant equals the resonant wavelength in the substrate ($\lambda/n_{\text{sub}}$, where $\lambda$ is the wavelength in vacuum, and $n_{\text{sub}}$ is the substrate refractive index.) Under this condition, scattered fields experience $2\pi$ of phase oscillation before encountering the neighboring resonator, resulting in both incident and scattered fields driving resonators in phase. At this critical pitch, the grating-induced evanescent modes more strongly couple individual array elements to each other leading to band narrowing and a blue-shift of the resonant peak [12, 24]. Working in the infrared with square arrays of nanoantenna resonators, we characterize this transition similarly to others [12, 15, 22, 23], but also compare directly the array resonant characteristics between silicon and sapphire substrates that differ substantially in $n_{\text{sub}}$. The line-narrowing accompanying the evanescent regime suggests that more of the excitation couples into the array elements, which reduces scattering and reflection resulting in a longer lifetime [23]. Such enhancements in the residence time of the incident optical energy within the array may provide advantages for applications such as light harvesting and photocatalysis that depend on the utilization of absorbed radiation rather than simply locally enhanced field intensities.

Here, we also report on a third fundamental coupling regime for arrays of half-wave antennas. This regime is characterized by field localization between adjacent antennas along the longitudinal direction (i.e., end-to-end) and occurs for our antennas when the longitudinal inter-antenna gap is $\sim 400 \text{ nm}/n_{\text{sub}}$ (i.e., $\sim 235 \text{ nm}$ for sapphire and $\sim 108 \text{ nm}$ for silicon). As this regime depends on interparticle separation and not array periodicity, we refer to this as the near-field regime, similar to the well-known plasmonic near-field coupling regime that has been reported in systems of colloidal aggregates [25, 26], periodic arrays of closely spaced circular plasmonic resonators [16], and individual resonators with nanoscale gaps [27]. At and below this transition, the antenna resonance broadens dramatically, assumes a symmetric lineshape, and shifts red, traits again similar to near-field coupling within plasmonic nanoparticle assemblies. Given the similarities with near-field coupling in plasmonic systems, we note that much of the physics of near-field coupling within large-area, coupled systems can be explored within infrared (IR) antenna arrays, without the need for heroic lithographic efforts.

Because the dominant coupling mechanism among array elements influences the spectral resonance-position, linewidth, and near-field intensities, understanding the various coupling regimes is important for field-enhanced molecular spectroscopies, excited-state reactivity, and energy harvesting. However, although arrays responding in the mid-IR are particularly important for enhanced vibrational spectroscopy, they have received only modest attention [28] compared to systems that are resonant in the visible. This work emphasizes antenna coupling within square arrays resonant from $\sim 2.3$ to $7 \mu\text{m}$ and on different substrates, and establishes a generalized model from which such pitch-dependent transitions can be predicted. Finally, we have compared our results to numerical solutions to Maxwell’s equations that reveal the underlying field distributions accounting for the observed spectral features.

2. Methods

Rectangular nanoantennas were fabricated via electron-beam lithography and lift-off (5/65 nm Ti/Au) on sapphire and silicon substrates, allowing for the analysis of substrate index effects [29]. Additionally, sapphire substrates offer IR transparency and a lower index of refraction than the silicon used in other studies [15]. On each substrate, arrays of both randomly and periodically distributed particles were produced. All antennas were nominally 65 nm thick.
To extract the modal index and investigate the effects of antenna width free from periodic-array induced effects, three series of randomly distributed parallel antennas were patterned on each substrate, with each series having a different fixed width (65, 130, and 260 nm) but varying lengths (aspect ratios ranging from 3:1 to 20:1).

The bulk of the experimental work concentrated on periodically arrayed antennas to probe the pitch-induced coupling regimes. Periodic arrays with varied pitch were patterned in two size series. The targeted particle size for the series were 1100 × 260 × 65 nm and 550 × 130 × 65 nm (length × width × thickness). Each array comprised a square 300 × 300 μm area with targeted pitches spanning ~1.07 to 3 times the particle length (smallest longitudinal gap attained ~35 nm). This broad sample set enabled identification of inter-antenna coupling regimes for nanoantennas with resonances occurring in the mid- and near-IR. Transmission and reflection spectra were acquired with a Nicolet Continuum FT-IR microscope using matched top and bottom Schwarzschild reflective objectives (15x, 0.58 numerical aperture) that illuminated the entire array over a range of incidence angles spanning ~10° to 35° from normal. While the reported results were obtained without using a polarizer, studies with polarization control demonstrated that the predominant response was parallel to the long axis of the nanoantenna arrays.

Numerical simulations were performed by using finite-difference time-domain (FDTD) software (Lumerical Solution, Inc.) [30]. This numerical method computes full vectorial solutions to Maxwell’s equations and is well established for calculating the optical response of nanostructures [31, 32]. In the simulations, the permittivity of gold from Palik’s reference was used [33]. Periodic boundary conditions were employed in the in-plane directions to accommodate the periodicity of the antenna array structure, and the incident plane wave was at normal incidence. Perfectly matched layers (PML) above and below the antenna structures, with the lower PML being in the substrate. To obtain the reflection, a field monitor plane was placed above the array at a location between the source and the upper PML. This arrangement eliminated spurious reflections which are possible in finite size geometries. The reflection was obtained from the normal component of the power passing through the plane.

3. Results and discussion for random arrays

To measure antenna properties free from inter-antenna coupling effects due to periodicity, reflection spectra were acquired for randomly distributed nanoantennas of three widths (~65, 130, and 230 nm) on sapphire and Si. Representative data for the 130 nm wide antennas on sapphire are displayed in Fig. 1(a). The randomly distributed antennas all exhibited similar general features that consist of a strong, asymmetric resonance that shifts to longer wavelengths with increasing antenna length (higher aspect ratio), while the longer antennas also exhibit higher order modes within our spectral window (indicated by blue arrows).

The primary resonances observed in Fig. 1(a), and array resonances discussed later, are well described by the Fano line shape [34–36]

\[
I(\omega) = I_0 + \frac{A}{q} \frac{2\Delta + q \gamma}{(4\Delta^2 + \gamma^2)}
\]

where \(I_0\) is an offset, \(A\) is the peak amplitude, \(q\) is the Fano parameter originally developed to represent the ratio of the resonant to background transition amplitudes [35], \(\gamma\) is the full-width at half-maximum, and \(\Delta = \omega - \omega_0\) is the detuning from the resonance frequency \(\omega_0\). The second term on the right side of Eq. (1) can describe the intensity lost through resonant scattering and absorption in a transmission measurement, or the intensity scattered in a reflection measurement as reported here. The parameters of Eq. (1) were extracted by least-squares fitting for each spectral curve acquired. Representative fits are displayed in Fig. 1 and 2. All parameter values, excepting the peak amplitude, \(A\), and offset, \(I_0\) for all periodic data sets are presented in Fig. 3.

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Although we cannot definitively ascribe a Fano mechanism to our asymmetric lineshape, use of the Fano lineshape is suggested by previous research [37, 38] establishing it as a common occurrence arising from interference between a discrete plasmonic resonance and other modes (e.g., substrate scattering or direct transmission [39, 40], plasmonic dark modes activated through broken symmetries [41, 42], or higher order Fabry-Perot antenna modes on the same antenna [43]). Fano-like interference between primary and higher order plasmon resonances supported on individual dipole antennas [43] has been shown analytically and numerically, suggesting that a Fano resonance may provide a suitable functional description for our system. Similarly, Fano-like lineshapes (i.e., skewed half-wave mode, negative-going lobes in the higher order modes) are also typical for scattering from non-plasmonic half-wave antennas. In fact, the analytical treatment from reference [44] was used to generate the scattering profile for a single antenna which reproduces the pertinent features of our random antenna results and is presented as a dashed curved in Fig. 1(a). Given our inability to state definitively that underlying Fano interferences are producing our measured lineshapes, we emphasize again that we regard the quantity $q$ in our fits simply as an asymmetry parameter that future research may nonetheless associate with Fano-interfering modes. We, therefore, employ the Fano lineshape as a method to extract band parameters and track spectral changes indicative of the different coupling regimes.

![Fig. 1. (a) Reflection spectra (red) and Fano fits (blue) for random arrays of 130 nm wide antennas on sapphire. Each curve is labeled with its corresponding nanorod antenna length. Blue arrows indicate higher order antenna modes for the 1.58 μm long antenna. Dashed black curve corresponds to the normalized scattering cross-section computed with microwave scattering theory for a single, isolated antenna with an effective length and diameter of 1.3 and 0.06 μm, respectively. (b) Resonance position via Fano fits for 65, 130, and 260 nm wide antennas on sapphire as a function of antenna length. As antenna length is increased, resonance shifts to longer wavelengths. Linear fits (solid lines) indicate antennas are well-behaved half-wavelength resonators, with $\lambda_{res} = 2n_{eff}(L + 2\delta)/m$ as defined in text. $n_{eff}$ decreases for wider antennas as shown in inset of (b).]

The fitted resonant wavelengths of random arrays for different antenna widths are plotted as a function of antenna length in Fig. 1(b). The linear dependence of the resonance wavelength on the antenna length indicates that our particles act as half-wave dipole antennas with resonances determined primarily by their length rather than aspect ratio [45]. Plasmonic half-wave antennas can be viewed as Fabry-Perot cavities supporting a circulating surface plasmon polariton (SPP) characterized by an effective modal index $n_{sub}$ [46–49]. Accordingly, we extract $n_{sub}$ according to $\lambda_{res} = 2n_{eff}(L + 2\delta)/m$, where $\lambda_{res}$ is the observed resonance wavelength, $m$ is the antenna standing-wave order supported on the rod, $L$ is the rod length, and $\delta$ accounts for the modal extension from the rod end, which increases the effective antenna length [46, 47]. Our fitted width-dependent modal indices on sapphire vary from $n_{sub} = 1.3–1.55$ (see inset to Fig. 1(b)), and on Si from $n_{sub} = 2.7–2.9$. This $n_{eff}$ range is close to the approximation of $n_{eff}$ based on the average dielectric constant [50] $n_{sub} = (0.5(1 + n_{sub}^2))^{0.5} = 1.46$ for sapphire and $n_{sub} = 2.57$ for Si. The extracted $\delta$ values increase with antenna width and vary from 86 to 220 nm on sapphire and 9–107 nm on Si as widths vary from 65 to 260.
nm. The smaller values for Si reflect a stronger SPP confinement expected for an environment with a larger dielectric constant. Interestingly, below we note that the transition to longitudinal near-field coupling between adjacent nanorods occurs when antennas approach one another to within ~2δ.

Finally, we point out that both even and odd higher-order resonances were observed. For example, the longest antennas evaluated (1.58 μm) on sapphire showed peaks at 5.26, ~2.74, and ~1.92 μm. These are in approximate agreement with the \( m = 1, 2, \) and \( 3 \) resonances predicted to occur at \( \lambda_{res} = 5.3, 2.65, \) and \( 1.77 \) μm, respectively, assuming a wavelength-independent modal index \( n_{sub} = 1.44 \). The \( m = 2 \) mode at 2.74 μm corresponds to a full wavelength oscillation supported on the antenna and thus contains no net transition moment for normally incident light. However, this mode is excited under oblique illumination [46, 47], which necessarily occurs with our 0.58 NA Schwarzschild reflective objective. Even-order modes have also been observed in far-field [37] and near-field [51] measurements of half-wave antennas.

4. Results and discussion for periodic arrays

Figure 2 presents representative reflectance spectra of the periodic arrays of 1100x260x65 nm antennas on (a) sapphire and (b) p-type silicon (0.02-0.04 Ω–cm). The lineshapes of the more widely spaced arrays are clearly asymmetric (high energy tail) and, as with the random samples of Fig. 1(a), were adequately described by a Fano expression [34]. The general lineshape may be altered by the presence of an asymmetric versus symmetric dielectric surrounding the resonators [36]. In our asymmetric system (substrate below and air on top) no sharp diffraction-induced features are observed. Qualitatively, as the grating period is reduced, the resonance feature first shifts to the blue and exhibits a line narrowing. Further reduction in pitch results in a subsequent line broadening, a loss of asymmetry, and finally a red-shift at the smallest pitches. These general features were observed for arrays of 1100 and 550 nm long antennas on both sapphire and silicon. The dependence of the resonance position, oscillator quality factor \( Q \), and asymmetry-parameter \( q \) obtained by fitting Eq. (1) to the spectra forms a basis for identifying and assigning the operative coupling mechanisms and is presented in Fig. 3. A horizontal dashed line indicates the resonance position for the same length antenna without periodic coupling effects as predicted by the linear fits of Fig. 1. A simplified prediction of the transition from radiative to evanescent coupling [22–24, 52] can be defined by application of Bragg’s law for normal incidence and first-order in-plane diffraction generating the critical condition for evanescent coupling \( \lambda_{cr} = d_{cr} (n_{sub}m) \), where \( \lambda_{cr} \) is the wavelength of interest in air, \( d_{cr} \) the critical array pitch, and \( n_{sub} \) the substrate refractive index, and \( m \) is the diffractive order [22, 23]. However, this treatment ignores the experimental fact that illumination through Schwarzschild reflective optics is not normal to the substrate. The correct condition [12, 53] for first-order in-plane diffraction resulting from incidence of light at angle \( \theta \) relative to normal through air into a substrate of index \( n_{sub} \) is \( \lambda_{cr} = (d_{cr}/m) \left[ n_{sub} (1 - \sin \theta / n_{sub}) \right] \) and is plotted as two slanted dashed lines for the \( m = +1 \) and \( -1 \) diffractive orders for the smallest angle of incidence for our system of 10°. Inspection of the above relation shows that the impact of angled incident light is reduced for high index substrates (i.e., silicon).
Fig. 2. Typical reflection spectra (red) and Fano fits (blue) for square arrays of 1100 nm long antennas on (a) sapphire and (b) silicon. The subset of data presented includes pitches, $p$, of 1.2, 1.275, 1.35, 1.4, 1.6, 1.8, 2, 2.2, 2.4, 2.6, and 2.8 $\mu$m for both substrates. (Insets) SEM images of 1100 nm antenna array with $p = 1.6$ $\mu$m and 550 nm antenna array with $p = 0.8$ $\mu$m.

In addition to the blue shift and reduced linewidth which typically accompany the transition from radiative to evanescent coupling, a substantial line broadening, red shift and loss of asymmetry is observed at very small pitches.

Two signatures announce the onset of evanescent coupling as pitch is reduced: (i) a relative blue shift and (ii) line narrowing. It is observed that the resonance position of the widely-spaced arrays is red-shifted from that predicted for non-interacting antennas. This is consistent with a coupling between antennas dominated by a transverse (side-by-side) dipolar interactions when the dipole fields on nearest neighbors are aligned to reduce the restoring force (or spring constant) of the antenna of interest causing a resonance red-shift. A relative blue shift, or reduction of red-shift, is observed when the pitch is reduced sufficiently to enter into the evanescent coupling regime (right to left in Fig. 3) [12, 15, 23]. The resultant blue-shift has been described for excitons in H-aggregates of dyes [54, 55], coupled oscillations in plasmonic particle pairs [56, 57], and associated arrays [12, 15, 23]. The second signature of the radiative to evanescent transition is a line narrowing which indicates reduced losses as radiation that had been diffracting out of plane at the resonant frequency now propagates as in-plane mode with evanescent tails above and below the substrate [12].

The data of Fig. 2(a) and 2(b) also illustrate that when the array pitch is reduced well below the radiative-evanescent transition, a third coupling regime, heretofore unreported for square arrays, becomes apparent as indicated by three additional modifications to the lineshape: (i) a band broadening, (ii) development of a symmetric lineshape, and (iii) a red shift. This third coupling regime was observed for the 550 and 1100 antenna arrays on both sapphire and silicon substrates illustrating that this transition should be universally observed.

To emphasize the common characteristics of the inter-antenna coupling regimes, we provide in Fig. 4(a) and 4(b) universal plots of the pitch dependence of the resonance wavelength and Q for all array sets. Here, the pitch has been scaled by the substrate index and non-interacting resonance position as predicted by the results for random ensembles (Fig. 1). Similarly, the ordinates are scaled by the corresponding values measured for the random arrays. This analysis demonstrates that the pitch-dependent transitions scale with substrate index and antenna length and can be generalized to any antenna array system, regardless of the material makeup, resonant frequency and substrate used. The spectral characteristics we attribute to this final near-field coupling regime, i.e., a red-shifted and broadened resonance, are explained by the onset of longitudinal near-field coupling, as discussed below.
Fig. 3. Summary of spectral properties for square arrays of 550 and 1100 nm antennas on sapphire and Si. All systems exhibit comparable behavior. The relevant features associated with the radiative to evanescent transition with decreasing pitch (indicated by slanted dashed lines for the $m = +1$ and $-1$ diffractive orders) are a relative blue shifting of the peak and increased oscillator quality factor $Q$. Our results demonstrate additional significant modifications to line shape when pitch is further reduced, which consist of line broadening (reduced $Q$), loss of asymmetry (increased Fano parameter $q$), and a relative red shift. Note that the most widely-spaced arrays studied have a resonance red-shifted relative to that of non-interacting antennas as predicted by the results of Fig. 1 (horizontal dashed line). Blue arrows indicate pitch at which longitudinal current extension ($\delta$) of adjacent antennas overlaps.

The evolution of the resonance asymmetry as array pitch is varied is not described in the literature. The asymmetry is conveniently reported through our fitted Fano parameter, as plotted by the blue curves in Fig. 3. At large pitches, the bands exhibited a modest Fano character ($q \sim 3$). When the pitch was decreased through the radiative-to-evanescent transition (right to left in Fig. 3), the lineshape is brought closer to the Lorentzian limit realized at large $q$. Although it is tempting to associate variations in the Fano parameter to scattering amplitudes from resonant and background states, there is insufficient information to make such claims here. Instead, we use the Fano parameter as an objective measure of the peak asymmetry.
5. Numerical simulations

Our interpretation that longitudinal near-field coupling dominates at the smallest array pitches investigated is supported by numerical modeling. These numerical results demonstrate (i) the roles of transverse and longitudinal interparticle coupling, (ii) field intensity distributions relevant for molecular spectroscopy and sensing, and, (iii) direct longitudinal interaction at the smallest pitches. Figure 5 shows the resonant response of arrayed 1100 nm antennas on (a) sapphire and (b) Si generated through finite-difference time-domain (FDTD) simulations. These simulated structures model those which generated the experimental results plotted in Fig. 2 and exhibit all of the pertinent features. The simulated arrays exhibit the relative blue shift and line narrowing associated with the evanescent coupling regime as well as the line broadening, loss of asymmetry, and red shift at the smallest array pitches that we attribute to longitudinal near-field coupling. The fitted resonant wavelengths of the simulated and experimental responses are compared in Fig. 6 and provide reasonable quantitative agreement.
Fig. 6. Peak positions extracted from FTDT results (open dots) compare very well with those from the experimental results (solid dots) for 1100 nm antenna arrays on (a) sapphire and (b) silicon. This agreement demonstrates that simulations provide an accurate description of the real system.

Since the numerical results faithfully reproduce the observed pitch-dependent spectral features, it is reasonable to inspect the simulated electric field distributions to gain insight into the coupling processes responsible for the observed behavior. The contour plots in Fig. 7 are a subset of the simulated data and show the x-component of the field intensity for 1100 nm antennas on sapphire, where the x-direction is oriented along the antenna axis and is the direction of the transition moment for these halfwave antennas. The section plane chosen is a horizontal plane (parallel to the substrate) 1 nm below the substrate surface. The profiles are taken on resonance and all are plotted on the same logarithmic scale (the antenna is located in the center of each image as indicated by a black dotted rectangle). There are several key features in Fig. 7. First, the most widely-spaced array (a; p = 2.8 μm), which corresponds to the radiative regime where diffractive losses are significant, exhibits maximal values for $|E_x|^2$ of ~800$|E_0|^2$, where $E_0$ is the incident field. Next, (b; p = 2.4 μm) and (c; p = 2.0 μm) correspond to the evanescent regime. These structures generated the highest field intensities overall (~1250$|E_0|^2$ and ~1050$|E_0|^2$, respectively) with (c) corresponding to the array with highest Q. When pitch is further reduced (d; p = 1.6 μm), line broadening occurs in both the experimental and numerical results which coincides with increased field strength in the longitudinal gap as revealed in the numerical results. Finally, (e; p = 1.3 μm) and (f; p = 1.2 μm) reveal the dominance of longitudinal coupling occurring at the smallest pitches with fields tightly localized between the ends of longitudinally adjacent antennas.

The aspects of the pitch-dependent field distribution most important to the current report are summarized in Fig. 8. Here, we have extracted the field intensities at relevant positions on the boundary of the unit cell used to define the FDTD periodic-boundary conditions. These positions are marked $T$ (transverse) and $L$ (longitudinal) in Fig. 7(a). These values are indicators of field localization and coupling along the directions transverse to and aligned with the longitudinal antenna axis and are plotted for arrays of 1100 and 550 nm antennas. Several informative features appear in Fig. 8. First, the pitch at which maximum Q occurred for the simulated structures (indicated as a vertical dotted line) correlates well with the pitch at which longitudinal fields begin to overtake transverse fields. This is consistent with the assertion that a dominant longitudinal coupling mediates the observed line broadening and is also consistent with the response of linear chains of resonant spheres [58]. The maximum transverse field strength at position $T$ is also roughly correlated with this maximum Q corresponding to the pitch within the evanescent regime where energy is best coupled to the array system. Finally, the longitudinal field strength quickly increases by over an order of magnitude and dominates the antenna interactions at small pitches. This coincides with the red-shifting we observe and supports the assertion of longitudinal near-field coupling.
controlling array behavior in this regime. These features are common for both the 1100 nm and 550 nm antennas on sapphire.

Fig. 7. Contour plots of $|E_x|^2$ for 1100 nm long antennas calculated for a plan view section taken 1 nm below the substrate surface. Values are plotted on a common logarithmic scale relative to incident intensity (0.01–1200 $E_0$). Position of a single antenna is indicated by a dotted rectangle and periodic boundary conditions were used to generate infinite array. Plots correspond to array pitches of (a) 2.8, (b) 2.4, (c) 2.0, (d) 1.6, (e) 1.3, and (f) 1.2 μm.

Further details of the longitudinal field distributions and their role in antenna coupling are revealed by inspecting field strengths in the substrate versus the air. To this end, the fields on a vertical cross-section taken through the middle of the 1100 nm antennas were calculated. From these, single line profiles were extracted at the longitudinal mid-gap position along the direction normal to the substrate. These results are summarized in Fig. 9(a), where we have plotted the field strength at the longitudinal mid-gap position as a function of vertical distance for arrays of 1100 nm antennas on sapphire. These data reveal that the region of highest longitudinal field strength resides in the substrate for larger pitches but approaches the surface as the pitch is decreased, and eventually shifts from the substrate into the air. Figure 9(b) demonstrates this transition by plotting the z-position at which the highest field strength occurs as a function of pitch for arrays of 1100 and 550 nm antennas. The maximum field transitions from a position within the substrate to the air gap between the antenna ends at $p \approx 1.5$ and $p \approx 0.86$ μm for arrays of 1100 and 550 nm antennas, respectively. These values compare very closely with the pitch at which the longitudinal mode extension ($\delta$) overlaps as indicated by blue arrows in the raw data of Fig. 3, and correlate well with the onset of the red-shifting that we attribute to longitudinal coupling. This result strengthens the case for assigning direct responsibility to end-to-end coupling for the spectral modifications observed at the smallest pitches investigated.
Fig. 8. Comparison of field intensity at the longitudinal and transverse mid-gap positions (marked by red dots labeled L and T in Fig. 7(a)) for arrays of (a) 1100 nm antennas and (b) 550 nm antennas on sapphire. Vertical dashed lines indicate array with greatest oscillator quality factor, Q.

Fig. 9. (a) Vertical field profiles taken at longitudinal mid gap for 1100 nm antennas on sapphire for pitches from 1.2 to 3 μm. Dashed black line indicates air-substrate boundary. Red box indicates height of antennas. As pitch is reduced, the field maximum moves up from the substrate eventually reaching a peaked value in the air between antennas. (b) Pitch-dependent position of maximum field for arrays of 1100 (black) and 550 nm antennas (red) on sapphire. The maximum-field transitions from substrate to air at p~1.5 and p~0.86 μm for arrays of 1100 and 550 nm antennas, respectively (indicated by vertical black dashed line). These pitches correlate well with the onset of red-shifting observed in Fig. 3 which we attribute to longitudinal coupling.

6. Further discussion

Considering the system as a whole, simulations show that transverse coupling is maximized in the evanescent regime for pitches near the evanescent/radiative transition, where in-plane diffracted modes couple array elements to one another, resulting in maximum oscillator quality factor Q, in accord with experiment, and maximum computed field intensities. It is important to note that although the mid-gap field is highest for our smallest modeled pitch (within the near-field coupling regime), the greatest localized field intensity is found in the evanescent regime, for fields at the antenna itself facing the longitudinal gap, where an intensification factor $|E_x|^2/|E_0|^2 \sim 1000x$ occurs. Localizing fields at the antenna surfaces may be desirable for sensing applications where molecular bonding to metal surfaces via thiol or similar surface functionalization chemistries is commonly used. On the other hand, cooperative oscillations of arrays of coupled particles, strongest when the array pitch equals $\lambda_{sub}$ and evidenced by maximum Q, may be preferable for applications relying on energy utilization such as optical detection, energy harvesting, or catalysis.
As the array pitch decreases further, near-field interactions in the longitudinal direction compete with and eventually dominate inter-antenna coupling (Fig. 7), giving rise to the near-field coupling regime discovered in this report. This regime is characterized by a rapidly decreasing Q accompanied by a red shift. A number of mechanisms may be responsible for these effects. One which we can reject is variability in the inter-antenna gap width through lithographic errors. Errors in gap width even as large as 5 nm would not produce resonance shifts large enough to generate the observed broadening, even considering the strong exponential dependence of resonance position with antenna separation as demonstrated in Fig. 10. Instead, intrinsic mechanisms are in play, as also indicated by the broadening and red shift found in the FTDT simulations.

At small pitches, an antenna is no longer a point, and probably experiences a range of field strengths over its length in, or out of, phase with the restoring force. In this regime, the notion of moderately coupled oscillators starts to break down. Additional broadening may occur as SPPs circulating on an antenna leak to adjacent antennas with increasing efficiency as the gap decreases [59]. For strong enough coupling, mode hybridization leads to a description in terms of a particle waveguide [60, 61], which is characterized by a band that spreads in frequency from the single-particle resonance as wavevector increases. Hence for our smallest gaps, the array response is better described as an ensemble of one-dimensional SPP waveguides than a two-dimensional lattice. For example, a waveguide comprising a linear chain of spherical metal particles produces red-shifted resonances when coupled in the longitudinal direction (parallel to direction of chain). Similar red-shifting and broadening due to longitudinal coupling in linear arrays of half-wave antennas placed in slit arrays has also been reported [62]. Computations for a dispersive interrupted SPP-waveguide for the longitudinal mode exhibits a red shift for the small wavevectors that can couple to our excitation scheme, which may contribute to the experimentally observed red shift [60, 61, 63]. For such a waveguide, band dispersion and losses from re-radiation of the traveling-wave SPP may also contribute to the measured increase in resonant breadth.

7. Conclusions

In summary, we have fabricated random ensembles and periodic square-arrays of half-wave nanoantennas with tight control of dimensions, and systematically varied pitch on substrates with very different refractive indices (silicon and sapphire). Reflection spectra were measured, analytically and numerically modeled to reveal three inter-antenna coupling regimes. These were described by: (i) at array pitches > λ_{sub}, weak dipolar interactions among periodically arrayed elements that caused a red shift relative to the resonance of antennas arrayed randomly, (ii) enhanced in-plane coupling for pitches ~λ_{sub} that induces spectral
narrowing and blue shifting of the nanorod absorption band, and finally (iii) a near-field coupling regime characterized by a broadened symmetric lineshape and red shifting at the smallest array periodicities explored in this work. This final coupling regime is termed “near-field” coupling and is associated with the predominant interparticle coupling switching from the transverse to longitudinal direction. The role of array pitch on coupling mechanism and spectral character indicates its importance for applications such as energy harvesting, optical detection, and photo-induced chemistry.

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