Bonding and Antibonding Modes in Metal–Dielectric–Metal Plasmonic Antennas for Dual-Band Applications

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Resonant optical antennas supporting plasmon polaritons (SPPs)—collective excitations of electrons coupled to electromagnetic fields in a medium—are relevant to sensing, photovoltaics, and light-emitting devices, among others. Due to the SPP dispersion, a conventional antenna of fixed geometry, exhibiting a narrow SPP resonance, cannot simultaneously operate in two different spectral bands. In contrast, here it is demonstrated that in metallic disks, separated by a nanometric spacer, the hybridized antibonding SPP mode stays in the visible range, while the bonding one can be pushed down to the mid-infrared range. Such an SPP dimer can sense two materials of nanoscale volumes, whose fingerprint central frequencies differ by a factor of 5. Additionally, the mid-infrared SPP resonance can be tuned by employing a phase-change material (VO₂) as a spacer. The dielectric constant of the phase-change material is controlled by heating the material at the frequency of the antibonding optical mode. These findings open the door to a new class of optoelectronic devices able to operate in significantly different frequency ranges in the linear regime, and with the same polarization of the illuminating wave.

Optical antennas are used to couple freely propagating optical fields to fields in matter and already present an established concept in nanophotonics.[1,2] They can be used for nanoscale imaging, light emission, optical detection, coherent light control, as well as for life sciences and medical applications.[3,4] Optical antennas are typically made of metals supporting SPPs (plasmonic antennas)[5] and can be designed for a very broad frequency range, from visible (VIS) to terahertz frequencies. At mid-infrared (mid-IR) frequencies, novel 2D and van der Waals materials have been suggested as an alternative for optical antennas, as for instance graphene[6,7] and topological insulators[7] (supporting Dirac plasmon polaritons) or h-BN (supporting hyperbolic phonon polaritons).[8,9] The latter materials, on the one hand, can be more interesting compared to metals due to both much higher plasmon confinement and active tuning of plasmon wavelength (and thus antenna resonance). On the other hand, they are very limited to relatively narrow spectral intervals in which they support polaritons.

A particularly interesting application, for which optical antennas present a powerful tool, is surface-enhanced spectroscopy.[10] Strong electromagnetic near-fields created by the antennas can dramatically (by orders of magnitude) enhance the absorption resonances of the placed nearby molecules. The molecular fingerprints are recognized either by analyzing Fano-like features appearing in the SPP resonances in the spectra of the extinction cross-section of the antennas (surface-enhanced absorption spectroscopy[10]) or by monitoring Raman signals (surface-enhanced Raman scattering[11]). Surface-enhanced spectroscopy is used both in the mid-IR frequency range, in which many organic materials have vibrational resonances,[10,12,13] and in the visible one, where electronic transitions in molecules are more relevant.[14,15] Since metallic antennas exhibit SPP resonances in a broad frequency range (with the resonance frequency depending upon antenna’s geometry), they seem to be more universal for surface-enhanced spectroscopy applications, than antennas made of alternative materials. At the same time, due to a big difference between SPP wavelengths at VIS and mid-IR frequencies, one and the same conventional SPP antenna cannot simultaneously operate in both spectral bands. For enabling dual-band performance, one has to design antennas with large geometric aspect ratios (e.g., rod antenna).[16] In this case, the antenna responds differently to illuminating waves of different in-plane polarizations.
Here we show that by using a simple vertical SPP dimer composed of two metallic disks separated by a nanometric spacer, it is possible to achieve well-pronounced SPP resonances simultaneously in the VIS and mid-IR ranges. By numerical simulations, we demonstrate that each of the resonances can be used for surface-enhanced spectroscopy. The frequencies of the emerging SPP resonances are predominantly defined by strong hybridization between the SPPs supported by each disk. Therefore, the resonances of the vertical SPP dimer can be tuned by the thickness of the spacer and its dielectric permittivity. As an example, we tune the position of the mid-IR resonance by filling the spacer of the antenna with VO$_2$ (phase-change material having temperature-dependent dielectric permittivity). Importantly, thanks to the rotational symmetry of the antenna, antenna’s electromagnetic response is totally independent of the in-plane polarization of the incident wave.

In Figure 1a, we illustrate the concept of a dual-band antenna: two gold disks (of height $h = 40$ nm and radius $R = 120$ nm) are separated by a dielectric spacer. The antenna is placed on a standard SiO$_2$ substrate, transparent in both VIS and mid-IR ranges. For simplicity of simulations, we consider a periodic array of such antennas. Taking a subwavelength period, $L = 400$ nm, in the whole studied range of wavelengths (from 0.55 to 5.5 $\mu$m) we avoid diffraction into higher orders except the fundamental (zero) one. On the other hand, the chosen period is much larger than the characteristic confinement length of the SPPs in the disks, $L \gg \delta_{SPP}$, where $\delta_{SPP} \leq \lambda_p/2\pi$ (with $\lambda_p$ being the wavelength of the SPP on an infinite metal surface). Hence, the coupling between the SPP modes of different antennas is negligible. The extinction (defined as $1 - |T|^2$, with $T$ being the amplitude transmission coefficient) spectra for different values of the spacer thickness, $d$, is shown in Figure 1c. As a reference, the extinction for a single gold disk is represented by the black curve, showing one dipolar SPP resonance around $\lambda = 760$ nm ($\omega = 13\ 158$ cm$^{-1}$). When the antenna is composed of the two disks, the dipolar SPP modes of the upper and lower disks couple, building up the hybridized bonding and antibonding modes.$^{[17]}$ Accordingly, the extinction spectrum of the dimer manifests two peaks (colored curves in Figure 1c), with the distance between them being increased as $d$ decreases. While the antibonding (high-frequency) mode remains almost at the same spectral position (near $\omega = 14\ 500$ cm$^{-1}$), the bonding (low-frequency) mode quickly moves away toward mid-IR frequencies. The effective repulsion of the two resonant peaks is more clearly visible in the color plot representing the extinction as a function of both $\omega$ and $d$ (Figure 1d).

As it is clearly seen from Figure 1d, for $d > R$ the resonant wavelengths of the bonding and antibonding modes are symmetrically shifted to longer and shorter wavelengths, respectively, with respect to the resonant wavelength of a single disk. These shifts are the manifestation of the interaction between the two disks via the common dipole field, see the Supporting Information. It turns out that according to
the quasistatic approximation (assuming that the disk is small compared to the resonant wavelength of the mode) the resonant wavelengths of the vertical dimer for \( d > R \) are
\[
\lambda_1 = \lambda_0 (1 + \beta/2).
\]
Here, \( \lambda_0 \) is the resonant wavelength of a single disk (Section S4, Supporting Information) and \( \beta \) is the coupling between the disks. This coupling is proportional to \( (1 + d/w)^2 \) so that the separation between the resonant wavelengths increases as the distance between the disks \( d \) decreases. The model is developed for \( d > R \) but the same functional dependence on \( d \) can be used for the bonding mode in a wider parameter space: \( \lambda_0/\lambda_0 = 1 + a/(1 + d/w)^2 \). Here, \( \lambda_0 \) is the resonant wavelength of the bonding mode; \( a \) is a constant defining the integrated spatial overlap of the dipolar modes and \( w \) is the effective size of the overlap. Fitting the parametric dependence \( \lambda_0(d) \) to the simulation data (Figure 1d, color plot), we get the values \( a = 4 \) and \( w = 8.33 \) nm. The result of the fit is shown in Figure 1d, by the black dashed curve. Our simple expression for the wavelength of the bonding mode is useful for a quick estimate of the wavelength of the bonding mode prior to numerical simulations. Moreover, the dependence \( \lambda_0(d) \) can be used for an order-of-magnitude estimates for disks of different radii since \( w = R/10 \) (for details, see the discussion about \( w \) after Equation S6, Supporting Information).

Importantly, the strong dependence of the bonding resonance on the spacer thickness allows for its significant shift toward low frequencies, down to the mid-IR range. This dependence can be used for efficient tuning of the antenna, for example by applying strain or by thermally induced melting of a self-assembled layer placed inside the spacer. The coupled oscillators model (see Section 1.3, Supporting Information) also qualitatively provides the spatial field distribution of the hybridized SPP modes: the effective electric in-plane dipoles induced in the upper and lower disks are either parallel (antibonding mode) or antiparallel (bonding mode). This result is fully consistent with the in-plane electric field spatial distributions found by means of wave electromagnetic simulations (Figure 1b, black arrows distribution). The bonding and antibonding modes can also be easily recognized by the antisymmetric and symmetric spatial distribution of the real part of the vertical component of the electric field, \( E_z \) (being proportional to the surface charge density), on the top face of the lower disk and on the bottom face of the upper disk (color plot in Figure 1b).

Due to the antisymmetric in-plane electric field distribution (and thus the reduced effective in-plane dipole moment, preventing an efficient coupling with the incident wave), the peak intensity of the bonding mode is lower as compared to the antibonding one. In a planar SPP dimer (two gold disks located in the same plane next to each other), one of the modes is always dark, i.e., it cannot be excited by a normally incident light. In contrast, for our vertical SPP dimer, the situation is different thanks to the retardation effect (phase shift) between the effective dipoles induced in the disks. Therefore, both modes can be excited by a normally incident plane wave even in the case of the symmetric dielectric environment of the vertical SPP dimer. Apart from the different symmetry of the fields of the hybridized SPP modes, the spatial distribution of the electric field intensity, \(|E|\), is significantly different as well. Namely, while the maxima of \(|E|\) of the antibonding modes are concentrated around the edges of the bottom disk (right panel of Figure 1e), the \(|E|\) of the bonding mode is strongly “pushed” into the spacer (left panel in Figure 1e). The spatial distribution of \(|E|\) provides a hint to the best spatial allocation for the sensed material. In particular, the spectral position of the bonding mode should be very sensitive to the dielectric permittivity of the spacer. The concept of probing minute amounts of materials inside the spacer has recently been suggested for similar “screened” plasmonic modes in graphene resonators above a metal pad and later realized experimentally.

In order to test the sensing functionality of our dual-band SPP dimer antenna, we use two different materials: octane and j-aggregate, with their dielectric permittivities \( \varepsilon_{oct} \) and \( \varepsilon_j \) taken from refs. [22] and [15], respectively. While octane shows a typical for alkenes absorption resonance of the stretching vibration of the C–H bond at mid-IR frequencies (around \( \omega = 3000 \) cm\(^{-1}\), see Figure 2a), j-aggregate has an excitonic absorption peak in the visible range (around \( \omega = 14 500 \) cm\(^{-1}\), see Figure 2b). For simplicity of the proof of principle, we consider cylindrically symmetric shapes of the probed materials, preserving the symmetry of the antenna. According to the spatial positions of the \(|E|\) maxima (Figure 1e), we place 1.4 nm thick layer of octane (in the form of a disk) between the gold disks and 3 nm thick ring of j-aggregate around the bottom gold disk, as shown in the insets to Figure 2c. The octane disk radius coincides with that of the gold rings, so that its volume is \( 63.3 \times 10^{-3} \) nm\(^3\) (i.e., \( 3.9 \times 10^{-19} \) mol) and thus fits \( 2.35 \times 10^5 \) octane molecules. In contrast, the j-aggregate ring has the internal radius coinciding with the radius of the gold rings and a width of 3 nm (so that its volume is \( 6.9 \times 10^{-3} \) nm\(^3\)), and mimics a single j-aggregate rod (typically found in solutions), rolled around the antenna. Figure 2c shows the extinction spectra of the SPP dimer antenna with the molecular layers (red solid curve) and with the reference layers having the constant dielectric permittivities \( \varepsilon_1 \) and \( \varepsilon_2 \) (black dashed curves). The values of \( \varepsilon_1 \) and \( \varepsilon_2 \) correspond to the average of \( \varepsilon_{oct} \) and \( \varepsilon_j \), respectively, in the shown frequency range. The comparison between the spectra clearly reveals the absorption fingerprints in both VIS and mid-IR spectral bands. Remarkably, the visibility of the absorption fingerprints exceeds the absorption by the octane disk and j-aggregate ring by about two orders of magnitude (see orange and violet curves in Figure 2c). Interestingly, apart from the excitonic resonance (approximately repeating the peak of \( \text{Im}(\varepsilon_j) \)) the absorption by the j-aggregate ring also shows a broader exciton-polaritonic resonance at higher frequencies, where \( \text{Re}(\varepsilon_j) \) takes negative values. The observed significant fingerprint enhancement justifies the use of our dual-band dimer SPP antenna for surface-enhanced spectroscopy. Notice that from the practical point of view, the delivery of the sensed materials in between the gold disks, as well as around the antenna, can potentially be realized via nanofluidics.

The strong field confinement inside the spacer of the SPP dimer can enable the spectral tuning of the bonding resonance by changing the dielectric permittivity of the spacer. An interesting possibility to control the dielectric permittivity is via heating of phase change materials, such as, for instance, VO\(_2\). At the rutile to monoclinic transition temperature (\( T_{M} = 67 \) °C), VO\(_2\) exhibits a metal to semiconductor transition (Mott transition) in its electronic structure: the rutile phase is metallic while the monoclinic phase is semiconducting. As a result,
its dielectric permittivity, $\varepsilon_{\text{VO}_2}$, strongly changes with the temperature, $T$, around $T = T_M$, particularly in the mid-IR frequency range (Figure 3a).\textsuperscript{[27,28]} For this reason, $\text{VO}_2$ has recently been used for active switching of SPPs\textsuperscript{[29]} and reconfigurable control of in-plane phonon polariton propagation.\textsuperscript{[30]} To demonstrate the tunability of our SPP dimer antenna, we perform the simulation of its extinction spectra, placing $\text{VO}_2$ between the gold disks (see Figure 3b). As seen in the figure, in the temperature range 50–60 °C (i.e., heating up the antenna by 10 °C) the mid-IR resonant peak blueshifts by 240 wavenumbers. The blueshift of the resonance with $T$ can be explained by the reduction of the real part of $\varepsilon_{\text{VO}_2}$ (Figure 3a, solid curves). On the other hand, as the imaginary of $\varepsilon_{\text{VO}_2}$ increases with $T$ (Figure 3a, dashed curves), the amplitude of the mid-IR peak decreases.

From the results presented in Figure 3, we can directly estimate the figure of merit of the bounding resonance as $\text{FOM} = \Delta \lambda / \Delta n \cdot \text{FWHM} = 4$, where $\Delta \lambda$ is the wavelength shift per refractive index change, $\Delta n$, and FWHM is the full width at half maximum. In contrast, the antibonding resonance at the VIS frequencies does not display any significant change with $T$. Thus, the antibonding SPP resonance in the VIS range can be used for controlling the bonding SPP resonance in the mid-IR range by means of optical pumping.\textsuperscript{[31]} Such pumping can be
practically realized with a basic, mW-scale, commercial diode laser. For instance, for a thin silicon substrate, the heat flux across the face 1 mm in height and 1 cm in width amounts to less than 1 mW. The main expected mechanism of thermal losses is due to blackbody radiation, which for a sample temperature of 40°C above the ambient, results in 30 mW of losses. Notice that previously SPP resonances in plasmonic antennas have already been explored for the experimental demonstration of antenna-assisted, optically triggered phase transition of VO₂ at the near-IR frequencies.[12]

In conclusion, we have suggested a simple dual-band vertical dimer antenna exhibiting SPP resonances simultaneously in the VIS and mid-IR frequency ranges. We have shown the tuning of the mid-IR resonance by means of heating the phase-change material (VO₂) placed in the spacer between the gold disks. The heating of VO₂ can be realized by resonant pumping of the antibonding SPP mode with an mW-scale, visible laser. We have demonstrated the potential of the SPP dimer antenna for dual-band surface enhanced spectroscopy. Although we have illustrated the identification of the fingerprints of two different molecules, such dual-band spectroscopy can also be used for identification of the same material (molecules) having its fingerprints in the VIS and mid-IR frequency regions. Moreover, with proper matching of the oscillator strength of the SPP resonances to that of the molecular absorption resonances, one can potentially achieve strong coupling between the SPPs of the antenna and the molecule, simultaneously in the VIS and mid-IR ranges. From a different perspective, our findings can pave the way to enhancing the efficiency of the Förster resonance energy transfer or photon upconversion applications (e.g., solar spectrum conversion for photovoltaics).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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