THE JOURNAL OF PHYSICAL CHEMISTRY C

ARTICLE

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Near Field Enhancement in Ag Au Nanospheres Heterodimers

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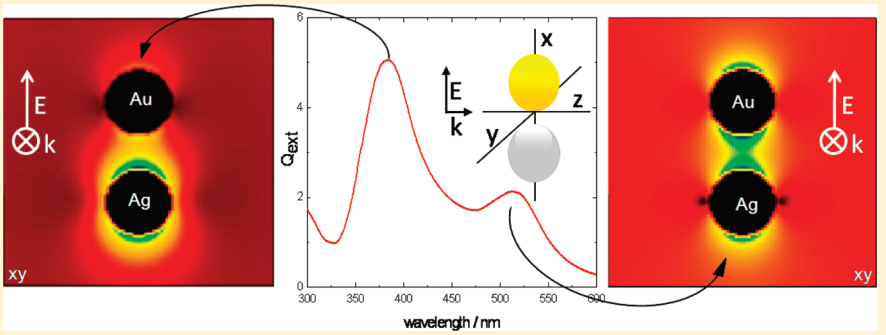
Supporting Information

ABSTRACT:



The near field enhancement in Ag Au nanospheres heterodimers excited at their respective resonance wavelengths is studied in detail using rigorous electrodynamics calculations based on the Generalized Multiparticle Mie theory. The effect of incident polarization, nanosphere radius, and interparticle separation on the distribution pattern and magnitude of the near field enhancement is analyzed. As in the homodimer case, the highest enhancement values are found for incident polarization parallel to the dimer axis. However, there are significant different enhancement patterns around the dimer according to the excitation wavelength. Analyzing the vector field plot of the enhancement, and comparing it with those corresponding to Ag and Au nanospheres homodimers, the differences observed are rationalized in terms of multipole excitations to explain the effect of breaking the symmetry of the plasmonic heterodimer. The results presented could be a useful tool for future design and engineering of plasmonic devices based on the near field properties such as substrates for enhanced spectroscopies and sensing.

INTRODUCTION

The optical properties of noble metal nanoparticles (NPs) are characterized by coherent oscillations of the conduction electrons upon illumination with an electromagnetic field of a given frequency, the so-called localized surface plasmon resonance (LPSR).[1] One of the most significant features is that when LSPRs are excited enhancements of the extinction cross section and of the electric field around the NP are observed.[2] In addition, the LSPR resonance frequency is size and shape tunable.[3] These characteristics have motivated numerous theoretical and experimental studies concerning the optical properties of NPs during the past decade, due to their relevance from both fundamental and technological standpoints.[4−7] The synergy of the availability of physical and chemical preparation methods and techniques able to measure the optical response and to morphologically characterize individual NPs, along with the current capability to theoretically calculate their optical response, has triggered important advances in our knowledge of the optical properties of isolated NPs.[8,9]

As mentioned above, excitation of LSPR leads to a significant enhancement of the electric field generated in the local vicinity of the NP with respect to the incident electric field. In turn, this enhanced electric field is able to amplify the optical signals of molecules located on the surface of the NP,[10,11] to such an extent that in some cases it is possible to detect the Raman signal of an individual molecule.[12] This feature gives rise to the development of a better control of surface-enhanced spectroscopies such as SERS and SEIRA.[13,14] In this context, the design of nanostructures that maximizes this enhancement at a given wavelength λ constitutes one of the current challenges of nanoplasmonics.[15]

A pair of NPs or dimer constitutes a prototype system where a strong field electromagnetic field is generated in the gap between the NPs. This optical interaction, which occurs mainly through plasmon coupling, has been addressed by several authors.[16−21] For example, systems composed of two Au or Ag NPs (homodimers) have been studied in detail, and it has been stated that it can be used as a device, the so-called *plasmonic ruler*, that could be used to measure distances in the nanoscale.[22,23] In general, the homodimers mostly studied are symmetric nanostructures. In contrast, nonsymmetric nanostructures composed

Received: June 1, 2011
Revised: July 5, 2011
Published: July 13, 2011

of two different metals have received less attention, and, as far as we know, there are only a few studies reported that focus on this kind of system.

In this respect, Bachelier et al. have theoretically studied the far optical properties of heterogeneous dimers of Au and Ag nanospheres, heterodimers (HD).[24] In this work, a Fano profile in the absorption cross section of the Au NP has been found as a consequence of the near field coupling between the Ag LSPR and the Au interband transitions. Recently, Sheikholeslami et al. have experimentally studied the coupling of LSPR resonances in compositionally asymmetric plasmonic NP dimers and have interpreted their results according to the plasmon hybridization model.[25] These authors observed that the antibonding modes are red-shifted with respect to the Ag LSPR and attribute this shift to the coupling of the Ag LSPR to the quasi-continuum of interband transition in Au. These authors also state that the plasmon hybridization model fails to account for this coupling, as it only considers free electron behavior of the metals. More recently, Norrlander and co-workers have shown how the plasmon hybridization method can be extended to include realistic permittivities for metals and how this concept can be applied to understand the formation of plasmonic Fano resonances in strongly coupled metallic nanostructures.[26]

In a previous work we have also theoretically studied the far field optical properties of this system.[27] We found that the most attractive optical features appear for incident polarization parallel to the heterodimer axis. In such a case, the extinction spectrum is characterized by two peaks associated with the dipole LSPR of the Ag and Au nanosphere, respectively. In turn, these two extinction peaks are significantly red-shifted as the interparticle distance is decreased and as their size and dielectric constant of the environment are increased. In addition, based on the Generalized Multiparticle Mie theory, we were able to analyze the contributions to extinction from each individual nanosphere and verified the presence of Fano profiles coming from the relative contribution to the absorption cross section coming from the Au nanosphere, in agreement with Bachelier et al.

The near field enhancements of dimers of NPs have been studied both theoretically and experimentally by several authors. These studies have been mainly focused on symmetric nanostructures. Hao and Schatz used the discrete dipole approximation to investigate the electromagnetic fields induced by optical excitation of LSPR of Ag dimers and found that the enhancement is a strong function of interparticle separation and it scales with particle size.[28] In addition, they found that the largest enhancements are generally found for dimers that have the most red-shifted wavelength dipole plasmon resonances. Talley et al., using the finite difference time domain method, have calculated the near field enhancement induced in Au dimers and found that the integrated quartic local electromagnetic field calculated correlates with the SERS intensity measured,[29] the maximum field for a dimer being much larger than the maximum field at the surface of an isolated sphere. The "hottest" spot is produced for incident polarization parallel to the dimer axis, while for incident polarization perpendicular to the dimer axis, the maximum field at the surface of the adjacent particles can be slightly lower than that of an isolated sphere. Taking into account these previous studies, it should be of interest to address the question of how the spatial distribution of the electric field is modified in NPs pairs of different composition.

In this work we study, by means of generalized Mie theory calculations, the near field enhancement in Ag−Au nanospheres heterodimers excited at their respective resonance wavelengths. We analyze the effects of incident polarization, excitation wavelength, nanospheres radius, and separation on the magnitude and spatial distribution of the near field enhancement. We find that breaking the symmetry of the nanostructure has important consequences on the enhancement pattern and also that by studying the multipole nature of the modes excited in each nanosphere, some features of the far field optical properties can also be explained.

METHODOLOGY

The Generalized Multiparticle Mie Theory formulation, developed by Xu, is an extension of the Mie theory that exactly solves the complex problem of interaction between an electromagnetic field and an aggregate of spheres.[30,31] This theory is implemented in the GMM code, which calculates far field quantities such as extinction and scattering cross section. The GMM method has been described in detail in several places, so we will only give a brief summary here. In this valuable method, scattered fields from each L individual sphere are solved in terms of the respective sphere-centered reference systems. In an arbitrarily chosen primary j_0th coordinate system, the Cartesian coordinates of the origins of these L displaced coordinate systems (i.e., the sphere centers) are (X^j, Y^j, Z^j), $j = 1, 2, ..., L$. In order to solve multisphere-scattering through the Mie-type multipole superposition approach, the incident plane wave is expanded in terms of vector spherical wave functions in each of the L sphere-centered coordinate systems. Then, the total electromagnetic field upon each point in the aggregate is obtained, which consist of two parts: (1) the initial incident plane wave and (2) the scattered waves from all other spheres in the aggregate. Recently, Ringler has extended this original GMM method in such a way that the near field can be also obtained and implemented it in the GMM-FIELD code.[32] This relevant contribution allows to compute the local electric field in each

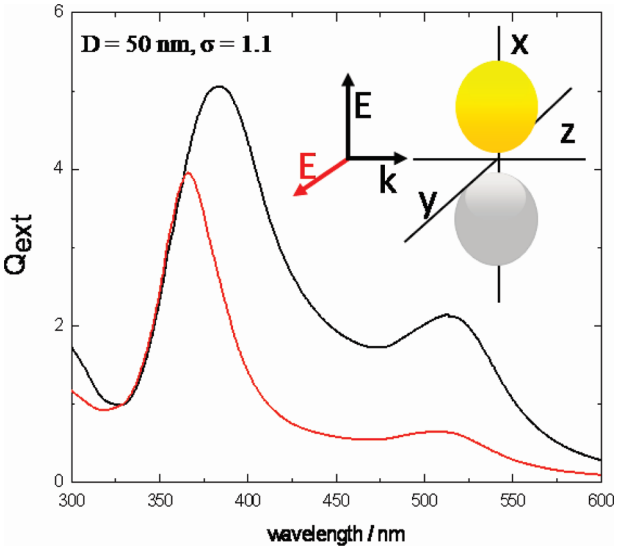


Figure 1. Extinction efficiency of a heterodimer in vacuum (D = 50 nm, σ = 1.1) for incident electric field parallel (black curve) and perpendicular (red curve) with respect to the dimer axis. The inset represents graphically the configuration of the system, showing a correspondence between the color of the different incident electric field and the respective extinction efficiency.

point by adding the incident field and the partial scattered fields in the original Cartesian coordinate system.

In this work we have employed the GMM-FIELD code to calculate the near field enhancements in Ag−Au heterodimers composed of equal diameter D nanospheres. In all the calculations presented here, the direction of the incident wave-vector k is parallel to the z axis, while the line that connects the spheres centers (from now on, dimer axis) is parallel to the x axis (see inset in Figure 1). The dielectric functions tabulated by Palik for Ag and Au were employed as input in the calculations to represent the respective metals.[33] For each dimer analyzed, the separation parameter between the nanospheres σ, defined as the ratio between the spheres center to center distance S and the nanospheres diameter ($\sigma = S/D$) is large enough ($\sigma \geq 1.05$) so that nonlocal effects on the dielectric constant can be neglected.[34]

RESULTS AND DISCUSSION

Effect of the Incident Polarization on the Near Field Enhancement. The extinction spectrum of a D = 50 nm and σ = 1.1 heterodimer in vacuum is shown in Figure 1 for incident polarization parallel (black line) and perpendicular (red line) relative to the dimer axis. In both spectra two peaks centered at around 370 and 510 nm are observed, which are attributed to the relative contribution coming from the Ag and Au sphere, λ_{Ag} and λ_{Au}, respectively.[27] From now on, we will focus on the near field originating around the nanostructure surface at each resonance, i.e., when it is excited at those wavelengths where the extinction shows the highest values. Figure 2 shows, in a color-coded graph, the spatial distribution and values of the modulus of the electric field $|E|$ in the plane $x-y$ (see inset in Figure 1) when the incident polarization is perpendicular to the dimer axis, at illumination wavelengths equal to 366 nm (A) and 507 nm (B), respectively. Irrespective of the incident wavelength value, the enhancement patterns resemble that of homodimers,[29] showing for each sphere two slight enhancements of $|E|$ in the direction of the incident polarization. In addition, if each sphere is considered individually, their enhancement patterns are very similar to that of a dipole, and the values of $|E|$ are very similar to those of the respective isolated spheres excited at the same wavelengths (see Figure 1 of the Supporting Information). These observations are in agreement with previous studies which state that the interaction between the nanoparticles is almost negligible under perpendicular excitation. On the contrary, quite different enhancement patterns are found for parallel excitation (Figure 3). Under this configuration the highest enhancement is found in the region between the nanospheres; however, a noticeable difference in the spatial distribution can be appreciated according to the λ value. At λ = 384 nm (Figure 3A), the electric field is asymmetric with respect to the yz plane, and it is concentrated around the Ag NP. On the other hand, at

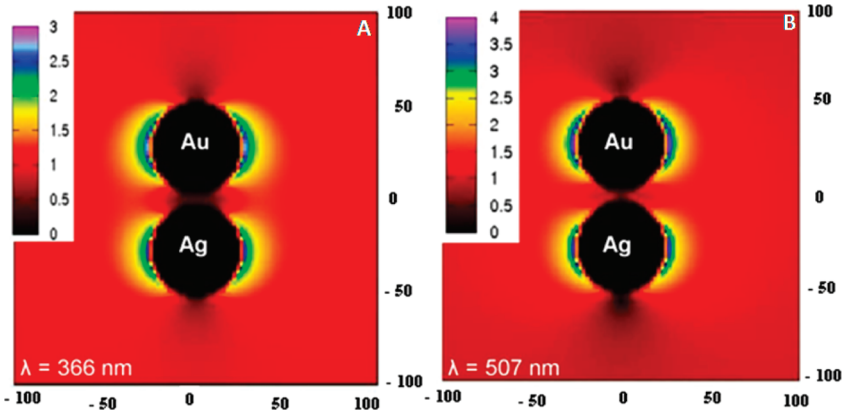


Figure 2. Near field enhancement in the xy plane (see inset Figure 1) for a heterodimer in vacuum (D = 50 nm, σ = 1.1) when it is excited with incident polarization perpendicular to the dimer axis. The excitation wavelength is indicated in each panel.

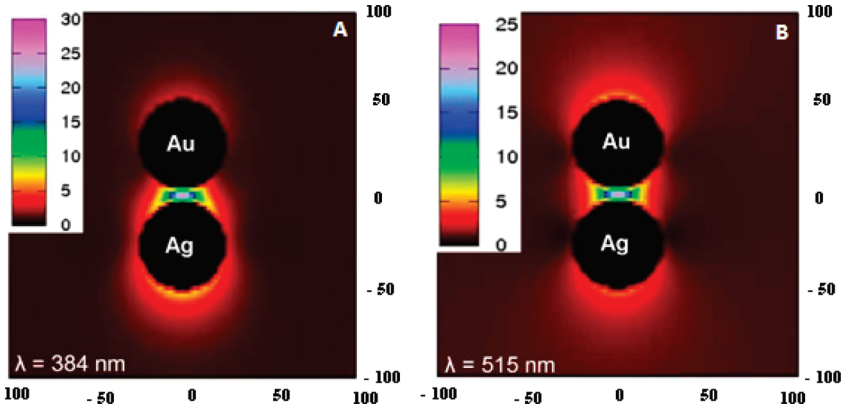


Figure 3. Near field enhancement in the xy plane (see inset to Figure 1) for a heterodimer in vacuum (D = 50 nm, σ = 1.1) when it is excited with incident polarization parallel to the dimer axis. The excitation wavelength is indicated in each panel.

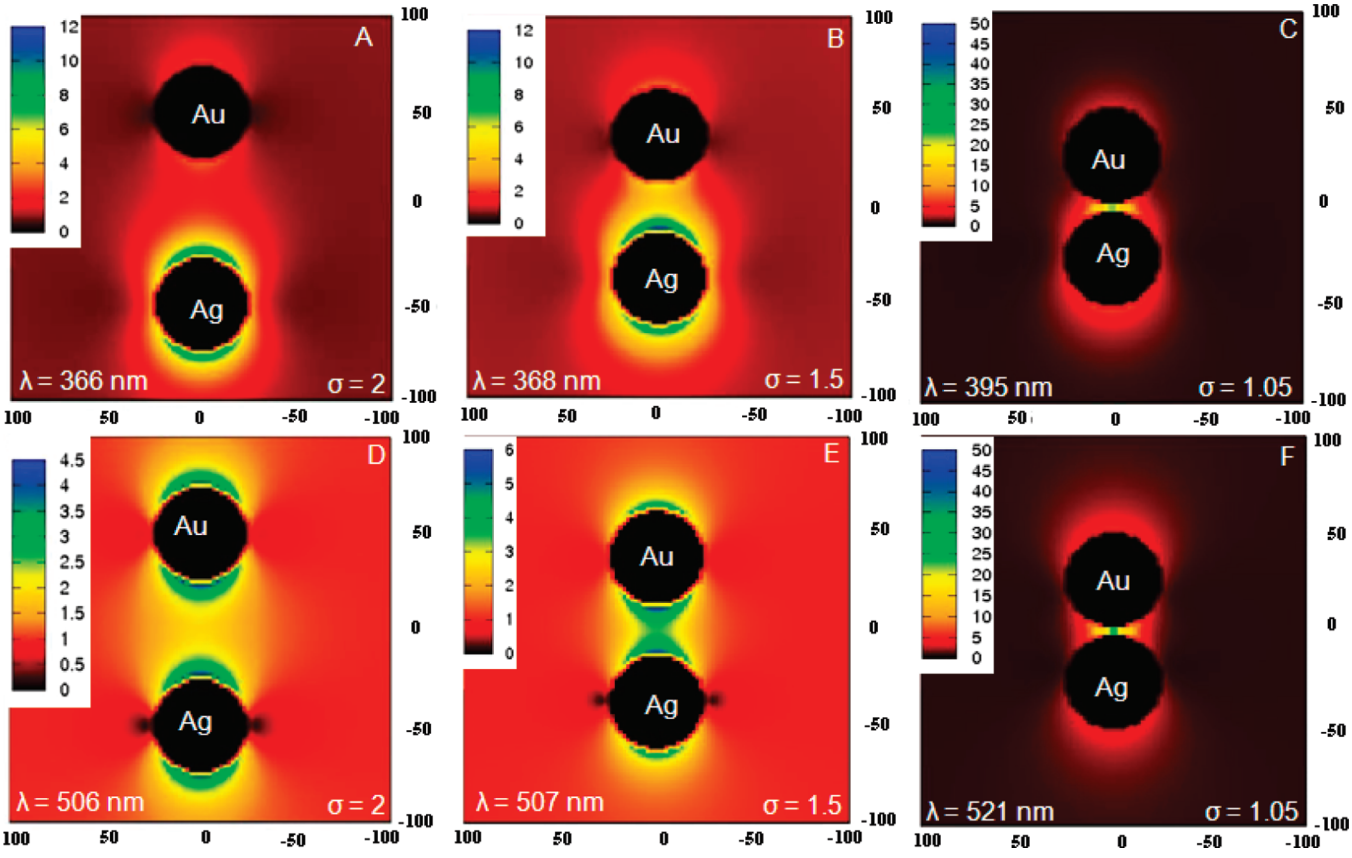


Figure 4. Variation of the near field in the *xy* plane for $D = 50$ nm Ag and Au spheres at different interparticle separation (A, D) $\sigma = 2$, (B, E) $\sigma = 1.5$, and (C, F) $\sigma = 1.05$. The respectives excitation wavelengths are indicated in each panel.

λ = 515 nm (Figure 3B), the electric field is symmetrically distributed around the hole nanostructure and resembles the pattern found for homodimers.[28,29] To better describe this phenomena, it is useful to analyze the evolution of the spatial distribution of the near field enhancement as the spheres are getting closer. Therefore, hereafter we will focus on the configuration corresponding to incident polarization parallel to the heterodimer axis.

Effect of the Nanospheres Separation on the near Field Enhancement. As mentioned previously, as the Ag and Au NPs approach each other, two simultaneous red shifts of the extinction peaks are found.[27] Figure 4 shows the enhancement pattern around the D = 50 nm heterodimer at different σ values for the corresponding resonance wavelengths. Panels A−C show the results obtained for λ_{Ag} LSPR. Again, from this sequence it can be clearly appreciated that, at $\lambda \approx 384$ nm, the main contribution to the field enhancement comes from the Ag LSPR. Besides the fact that the field is concentrated around the Ag sphere, the presence of the Au one is crucial for the system to be able to enhance significantly the electric field in the local vicinity of the nanostructure, as for isolated Ag spheres the near field enhancement is much lower. In addition, note how the magnitude of the enhancement is remarkably increased as the Au sphere approaches the Ag one. On the other hand, when the heterodimer is excited at $\lambda_{Au} \approx 515$ nm (panels D−F), the magnitude and distribution of the enhancement are similar around both spheres, in spite of the fact that at this λ value the Ag sphere is, in principle, *off* resonance. In this case it is also observed that the electric field enhancement arises as a consequence of interparticle interaction. Whatever the excitation λ, it is remarkable how the near field is signifanctly increased and confined to a smaller spatial region as the nanosphere gap is decreased.

At first glance, this opposite response could be attributed to the compositional asymmetry of the heterodimer. However, to achieve further insight it is reasonable to look for an explanation by analyzing and comparing the respective dielectric functions of Ag and Au. At $\lambda \approx 384$ nm, the dielectric response of Au is dominated by interband transitions; therefore, it is reasonable to think that electrons in Au are significantly less sensitive to the electric field originated by the Ag LSPR, as they have less "free electron behavior". At $\lambda \approx 384$ nm the near field enhancement is practically only due to the Ag LSPR, and, therefore, it is found mainly around the Ag sphere. When considering $\lambda \approx 515$ nm, electrons in Ag exhibit a more free behavior. Thus, they can be more easily influenced by the near field generated by the Au LSPR, and even can couple with the Au dipole plasmon.

Effect of the Nanosphere Size. Figure 5 shows the values of $|E|$ along the axis of different size heterodimers with an incident λ matching the Ag LSPR (λ_{Ag}) (Figure 5A) and the Au LSPR (λ_{Au}) (Figure 5B). In this set of calculations the relative distance between the spheres is kept constant ($\sigma = 1.05$). The respective excitations λ for each HD are listed in Table 1, along with the corresponding maximum $|E|$ values ($|E|_{max}$). Note that the resonance wavelength values increase with nanosphere diameter for a constant σ value. In general, the enhancement profiles are independent of D for this size range, being particularly intense in the region between the nanospheres. In the middle region, $|E|$ is proportional to D when the HD is excited at λ_{Au}; in fact $|E|$

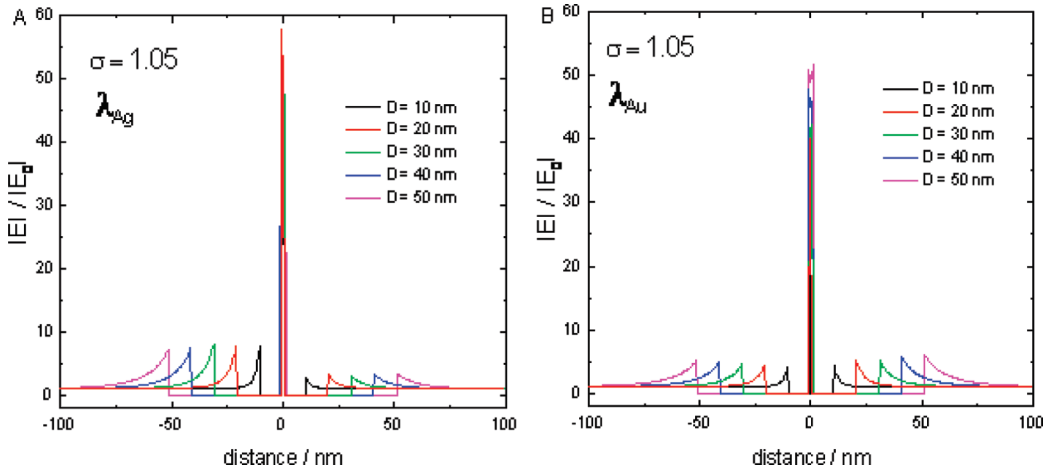


Figure 5. Variation of the near field along the dimer axis with the nanospheres diameter as indicated in each panel. The results depicted in panel A (B) are obtained by setting the incident wavelength in such a way that the Ag (Au) sphere is on resonance.

Table 1. Correlation between the Diameter *D* of the Nanospheres and the Maximum Near Field Value Observed When the Ag or Au LSPR Is Excited[a]

D/nm	λ_{Ag}/nm	$\lvert E\rvert_{max,\ \lambda Ag}$	λ_{Au}/nm	$\lvert E\rvert_{max,\ \lambda Au}$
10	364	48	510	35
20	368	58	513	40
30	372	52	515	42
40	383	53	518	47
50	395	50	521	51

[a] The excitation λ values for each case are also listed. Irrespective of the size of the HD, σ = 1.05.

increases almost 45% when D is increased from 10 to 50 nm (see Table 1). However, when the HD is excited at λ_{Ag} a clear trend between $|E|$ and D is not observed. As we will see and discuss in the next section, the respective same trends are found for both Au and Ag homodimers (see Figure 2 and Table 1 in the Supporting Information). A feature to be noticed is also that the enhancement in the external sides of the HD is around 10 times smaller than in the central region. The effect of D on $|E|$ is also significant in this region as the $|E|$ values diminish faster when moving away from the HD surface in the axial direction as the D is decreased. According to these calculations, HD of larger size would be preferable in plasmonic applications based on near field enhancements (such as SERS) not only because they produce a higher enhancement but also because the enhancement would be spread over a higher volume.

Comparison with Homodimers. The near field enhancements produced by the HD when excited at λ_{Ag} are almost three times smaller than the enhancements produced by the respective equal volume Ag homodimers. In contrast, the $|E|$ values for the HD excited at λ_{Au} are not significantly different (only a 10% lower) than the respective $|E|$ values for Au homodimers (see Figure 2 in the Supporting Information). Understanding this quite different qualitative behavior should give important insight into the optical response of asymmetric plasmonic systems. An analysis of the near field enhancement represented in a vectorial plot may help in this sense, as shown in Figure 6. In this figure, the values of the near field for hetero and homodimes (D = 50 nm, σ = 1.1 for all cases) in the xy plane are compared.

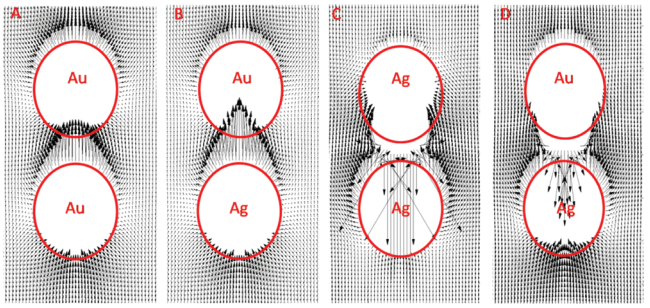


Figure 6. Vector plot of the real part of the near field enhancement in the xy plane for D = 50 nm (A) Au and (C) Ag homodimers excited at the respective LSPR, and for a D = 50 nm HD excited at λ_{Au} (B) and at λ_{Ag} (D).

According to the excitation wavelength, remarkable differences in the enhancement patterns are observed. For the longitudinal dipole resonance of the Au homodimer, the vector plot of the near field resembles that expected for the interaction between two head to tail dipoles (Figure 6A). This pattern is qualitatively the same as that obtained for the HD excited at λ_{Au} (Figure 6B), which indicates that the near field distribution is not modified by replacing a Au sphere by a Ag one. Besides, as mentioned above, the magnitude of the near field for the Au homodimer does not change significantly with respect to the HD excited at λ_{Au}. Thus, the interaction in the HD when the Au sphere is on resonance may be thought of as follows: the LSPR in the Au sphere has mainly a dipole character, which in turn is able to induce a dipole LSPR in the Ag sphere. Due to the free electron behavior of electrons in Ag, both dipole moments have a similar magnitude, leading to a symmetric distribution of the near field as shown in Figure 3B. These observations indicate that the major effect of breaking the symmetry of the dimer by replacing a Au sphere by a Ag one, for excitation at λ_{Au}, is just to modify the resonance wavelength, as the magnitude and spatial distribution of the near field remain practically unchanged. On the other hand, if we now consider the excitation of the longitudinal dipole LSPR of the Ag homodimer, the vector plot of the near field (Figure 6C) differs considerably from that obtained for the Au homodimer, indicating that a complex charge distribution, different from that corresponding to two head to tail dipoles, is generated.

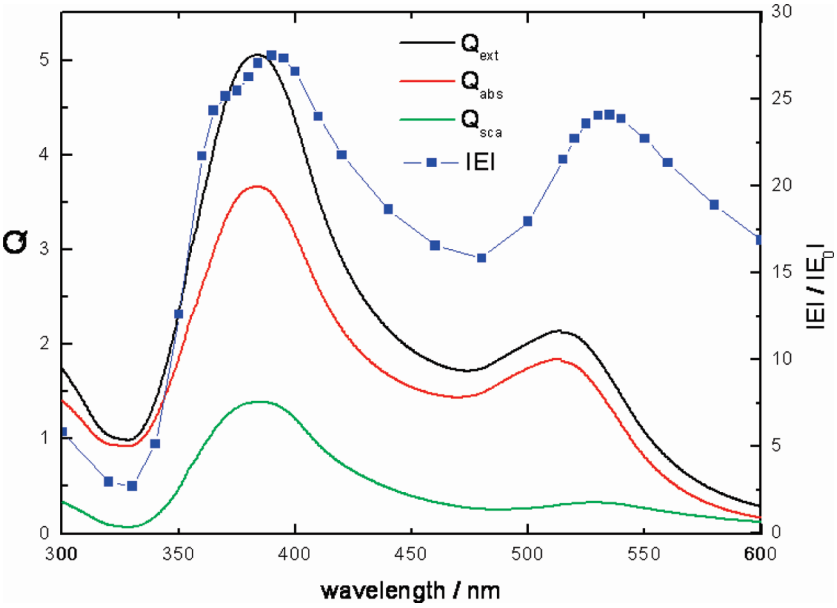


Figure 7. Extinction (black curve), absorption (red curve), and scattering (green curve) efficiencies spectra of a heterodimer in vacuum (D = 50 nm, σ = 1.1) for incident polarization parallel to the dimer axis, along with the enhancement spectrum (blue dots). The enhancement spectrum represents the average $|E|$ in the gap region for each wavelength (see text for the calculation details).

This complex charge distribution can be attributed to the interaction between dipoles and higher order multipoles excited in each sphere. It is important to note that this pattern arises at relatively short distances ($\sigma \leq 1.5$) while for $\sigma > 1.5$ the pattern is quite similar to the one shown in Figure 6A corresponding to the interaction between two dipoles. According to this analysis for Ag homodimers, the contribution of higher order modes is significant as the spheres are getting closer, which is in agreement with previous results.[22] In addition, note that these higher order contributions are mainly responsible for the larger red shifts in Ag homodimers compared to Au homodimers. In general, Ag nanostructures produce greater near field enhancements than Au nanostructures of similar shape. The same effect occurs for dimers, which could be attributed to the lower damping of the plasmon oscillation of Ag with respect to Au. Taking into account this statement and the results presented here, it is possible to suggest that as Ag has lower damping than Au, the former is able to support the excitation of higher order modes as the particles are getting closer, while this process would be suppressed in the latter. Then, as a result of the interaction of LSPR of higher order, Ag homodimers show greater near field enhancements than Au. If we now consider the HD excited at λ_{Ag}, the vector plot of the enhancement (Figure 6D) is qualitatively the same as that obtained for the Ag homodimer, but its magnitude is several times smaller. This result can be explained considering that the Ag sphere induces the excitation of dipole and higher order LSPR modes in the Au sphere; however, as Au has a larger damping, the multipole moments sustained in this sphere are smaller than the respective multipole sustained in the Ag sphere, which leads to a lower near field enhancement compared with the Ag homodimer. In addition, this behavior should produce a higher field around the Ag than in the Au sphere, which is in agreement with the asymmetric near field enhancement shown in Figure 3A.

Correlation with Far Field Optical Properties. Figure 7 represents the average $|E|$ value (averaged in the region defined by a sphere of 2.5 nm radius and located at the origin of the coordinate system) for several λ, from now on the "enhancement" spectrum (blue dots), and its correlation with the respective extinction spectrum (black curve). In general, the enhancement spectrum follows the same trend as the extinction one. However, as it has been previously reported, there is a red shift of $|E|_{max}$ with respect to the extinction peaks.[35,36] Another feature to be remarked is that there is not a direct relationship between the values of the Q_{ext} and the $|E|$ values. Note that changing λ from 384 to 515 nm, Q_{ext} reduces its value 60%, while $|E|$ only decreases 15% from its original value. In addition, it is important to mention that the maximum values of $|E|$ obtained for this heterodimer are similar to those obtained for homodimers using other theoretical approaches.[28,29] The correlation shown in Figure 7 is in agreement with a recent work[2] where the authors have elegantly shown that the red shift of the enhancement spectrum peak with respect to the extinction peak is a direct consequence of the fundamental properties of damped, driven harmonic oscillators. The red shift shown here is more pronounced for the excitation of the Au LSPR than for the Ag LSPR as the damping of the electrons oscillation in Au is higher than in Ag, which is consistent with the argument mentioned above.

As we have studied the far field optical properties of these broken symmetry nanostructures in a previous work,[27] it should be of interest to correlate them with the present results. In that work, we found appreciable values of the scattering efficiencies Q_{sca} for the off resonance nanospheres, i.e., when the Ag (Au) particle is excited at λ_{Au} (λ_{Ag}). In order to explain this observation we have already proposed a mechanism in which the on resonance sphere transfer the plasmon energy to the off resonance one through a near field coupling of the respective LSPR. The transferred energy is then converted into scattered light, giving rise to the Q_{sca} values observed. The near field results presented here are in complete agreement with the mechanism suggested previously.

CONCLUSIONS

In this work we have studied the near field enhancements in Ag−Au heterodimers by mean of electrodynamics calculations. According to the direction of the incident polarization with respect to the homodimer axis, two modes of resonance can be clearly identified, the highest near field enhancement was found for incident polarization found to be parallel to the dimer axis. In turn, for parallel configuration, the enhancement is particularly high when the LSPRs of the Ag and Au spheres are excited at λ_{Ag}, and λ_{Au}, respectively. The distribution pattern of the enhancement is symmetric (asymmetric) around the heterodimer when it is excited at λ_{Au} (λ_{Ag}). We have rationalized these qualitative different behaviors by analyzing the vector plots of the enhancement and by comparing them with those corresponding to the homodimers. This analysis indicates that when the HD is excited at λ_{Au} dipole dipole interactions dominate. In contrast, for excitation at λ_{Ag} the interaction between higher order multipoles becomes relevant. At λ_{Au}, electrons in Ag behave as free electrons in their response to the field generated by the Au sphere give rise to a symmetric distribution of the field enhancement. On the contrary, at λ_{Ag}, electrons in Au do not behave mainly as free electrons, and their response to the multipole field produced by the Ag sphere lead to an asymmetric field distribution. In summary, breaking the symmetry of nanosphere pairs by studying heterodimers of Ag and Au spheres make it possible to understand how the individual intrinsic material properties of each sphere, such as damping and interband transitions, produce significant changes in the near field patterns, a feature that is not easy to be addressed by only considering extrinsic properties such as size and interparticle distance.

ASSOCIATED CONTENT

Supporting Information. Color-coded graph of the near field enhancement generated by Ag and Au isolate nanospheres excited at several wavelengths and the near field enhancement values along the axis of different size Ag and Au homodimers when they are exited at their respective resonance wavelengths. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Financial support from CONICET, FONCyT, ANTORCHAS, SECyT-UNC, and MinCyT-Córdoba is greatly acknowledged. The authors thank M. Ringler for making available the GMM-FIELD code.

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