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Chiromagnetoptics of Au and Ag Nanoparticulate Systems

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Abstract: Photoelectron excitations into unoccupied energy states are fundamental in solid-state physics and many modern applications. The operation of such internal electronic transitions relies not only on photon absorption efficiency, which is pivotal in sensing, photovoltaics, active plasmonics, etc., but also on light–matter interactions and near/far-field spectroscopic techniques. Here, we report on a spectroscopic absorption fingerprint in magnetic circular dichroism (MCD) responses of various nanoparticulate systems. MCD spectra acquired at low temperatures on assemblies of uncoupled/coupled Ag and Au nanoparticles reveal asymmetric MCD spectral line shapes strongly depending on the nature and shape of nanoparticles and on their interparticle interactions. Assembling for instance the NPs into 2D networks with interparticle distances allowing dipolar interactions or transforming the spherical nanoparticles into disks was found to significantly alter the magneto-optic response in the spectral line shape. The findings are interpreted within the framework of chiral magneto-plasmonic effects by considering the k -dependent electronic states involved in both inter- and intraband electronic transitions.

1. Introduction

Plasmonic nanostructures have attracted great interest in the last 15 years due to their increasing potential for exceeding the diffraction limit in optics (1) and opening important perspectives in photonic applications. (2–5) At the heart of this research field is the ability of metallic nanostructures to temporarily store, confine, and release electromagnetic radiation. (6,7) In this context, one sought after effect is the possibility of externally controlling this process. (8–10) To realize such functionalities, the application of an external magnetic field appears as a promising approach, (11–14) leading to magneto-optical (MO) effects. (11,15,16) As a consequence, the recent advances in the research of plasmonic nanostructures continue to heighten magneto-optics, which has already been a blossoming field with respect to ferromagnetic (17–19) or semiconductor materials (20–23) for example. MO activity in non-ferromagnetic metals is nevertheless small, but the excitation of localized surface plasmon (LSP) dipoles can considerably enhance the magneto-optical coupling. (24,25) This enhancement is the result of the Lorentz force, which exercises a torque on the plasmon dipoles inducing a far larger MO activity in metal nanostructures presenting LSP resonances than in their bulk or thin-film counterparts. (25,26) MO activity associated with LSP resonances has also been found

leading to linear and nonlinear responses at relatively low light intensities. (27,28) Upon increasing the excitation densities, nonlinear effects become more important and a circularly polarized laser light at the localized surface plasmon (LSP) resonance may induce a current density proportional to the incident intensity of electric field and a net magnetic moment via the inverse Faraday effect. (29,30)

The Lorentz force is known to exert on moving charges exposed to magnetic fields. It is at the origin of many fundamental observations such as Hall and Zeeman effects but is also a key component for the development of advanced instrumentation such as cyclotron facilities or electron microscopy. For a charge moving at a fixed speed v , the Lorentz force reads as $\mathbf{F} = q(\mathbf{v} \times \mathbf{B})$. In the case of plasmonic excitations, the related oscillating dipole moment $\mathbf{p}(t)$ gives (25) $\mathbf{F} = d\mathbf{p}/dt \times \mathbf{B}$, and the associated energy may lift the degeneracy of electronic levels near the Fermi level (31) in a rather different way as in atomic systems. The difference resides in the fact that, in metals, the involved conduction levels form a continuous and k -dispersive sp-band, and the lift of the degeneracy is weak, barely observable by optical spectroscopy due to strong electron–electron correlations. When LSP excitations, induced by the oscillating electric field of the light, are associated with a large material polarisability, they can however significantly increase the unoccupied sp level splitting, facilitating the observation of a term-A signal in MCD spectroscopy, which is by nature rather independent of temperature. (32)

When circular left- and right-handed light propagates in nanoparticulate plasmonic materials exposed to an external magnetic field, the electron excitations may be different on the spin-split levels because of quantum selection rules. This has been experimentally revealed through a specific MCD signature showing an asymmetric peak derivative-like spectrum. (32,33) Furthermore, if a magnetic field splits the degenerate electronic levels of a nanoparticle by a quantity proportional to the field strength, the resulting magneto-plasmonic effect is maximal when the magnetic field is applied along the light propagation vector because the Lorentz force is perpendicular to the field. (34) In this picture, the importance of the nanometric size of the particles enters into play when considering the LSP modes. (35) Thus, the strong correlations between the electrons below the Fermi level are broken by the surface plasmon oscillations, as electrons are excited to the unoccupied states. This allows enough splitting of excited energy levels to induce an enhanced MCD signal with some asymmetry.

Electronic correlation effects were studied by Pineider et al. by analyzing in detail the asymmetry of the MCD spectra acquired on Au NPs. (33) There, it was quantitatively shown that interband transitions—being not part of plasma oscillations—impact the MCD signal by inducing a difference in left- and right-handed light absorption. As a result, the MCD signal appeared as an asymmetric double-peak feature of the opposite sign. From a fundamental point of view, when such a spectral fingerprint depends on the onset of interband transitions, it might represent a unique spectral feature for characterizing many other nanometer-sized materials, which is thus very valuable for gaining information on their electronic properties. This is also because such spectra appear to depend on the size (36) and shape (37) of the NPs or their mutual interactions when they are coupled. (38,39) These studies also demonstrate that MCD spectral line shape can reveal, at room temperature and low fields, the interplay between inter- and intraband transitions, which is central for spectra analyses. Another interesting study (40) has shown that magneto-optical effects can also be enhanced in natively magnetic Ni nanoparticles, particularly when they are organized into arrays or superlattices. All these examples suggest that magneto-optical activity might indeed be tailored to a good extent by a careful choice of the material nature, its internal structure, and/or organization. However, a study about the exact role played by the k -dependent electronic band distributions in the reciprocal space is still lacking, in particular when associated with spectra shifts, obstructing the access to additional information about the shape and orientation of nanoparticles.

Here, we present an MCD study performed at 3 K and under magnetic fields of up to 8 T on both Au and Ag nanoparticles differing in sizes, shapes, and organization. The motivation of using Ag NPs is triggered by the fact that their interband transitions are far less intense at the LSP frequency than those of Au NPs. We also show that the aforementioned asymmetry of the MCD signal increases linearly with the applied field of up to 8 T and that it can be systematically tailored by altering the shape of the nanoparticles, as well as by assembling them in networks with controlled interparticle interactions. Besides the fundamental point of view, these findings can be of particular significance for the exploration of the orientation of NPs in networks and for sensing and metrology in general.

Experiments have been performed in high magnetic fields of up to 8 T with a home-build MCD setup, which includes an Oxford cryostat equipped with a superconducting magnet and optical accesses. This allows us to measure the evolution of the signal from low to high fields. All experiments presented here were carried out at 3 K. MCD spectra have been obtained by measuring the MCD signal with the field parallel and antiparallel to the light propagation direction. The first set of experiments has been realized on spherical Au ($d_{\text{Au}} = 8.7 \pm 0.5$ nm) and Ag ($d_{\text{Ag}} = 7.5 \pm 0.5$ nm) NPs, which were dispersed in polyvinyl alcohol (PVA) polymer matrix, so that interparticle interactions can be neglected. The evolution of the MCD signal with the shape of the NPs has been obtained from experiments performed on Ag disks of 20–50 nm in diameter realized by anisotropic chemical etching of Ag NPs. The nanodisks were dispersed in a solution of PVA polymer and therefore were randomly oriented with respect to the substrate after drying of the film. The impact of interparticle interactions into the MCD signal was evidenced by performing experiments on few monolayers of Au NPs, where the distance between NPs was controlled by capping ligands, that is, oleylamine for Au and dodecanthiol for Ag.

2. Results and Discussion

The role played by interband transitions and plasmonic intraband excitations in standard absorption spectroscopy is schematically shown in [Figure 1](#). For fcc-crystallized noble metals, the first Brillouin zone ([Figure 1a](#)) contains an electronic band structure, which is known for bulk crystals, [\(41–43\)](#) especially close to Fermi energy (see [Figure 1c,d](#) for Au). Although these electronic states may slightly change in the case of nanoparticles, [\(44\)](#) they nevertheless represent a good starting point for understanding the electronic transitions upon light absorption. The particularity of Au and Ag metals is the partially occupied dispersive bands (6sp bands for Au and 5sp bands for Ag) supporting free-like electrons, and the localized d-bands (5d and 4d bands for Au and mostly 4d band for Ag), which are fully occupied, falling a few eV below the Fermi level. This electronic structure confers to these metals an interesting interplay between intraband and interband transitions, as the electrons from below the Fermi level can absorb visible light either by remaining within the dispersive band (intraband transitions) or by translating from occupied d-states to the first unoccupied states of the dispersive band (interband transitions), as schematically shown in [Figure 1c,d](#). We stress here that both types of transitions occur along specific high-symmetry crystal directions, thus being very appealing for acquiring information about the shape of nanoparticles or for the development of characterization tools sensitive to NPs in networks, as discussed below.

The effect of inter- and intraband excitations on the absorption spectra of Au is schematized in [Figure 1b](#), with the overall response (black line) depicted as a sum of LSP resonance (intraband collective excitations) and interband transitions. It is worth noting that in the visible spectral range, interband transitions are expected to first occur along the X– Γ direction, at a location labeled Δ_x , where one dispersive sp-band intersects the Fermi level. For Au, this location falls around 1.7 eV (730 nm) where the absorption spectra start showing the first signs of an increase in signal, as illustrated by the red

line in [Figure 1b](#). Increasing the photon energy, electrons from the d-bands can then be excited upper in the unoccupied sp-band (not shown), increasing even more the absorption, also because of the flatness of the band at the X-point. Above ~ 2.4 eV (516 nm), another interband transition Δ_L starts playing a role in the absorption spectra of Au, being localized in the L–W direction. These two effects explain the progressive but significant increase of absorption when approaching the UV spectral range (red line in [Figure 1b](#)) for bulk Au.

Figure 1. Band structure and electronic excitations upon absorption of light. (a) First Brillouin zone of fcc-Au showing the high-symmetry crystal directions. (b) Schematic of absorption spectra resulting from plasmon (intraband) resonance and interband contributions. (c, d) Band structure near X and L points revealing Δ_X and Δ_L thresholds for interband transitions falling in the visible range.

For bulk Ag, the shape of the electronic band structure is very similar to that of Au. The difference resides in the fact that the absorption due to interband transitions raises at higher energies, typically above 4.0 eV (~ 310 nm). In other words, the two interband transition thresholds (Δ_X and Δ_L) in Ag are roughly at energies 2.0 eV higher, that is, the d- and sp-bands near X and L points are more separated in energy. This is now a well-known band structure property of bulk Au and Ag discussed in several experimental [\[45–48\]](#) and theoretical works. [\[49–53\]](#)

In the case of NPs made from these metals, visible light can also be absorbed by LSP excitations arising from collective oscillations [\[54,55\]](#) of the electrons within the sp conduction bands (intraband excitations). [\[56–58\]](#) Also note that the difference in the LSP resonance modes for spherical Au and Ag NPs is only about 0.62 eV (Au: ~ 2.33 eV and Ag: ~ 2.95 eV). Altogether, these electronic phenomena discussed here in the context of standard absorption spectroscopy in the visible range constitute the essential background to interpret the MCD spectra described hereafter.

2.1. Noninteracting Au and Ag NPs

In [Figure 2](#), we show the MCD spectra for Au and Ag NPs acquired at 3 K for increasing values of the magnetic field. As expected, it is seen in both cases that the spectra display a positive and a negative

peak, with a crossing at around 530 nm for Au and at 420 nm for Ag. These values given here by the positions where the signal crosses zero correspond well to the known energies of the LPS resonances of Au and Ag NPs.

As seen, besides the spectral positions, another difference between Au and Ag spectra is the asymmetry between the amplitudes of the two peaks, which is critically larger for Au than for Ag. The low-wavelength (positive) peak is however smaller in both cases, which is therefore a common characteristic of Au and Ag. As first suggested in ref (32) for Au NPs, this double-peak shape in MCD spectra arises from the Zeeman splitting of the dispersive sp-bands by the external magnetic field, as sketched in the inset of Figure 2.a Left and right circularly polarized light are thus differently absorbed on the two spin-split levels because of selection rules. Equal amplitudes of the double-peak resonance would be expected if only sp-bands splitting is considered. The asymmetry of the peak amplitudes is consequently an additional effect, which cannot be explained through the quantum selection rules alone.

Figure 2. MCD characterization of noninteracting Au and Ag spherical NPs. (a, d) Magnetic field dependence of MCD spectra at 3 K for Au and Ag, respectively. Intensities of positive and negative peaks plotted as a function of the magnetic field for (b) Au and (e) Ag. Signal ratio obtained by dividing the intensity of the negative peak by the intensity of the positive peak for Au (c) and Ag (f).

The variation of the amplitudes of the peaks with the magnetic field is shown in Figure 2b,d along with the resulting asymmetry (Figure 2c,f) defined as the amplitude ratio of negative and positive peaks. It

is seen that both Au and Ag show a linear increase in the amplitude of the peaks with the magnetic field.

The asymmetry increases almost linearly with the field for Au (Figure 2c), remaining on the contrary rather constant around 1.1 for Ag (Figure 2f). Following Pineider et al., (33) this suggests that interband transitions impact to a larger extent the MCD spectra for Au than for Ag NPs. In fact, our comparative study on Au and Ag NPs can be seen here as a direct experimental demonstration of the model introduced by Pineider et al. (33) The inter- and intraband electronic transitions are known to impact on the dielectric tensor of metallic nanoparticles subjected to a magnetic field, (59) as considered in Section 2.3 for the modeling of the magneto-optical response.

2.2. Two-Dimensional Networks of Au NPs

In Figure 3, we show the MCD spectra for Au NPs organized in a hexagonal network. The interaction between the NPs was tailored by the capping organic ligands, whose length ensures a plasmonic coupling between first-order neighbors. Such interparticle interactions are known to slightly shift the energy of the LSP mode toward lower energies (red shift). (60,61) As the interband transitions are based on the internal crystal structure, they should not be affected much; one can therefore expect a reduction in the measured asymmetry as compared with isolated NPs (Figure 2). This is because the LSP mode falls at larger wavelengths, away from the energies where interband excitations occur.

Figure 3. MCD characterization of interacting Au NPs. (a) Magnetic field dependence of MCD spectra at 3 K for Au NPs assembled in a hexagonal lattice. Inset is an electron microscopy image. (b) Intensities of positive and negative peaks as a function of the magnetic field for the red-shifted LSP mode (580 m). (c) Signal ratio obtained by dividing the intensity of the negative peak by the intensity of the positive peak, revealing a reduced asymmetry, as compared to noninteracting Au NPs (see Figure 1a,c,d), effect induced by the interparticle coupling.

The data on interacting NPs from Figure 3 is therefore in a full agreement with the description made above for isolated NPs, again indicating that the asymmetry of the MCD spectra is based on the interplay between interband and intraband transitions.

2.3. Modeling the Magneto-Optical Response

To provide a theoretical description of the experimental observations presented above, we use the effective medium approximations (EMA) to obtain the reflectivity (and absorption) of the NPs assembly and the Voigt theory to account for the magneto-optic response. We first use the Maxwell–

Garnett (MG) model (62,63) $\frac{\tilde{\epsilon}_{eff} - \tilde{\epsilon}_M}{\tilde{\epsilon}_{eff} + (n-1)\tilde{\epsilon}_M} = f \frac{\tilde{\epsilon} - \tilde{\epsilon}_M}{\tilde{\epsilon} + (n-1)\tilde{\epsilon}_M}$, to take into account the short-range local field

effects, and second the Bruggeman model [\(64,65\)](#) $f \frac{\tilde{\epsilon}_A - \tilde{\epsilon}_{Br}}{\tilde{\epsilon}_A + (n-1)\tilde{\epsilon}_{Br}} + (1-f) \frac{\tilde{\epsilon}_B - \tilde{\epsilon}_{Br}}{\tilde{\epsilon}_B + (n-1)\tilde{\epsilon}_{Br}} = 0$, for the long-range dipolar interaction. For the MG model, $\tilde{\epsilon}_{eff}$ is the effective dielectric constant, $\tilde{\epsilon}_M$ is the dielectric constant of the matrix (MG model), and $\tilde{\epsilon}$ is the dielectric constant of the metal. For the Bruggeman model, $\tilde{\epsilon}_A$ and $\tilde{\epsilon}_B$ are the dielectric functions of the matrix and metal and $\tilde{\epsilon}_{Br}$ is the effective dielectric constant of the medium. In both the models, f is the volume fraction of the metal.

Figure 4. Calculated absorption (a, c, e) and MCD (b, d, f) responses of noninteracting (a–d) and interacting (e, f) NPs. Calculations were performed using the MG and Bruggeman models, as well as the Voigt formalism.

The bulk metal (Au) dielectric function is considered as consisting of two parts. The first one is related

to the intraband transitions described by the Drude model $\tilde{\epsilon}_f(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}$, where ω_p is the plasmon frequency, γ is the free-electron damping, and $\hbar\omega$ is the photon energy. The second contribution in the dielectric function is based on the interband excitations (Lindhard RPA theory)

$\tilde{\epsilon}_B(\omega) = 2K \int_{E_f}^{\infty} dE \frac{\sqrt{E - E_f}}{E} [1 - F(E, T)] \frac{1}{(\hbar\omega)^2 - E^2 - (\hbar\alpha)^2 - 2i\hbar\omega\hbar\alpha}$, where, E , F , $\hbar\alpha$, $k_B T$, E_f , and E_g are the interband energy, Fermi distribution function, damping constant, thermal energy, Fermi energy, and band gap energy, respectively. K is a constant parameter, which depends on the transition dipole moment and electron effective mass. These formulations are known to approximate well the effective response

(and hence the optical absorption signal) of composite media comprising noninteracting metal NPs. [\(66,67\)](#)

Finally, the Voigt model [\(68\)](#) was used for the calculation of the nondiagonal components of the dielectric tensor $\tilde{\epsilon}$ from which the time-dependent magnetic signal can be obtained $\tilde{\epsilon}_{xx} \approx \tilde{\epsilon}_{yy} \approx \tilde{\epsilon}_{zz} \approx \tilde{\epsilon}(\omega)$, $\epsilon_{xy} \approx \frac{\omega_p^2 \omega_i}{\omega(\omega + i\gamma)^2 - \omega_c^2}$, leading to an estimation of the MCD signal.

The calculated absorption and magnetic signals for noninteracting Au and Ag NPs are shown in [Figure 4a–d](#) and are in good agreement with the experimental results. Both the peak positions and the asymmetry are obtained using typical parameters for Au and Ag. These analytical models therefore represent an essential base for the emergence of simple fitting models, which could be used systematically for extracting parameters featuring the behavior of the isolated or coupled NPs.

2.4. The Role of the Shape: Ag Nanodisks

Given what has been said above for spherical noninteracting NPs, let us now imagine how changes in the plasmonic modes arising from shape modifications affect the interband transitions, since the collective resonances will fall at different energies. In contrast, the intraband transitions, strictly related to the band structures, are in turn expected to stay rather unaffected by the shape of the crystals. To gain additional insights into these electronic excitation phenomena, we performed MCD experiments on Ag nanodisks obtained by the chemical anisotropic etching of spherical Ag NPs. This shape modification is indeed expected to impact the LSP modes, [\(69,70\)](#) while the electronic band structure is not likely to change significantly.

The MCD spectra of the noninteracting Ag nanodisks are shown in [Figure 5](#). As expected, the “disk” shape brings an additional spectral feature in the visible range, at about 620 nm. This feature is assigned to the longitudinal LSP plasmonic mode falling now at lower energy than the transversal LSP mode, which remains at 420 nm, as for spherical NPs. The broadness of the MCD spectra feature at 620 nm is probably induced by the large lateral size distribution of the nanodisks, which as seen in the inset of [Figure 5a](#) is relatively large in our samples. This agrees with extinction spectra (not shown) which revealed a broad line shape at the respective energy (FWHM ~ 150 nm). Interestingly, the asymmetry of the MCD spectral feature at 420 nm displays now a significant enhancement as compared to spherical Ag NPs, increasing up to a ratio of 20. While several factors can participate in such a modification in the asymmetry, including absorption changes and/or multipolar plasmonic effects, we restrain our interpretation of k -dependent band structure effects, as introduced in [Figure 1](#).

Figure 5. MCD characterization of noninteracting Ag nanodisks. (a) Magnetic field dependence of MCD spectra at 3 K for Ag disks. Inset: electron microscopy image showing Ag nanodisks drop-cast on a microscope grid. (b, d) Intensities of positive and negative peaks as a function of the magnetic field for the transversal LSP mode (420

m) and for the longitudinal LSP mode (620 nm), respectively. Signal ratio obtained by dividing the intensity of the negative peak by the intensity of the positive peak for (c) transversal LSP mode and (e) longitudinal LSP mode.

2.5. *k*-Dependent Effects

The MCD signal of noninteracting Au and Ag spherical NPs increases linearly with the magnetic field up to 8 T, as a consequence of the dipolar origin of plasmon excitations and of band splitting. The magneto-plasmonic MCD peak asymmetry of Ag NPs is significantly smaller than that of Au NPs, demonstrating, as proposed by Pineider et al., (33) that the interband transitions are indeed responsible for the MCD asymmetric peak signals. In the light of these experimental findings and descriptions on noninteracting NPs, the spectra of nanodisks suggest that either the interband transitions are significantly enhanced or the intraband excitations in the *k*-dispersive sp-band are reduced. To interpret these experimental findings, we consider the anisotropic chemical etching of fcc nanoparticles, which in our case preferentially occurs along one of the less-compact crystal faces, that is, (100) crystal planes. (71,72) The band structure of Ag, which as stated above is qualitatively very similar to that of Au, has the *X*– Γ and *L*–*W* high-symmetry directions related to the (100) crystallographic planes (Figure 1a). When the chemical etching of Ag spheres produces nanodisks with two large (100) faces, the longitudinal LSP mode is oriented along (100), while the transversal LSP mode is oscillating perpendicularly. Looking at the first Brillouin zone (Figure 1a), it can be deduced that the sp-band that holds collective oscillations of electrons with a wavevector *k* perpendicular to the (100) plane is the one laying along the *X*– Γ direction. In contrast, electrons within the sp-band corresponding to the *L*–*W* direction are not expected to efficiently participate in this transversal LSP resonant mode. Again, it is worth noting that interband transitions are likely to remain unaffected by the shape of the NPs. The giant enhancement of asymmetry observed in Figure 5 therefore speaks in favor of weak intraband transitions in the dispersive sp-band along the *X*– Γ direction. In the case of nanodisks with preferentially (111) faces, the transverse LSP mode (420 nm) would correspond to intraband transitions along the *L*– Γ direction where, as observed in Figure 1d, no empty states are available. The low absorption due to the transverse LSP mode originates mainly from the weak component in the *X*– Γ direction. This results in a low MCD signal amplitude and a high asymmetry, as observed in Figure 5a. Whether this finding holds true for spherical NPs as well remains an interesting question, which might be of interest to be addressed in further work, by means of photoemission spectroscopy studies for example. It is also interesting to remark that the different effective masses of electrons in the two dispersive bands may play a role, since quasiparticle corrections are known to impact the photoelectron excitations. (47,73) Moreover, the fact that there is an abrupt change in the *k*-wavevector at the *X*-point in the unoccupied part of the Brillouin zone can also participate to inefficient intraband transitions in this region of the reciprocal space. It can nevertheless be stated that the shape-induced symmetry breaking that separates in energy the two LSP modes combined with MCD spectroscopy thus represents a very attractive technique to explore band structure effects in relation to photoelectron excitations. This is because the asymmetry of the MCD signal is linked to the balance between the inter- and intraband electron excitations. These findings indicate that MDC spectroscopy can be a very powerful tool for characterization of the shape of the NPs, as well as for the investigation of the *k*-dependent electronic states upon production of chemically synthesized NPs.

3. Conclusions

The MCD signal of noninteracting Au and Ag spherical NPs, featured by an asymmetric double-peak shape, has a linear dependence on the magnetic field. This particular line shape can be utilized as a

spectroscopic fingerprint informing about NPs nature or shape, as well as their mutual interactions when assembled in networks. Indeed, for a disk shape, the MCD spectra revealed that the plasmon resonance, typical for spherical NPs, falling at 420 nm is preserved, constituting the transversal LSP resonance mode. In turn, the MCD asymmetry presents a giant enhancement when compared with spherical Ag NPs. These results were interpreted by analyzing the electronic band structure of the fcc-crystalline lattice where both dispersive bands—supporting collective excitations of electrons—and localized bands—promoting interband transitions—are present close to the Fermi level. We have also shown that the organization of Au NPs in 2D hexagonal networks, which favor interparticle interactions, induces a red shift of the plasmon resonance frequency. As a consequence, the asymmetry of the MCD peaks is reduced, demonstrating that the interplay between intra- and interband transitions are responsible for the asymmetry. Overall, we propose here that the asymmetry of the MCD spectral features is a very powerful contrivance for studying structure–, shape–, or interaction–property relationships. Besides the fundamental point of view, these findings might be of great importance for deciphering electron-level contribution in light–matter interaction, analytical chemistry, sensing, or in the sturdily promising field of plasmon-based applications.

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Additional Note : Our MCD spectra as a function of temperature (3–300 K) indeed indicate that a C-term signal involving the splitting of the ground states is not important here.

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