

Low-field magnetic circular dichroism in silver and gold colloidal nanoparticles of different sizes, shapes, and aggregation states

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ABSTRACT

Considerable magneto-optical activity has been observed in aqueous solutions of colloidal noble metal nanoparticles (Au and Ag, 2–50 nm in diameter) in a magnetic field as low as 0.5 T parallel to the propagation of the incident light exciting localized surface plasmons in the nanoparticles. The magnetic circular dichroism (MCD) spectra show pronounced Zeeman splitting in the plasmon absorption bands. The observed magneto-optical effects is due to the enhancement of the magnetic Lorentz force for localized surface plasmons in resonantly excited strongly polarizable Ag and Au nanoparticles. The magnitude and the spectral position of the MCD signal depend on the contribution of scattering and absorption components in the extinction spectra of nanoparticles. Addition of pyridine into the colloidal solution of silver nanoparticles causes aggregation of nanoparticles and the appearance of a characteristic intense long-wavelength band in the extinction spectrum. The MCD spectrum also shows signals from short- and long-wavelength components. The possible method for MCD biosensing based on controlled aggregation of plasmonic nanoparticles in the presence of analyte followed by differential MCD detection in the long-wavelength region is discussed.

Keywords: Magnetic circular dichroism, metal plasmonic nanospheres, plasmonic nanorods, aggregates

1. INTRODUCTION

Nanoheterostructures with an enhanced magneto-optical (MO) activity are interesting from both fundamental and technological points of view as novel systems paving the way for active manipulation of plasmon propagation.^{1,2} Nanoparticles with MO properties open new prospects in light beaming, manufacturing plasmonic wave plates, magnetically controlled waveguiding, and biosensing.³⁻⁶ The ability of the surface plasmons to localize the electromagnetic field in very small volumes permit controlling the MO response in composite nanostructures made out of noble metals and ferromagnetics.⁷⁻¹² Multilayered ferromagnetic/noble metal structures have been found to exhibit Kerr rotation enhancement due to thin-film surface plasmon resonance of the noble metal.¹³⁻¹⁵ Recent experiments have shown that ferromagnetic films integrated with gold nanoparticles display enhanced Kerr rotation associated with localized surface plasmon resonance (LSPR) of the gold nanoparticles.^{8,12}

The MO activity of pure noble metal structures is very low, and measurable MO responses from these structures may be obtained only in strong magnetic fields.⁹ Recently, it was shown that nanostructures made of pure gold disks could have a considerable MO activity in low magnetic fields of about 1 T in the MO Kerr polar configuration, under the conditions when the magnetic field was parallel to the propagation of the incident light exciting the plasmon resonances in nanostructures.¹⁶ This effect was explained by a substantial enhancement of the magnetic Lorentz force induced by the collective movement of the conduction electrons when the LSPR of metal nanostructure was optically excited. The MO

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response of a plasmonic nanostructure or nanoparticle can be enhanced by creating coupled plasmon-ferromagnetic nanoheterostructures.^{17,18}

Solutions of functionalized noble metal nanoparticles (NMPs) may be used as sensors for the detection of various biomolecules, such as DNA, proteins, and low-molecular-weight compounds.¹⁹⁻²¹ The advantage of using nanoparticle solutions is the simplicity of their preparation using colloidal chemistry procedures and easy functionalization for biomedical and sensing applications.¹⁹ The detection techniques using solutions of NMPs are based on the possibility to change the optical properties of functionalized nanoparticles upon their interaction with biomolecules or between nanoparticles.²⁰⁻²³ The possibility to obtain an enhanced MO activity of NMPs in aqueous solutions may open the way to the development of a new generation of highly sensitive assays based on the detection of their MCD signals, which are the difference between the absorbance of the left- and right-hand circular polarized lights passing through a sample with a magnetic field applied to it (Figure 1). This differential setup is especially advantageous in studies on biological tissues, fluids, and cell suspensions with a strong light scattering, when the standard absorption spectroscopy suffers from a very large background. In the case of the differential MCD measurement, the changes in the MO responses from colloidal NMPs can be detected with little influence of the background light scattering (Figure 1). The magnitude and the spectral characteristics of the MCD response of NMPs directly correlate with the basic optical properties of NMPs (absorption, scattering, and extinction). On the other hand, absorption, scattering, and the total extinction spectra strongly depend on the size, shape, and aggregation state of NMPs in the colloidal solution or on the substrates. We have analyzed the correlations between the extinction and MCD spectra of Au and Ag spherical NMPs of different sizes, Au nanorods, and aggregates of spherical Ag NMPs produced by addition of two different types of reagents, the polyelectrolyte polyethylene imine (PEI) and pyridine. We demonstrate that the MCD signal may have a complex pattern, especially in aggregates and non-spherical particles with the multi-peak extinction spectra.

2. EXPERIMENTAL PART

Silver colloidal nanoparticles (AgNPs) with diameters of 2, 3, 30, 50, and 56 nm were synthesized according to the protocols adapted from the Refs. 24, 25. Briefly, silver nanoparticles with diameters of 30, 32, 50, and 56 nm were synthesized as follows: 13 mg of AgNO₃ was dissolved in 1 ml of water and injected into a boiling solution of 15 mg of ethylenediaminetetraacetic acid (EDTA) disodium salt and 15 ml of 0.2 M NaOH in 100 ml of water. After injection of AgNO₃, the solution was kept stirred at 95°C. The initially colorless solution turned brown, then yellow, and finally brown-red, which indicated the formation of colloidal Ag nanoparticles of different sizes. After different periods of reaction, aliquots containing Ag colloidal particles with mean sizes of 30, 32, 50, or 52 nm were sampled, characterized by means of DLS and SEM, and used in the studies. For optical experiments, colloidal solutions were used as is in order to avoid potential aggregation provoked by purification.

Small AgNPs with diameters of 2 or 3 nm were prepared by adding 0.75 mL of 10 mM AgNO₃ to 1.50 mL of tridistilled water. Then, the pH of the solution was adjusted to pH 10 with an ammonia solution. This solution was cooled to 0°C on an ice bath, and 0.75 mL of 10 mM NaBH₄ was added while intensely stirring. The reaction mixture was kept stirred at 0°C for 1–5 min to complete the reaction and to ensure homogeneity of the reaction throughout the reaction volume. The reaction mixture was kept at room temperature until the temperature equilibrated; then, it was used for the optical and magneto-optical measurements without additional purification.

Gold nanoparticles (AuNPs) 6 nm in diameter were purchased from Aurion Immuno Gold Reagents & Accessories (The Netherlands); AuNPs 10, 20, 30, and 40 nm in diameter were purchased from Nanocs Inc. (NY10001, USA). Colloidal AuNPs ca. 6 nm in diameter in aqueous solution were synthesized according to Ref. 26 and purified by ultracentrifugation.

AuNRs ca. 15 nm in diameter and 40–50 nm in length were synthesized in the form of aqueous colloidal solutions according to the protocol adapted from Ref. 27. Briefly, small Au seeds were synthesized first. To do this, we prepared 0.2 M hexadecyltrimethylammonium bromide and 0.001 M HAuCl₄ solutions in deionized water and cooled them on an ice bath to 0°C. Then, 0.6 ml of ice-cold 0.01 M NaBH₄ was added quickly while intensely stirring until the color of the mixture turned yellow. The reaction mixture was then stirred for additional 20 min on an ice bath to complete the reaction. Then, 10 ml of 0.2 M hexadecyltrimethylammonium bromide, 10 ml of 0.001 M HAuCl₄, 0.4 ml of 0.004 M AgNO₃, and 0.15 ml of 0.078 M ascorbic acid were mixed very quickly at room temperature, the mixture was heated to

30°C, and 0.025 ml of freshly prepared Au seeds was added to the mixture. The reaction mixture was strongly stirred at 30°C for ca. 30 min to complete the reaction. The mean diameter and the aspect ratios of Au NRs were controlled by varying the amount of AgNO₃ and Au seeds used in the reaction and monitored by SEM. For optical measurements, colloidal solutions of Au NRs were used without further purification and diluted ca. 10 times with deionized tridistilled water in order to achieve the optical density of the solution of about 1 optical density unit per centimeter of optical path length.

Aqueous colloidal solutions of AgNPs, AuNPs, and AuNRs were characterized at room temperature by optical absorption spectroscopy and MCD spectra recorded using a Jasco J-815 spectropolarimeter (Horiba Jobin Yvon SAS, France) equipped with a GMW 3470 electromagnet providing a static magnetic field of up to 0.7 T. The optical path for both absorption and MCD measurements was 5 mm, and the optical densities were about 1.0.

The sizes of nanoparticles were measured using Malvern Nano-Zetasizer and scanning electron microscopy. We used reference data for the optical extinction versus the size of the nanoparticles to express the MCD magnitude as the molar ellipticity normalized per tesla.²⁸⁻³⁰

3. RESULTS AND DISCUSSION

To experimentally probe eventual MO effects in noble metal colloidal nanocrystals at low magnetic fields, Ag and Au nanoparticles (AgNPs and AuNPs, respectively) of different diameters in the range from 2 to 60 nm were synthesized as described under “Experimental Part”. The MO responses from colloidal solutions of NMPs were detected using the Faraday geometry as shown in Figure 1.

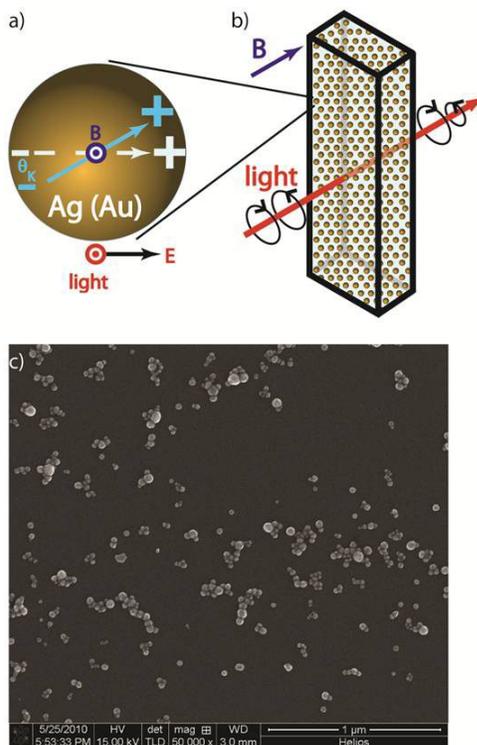


Figure 1. A schematic diagram of the experiment for measuring the magneto-optical activity in aqueous solutions of colloidal noble metal nanoparticles. (a) The magneto-optical effect induced in an optically excited metal nanocrystal in a static magnetic field. (b) The magnetic circular dichroism experimental setup for measuring the magneto-optical effects in aqueous solutions of colloidal nanoparticles. (c) A scanning electron microphotograph of 50-nm silver nanoparticles used in the study.

Figure 2 shows the optical extinctions and MCD spectra of AgNPs 2, 30 and 50 nm in diameter recorded at low magnetic fields (<1 T) under the experimental conditions where the direction of a static magnetic field was parallel to the direction of propagation of exciting light (Figure 1). The MCD bands appear at the same spectral positions as extinction peaks associated with the LSPR of AgNPs. The reference data on the optical extinction versus the size of the nanoparticles allow expressing the MCD value as the molar ellipticity normalized per tesla.²⁸⁻³⁰ The spectra show a pronounced Zeeman splitting accompanied by strong MO effects.

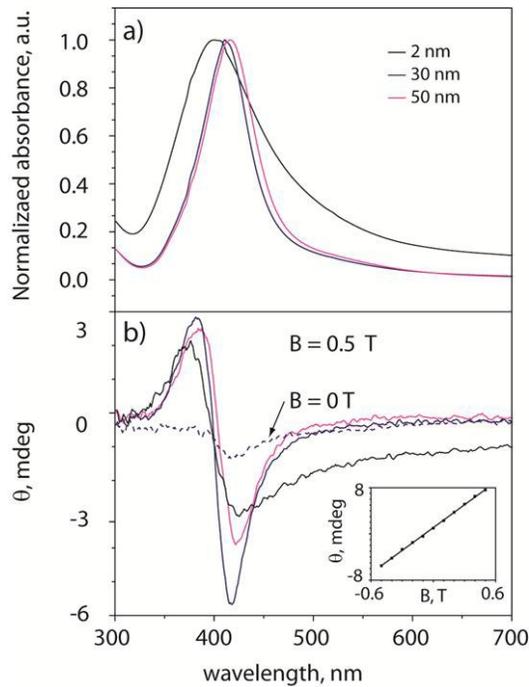


Figure 2. Optical and magneto-optical effects in colloidal silver nanoparticles (AgNPs) in aqueous solutions. (a) Extinction spectra. (b) Magnetic circular dichroism spectra at $B = 0.5$ T. The circular dichroism spectrum of 30-nm AgNPs at a zero field is shown as a dashed line. The inset in panel (b) shows the amplitudes of magneto-optical activities in a solution of 30-nm AgNPs as a function of the applied magnetic field.

The amplitudes of these effects linearly depend on the strength of the applied magnetic field, and the signs of MCD bands may be reversed by reversing the orientation of the applied magnetic field (the inset in Figure 2b). The extinction (Figure 2a) and MCD (Figure 2b) spectra exhibit similar red shifts with increasing size of AgNPs, thus demonstrating LSPR origin of both optical and MO effects. To verify that the observed derivative-like MCD spectral shapes were a magnetic field effect, the MCD spectrum of 30-nm AgNPs at $B = 0$ T was also (shown by a dotted line in Figure 2b). It is clear that in the absence of the external magnetic field AgNPs show only a very weak CD signal. Such a weak CD signal may be determined by intrinsic chirality of the metallic nanoparticles.³¹ The observation of $\Delta\epsilon_M \sim 0$ in the absence of the magnetic field confirms that there is no birefringence or other polarization effects in the aqueous solution of colloidal nanoparticles. The derivative-like MCD signals are therefore not due to the scattering effect as a result of an inhomogeneous refractive index in the colloidal medium. Moreover, the derivative-like shape of the MCD spectra for colloidal AgNPs in water has been shown to be asymmetrical; i.e., the negative portion of the MCD signal is larger than its positive portion. These observations indicate that the observed MO effect does not originate from a transition to a single degenerate excited state; instead, a strong intermixing of the excited spin-orbit states is suspected.³²

Figure 3 shows the optical extinction and MCD spectra of AuNPs 6, 10, 20, 30, and 40 nm in diameter recorded under the same conditions as those described above for AgNPs. AuNPs exhibit MO effects very similar to those for AgNPs in terms of experimental Zeeman splitting of their plasmon band, linear dependence of the MO effect on the magnitude of

the applied magnetic field, and the possibility of inversion of the sign of the MO effect by inverting the direction of the magnetic field (Figure 3b).

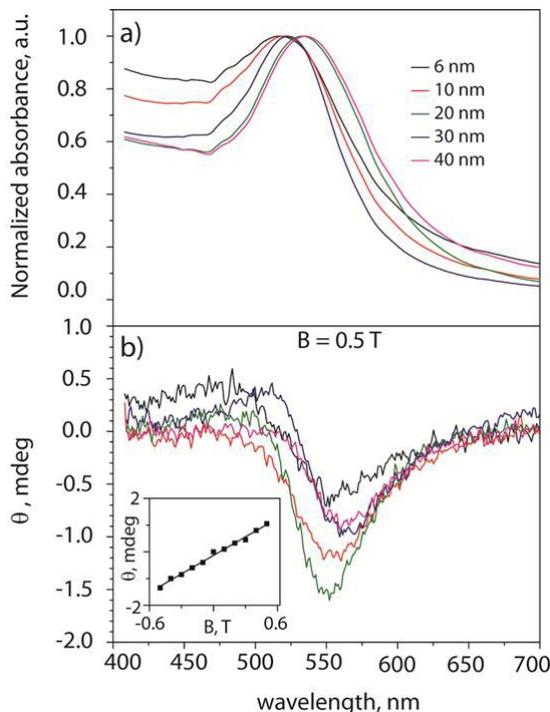


Figure 3. Optical and magneto-optical effects in aqueous solutions of colloidal gold nanoparticles (AuNPs). (a) Extinction spectra. (b) Magnetic circular dichroism spectra at $B = 0.5$ T. The inset in panel (b) shows the amplitudes of magneto-optical activities in a solution of 30-nm AuNPs as a function of the applied magnetic field.

Using the reference data on the molar extinction coefficient for Ag and Au spherical NMPs of different diameters, we normalized the magnitude of the MO signal to the molar concentration of NMPs and the magnetic field in each independent experiment (Figure 4). The MO effects have been found to be size-dependent, this dependence being correlated with for the dependence of the optical extinction coefficient on the NMP diameter for AgNPs (Figure 4a, dashed line) and AuNPs (Figure 4b, dashed line). The MO effect in AuNPs is weaker than in AgNPs due to the smaller extinction coefficient for AuNPs as compared to AgNPs of the same diameter.

For nanoparticles that are small compared to the wavelength of the exciting light, the dipole absorption (electric and magnetic moments) in the Mie equation mainly contributes to the extinction cross section of the surface plasmon transitions.³³ Moreover, the peak position of the surface plasmon resonance is a function of the real part of the dielectric constant of the metal particle and the dielectric constant of the surrounding medium. This provides the necessary conditions for the observation of a nonzero MCD spectrum.³² Analysis of the MCD spectrum supports the characterization of the excited electronic states where the transition from the ground state to the excited (degenerate or nondegenerate) state should have nonzero magnetic moment operator and electric moment operator and a strong mixing of the excited (spin and/or orbit) states involved if there is a magnetic field whose direction coincides with that of light propagation (Figure 1a).³²

We would like to emphasize that our results unambiguously disprove the explanation of the observed low-field MCD effects by the influence of some chiral molecules on the surface of our NMPs. Figures 4a and 4b clearly demonstrate strong linear dependences of MCD signals on the NMP molar extinction coefficients and sizes. The MCD signal grows with the diameter of NMPs within the studied size range. However, any surface effects should be most distinct in the smallest NMPs and become less visible with increasing NMP size. This is definitely not our case (Figure 4).

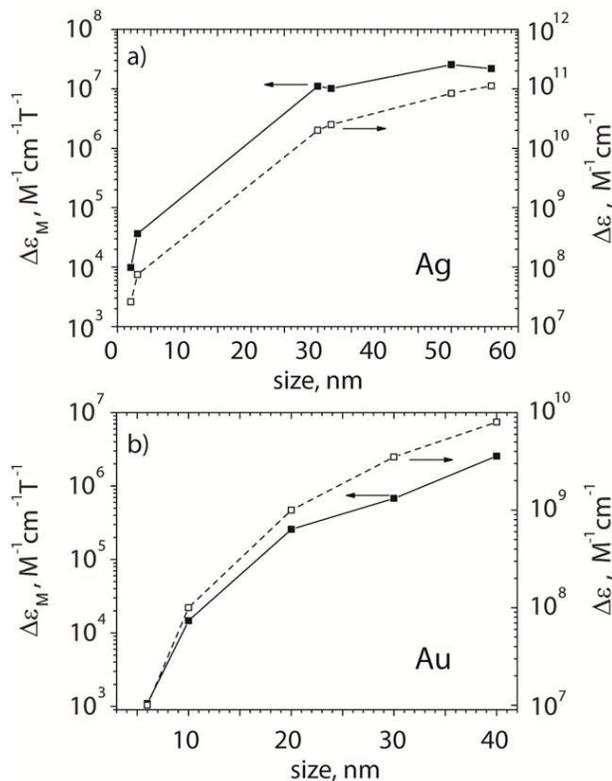


Figure 4. Dependences of the amplitudes of the MO activities of (a) AgNPs and (b) AuNPs normalized to the magnetic field and NMP molarities (solid lines, left Y axes) and dependences of the NMP molar extinction coefficients (dashed lines, right Y axes) on the size of the nanoparticles. The molar extinction coefficients for AgNPs and AuNPs were calculated according to Ref. 28 and Refs. 29 and 30, respectively.

In order to estimate the influence of the shape of colloidal NMPs on the corresponding MO responses, we synthesized two samples of Au nanorods (AuNRs), both ca. 15 nm in diameter and with lengths of 40 nm and 50 nm (see “Experimental Part” for more detail). Figure 5a shows the optical absorption and MCD spectra of colloidal solutions of AuNRs with different aspect ratios; Figures 5b and 5c show the SEM images of these AuNRs. Both types of AuNRs exhibit multi-peak absorption spectra, with high-energy peaks corresponding to the transversal plasmons and low-energy peaks corresponding to the longitudinal plasmons.²²

One can see from Figure 5a that the optical absorption spectrum of the dumbbell-like AuNPs 15×50 nm in size consists of two high-energy peaks at ca. 520 and 600 nm. The presence of two high-energy peaks may be explained by the dumbbell-like shape of these AuNRs (clearly seen in the SEM image in Figure 5c), where the 520-nm absorption band corresponds to the transversal plasmons located close to the thin centers of AuNRs and the 600-nm band corresponds to the transversal plasmons located closer to the AuNR tips, which have significantly larger diameters. The difference in the spectral positions of the low-energy bands between two AuNRs samples (710 and 790 nm) results from their different aspect ratios (ca. 2.6 and 3.3) and also may be affected by their difference in shape (Figures 5b and 5c). The MCD spectra of AuNRs (dotted lines in Figure 5a) show that the largest MO responses appear at the spectral positions of the maxima of the corresponding plasmonic bands, which, as in the case of spherical NMPs, unambiguously demonstrates correlation between the observed MO effects and plasmonic absorption.

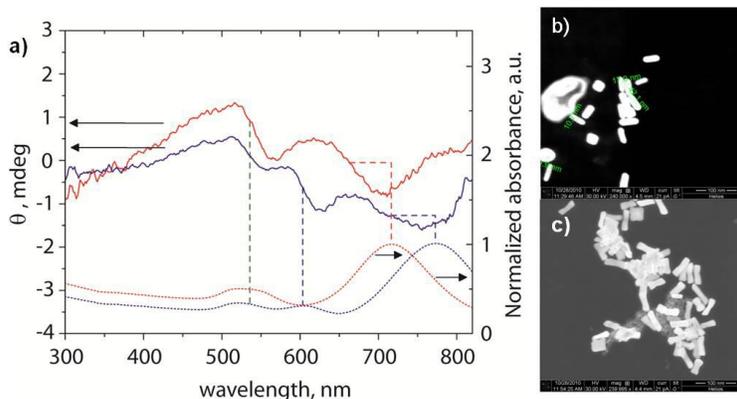


Figure 5. Extinction (solid lines) and magnetic circular dichroism (dotted lines) spectra of AuNRs 15×40 nm (red lines) and 15×50 nm (blue lines) in size. Panels (b) and (c) show the SEM images of (b) cylindrical AuNRs 15×40 nm in size and (c) dumbbell-like AuNRs 15×50 nm in size.

It should also be noted that in the solutions of AuNRs the less intense high-energy plasmonic bands and more intense low-energy plasmonic bands have almost the same magnitude of the corresponding MCD signals (Figure 5a). These data obtained for cylindrical and dumbbell-like AuNRs differ from the results presented in Figure 4 for spherical NMPs, where the normalized magnitude of MCD signals was proportional to their optical extinction coefficients. This difference is not surprising and may be explained by different contributions of the absorption and scattering components in the extinction spectra of NRs and spherical NMPs. For the spherical NMPs, which are much smaller than the wavelength of the incident light, absorption makes the main contribution to its extinction peak. This is also true for the short-wave extinction band of NRs, which corresponds to the excitation of transverse NR plasmons. Otherwise, the long-wave extinction band of the NRs corresponds to the excitation of the longitudinal NR plasmons and includes a much greater contribution of the light scattering component relative to the absorption component.³⁴

We further analyzed how aggregation of NMPs could influence the MO activity of their colloidal solutions. Nanoparticle aggregation is often used in sensing as an indicator of a positive binding event.²² Pyridine is a well-known agent causing the aggregation of Ag or Au colloidal nanoparticles in aqueous colloidal solutions. Pyridine-produced aggregates of Ag NMPs may serve as a useful model system for studying the MCD response. Figure 6 shows the extinction and MCD spectra of Ag NMPs in water before and after addition of pyridine.

Addition of pyridine into the colloidal solution of Ag NMPs results in the appearance of multi-peak structure in the extinction spectrum. This effect is well-known, and the additional long-wavelength peak corresponds to the excitation of collective plasmons in the aggregates of Ag NMPs.³⁵ In the corresponding MCD spectrum, one can see a noticeable decrease in the MCD signal at the fundamental plasmonic band of Ag NMPs around 400 nm and the appearance of a new signal in the spectral region of the long-wavelength excitonic band. The intensity of the long-wavelength MCD signal is much smaller than that of fundamental plasmonic transition, but it is still well-detectable with standard MCD equipment. We may propose an optical differential detection method based on this effect. The aggregation of silver or gold nanoparticles in aqueous colloidal solutions can be promoted by the presence of different analytes in the solution (inorganic ions, DNA, proteins, and small organic molecules, such as pyridine). The direct optical detection of the aggregation event requires clear solutions and relatively high concentration of plasmonic nanoparticles. In muddy solutions (culture suspensions etc.) the reliable detection of new long-wavelength plasmonic bands is not very efficient. In contrast, the differential method of MCD signal recording is independent of the background scattering and absorption and makes it possible to estimate a pure plasmonic response.

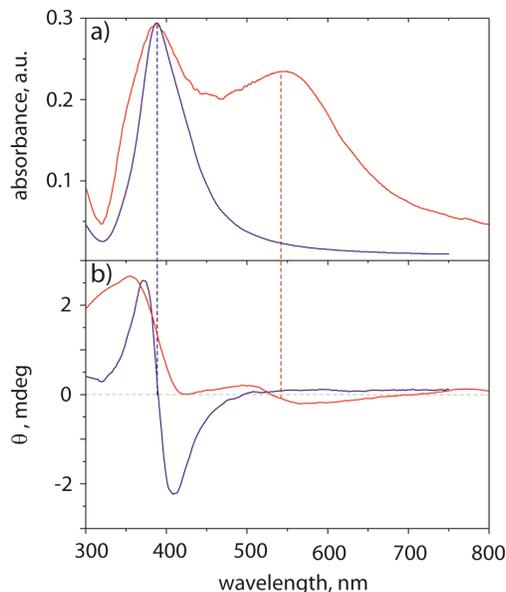


Figure 6. Optical (a) and magneto-optical (b) effects in solutions of colloidal silver nanoparticles 30 nm in diameter (blue lines) and the same nanoparticles aggregated with the pyridine (red lines). The extinction and MCD spectra of NMPs and NMP–pyridine aggregates are normalized to the intensity of extinction and MCD bands of free NMPs at 390 nm, respectively. The MCD spectra were recorded at $B = 0.5$ T using the setup shown in Figure 1.

4. CONCLUSIONS

Despite the spectacular progress in the development of solid-state plasmonic sensors, one should take into account that biological molecules are in the aqueous phase, and it is desirable to have a sensitive and specific detection system that is homogenous with the phase of the target molecule. Diagnosis in biological fluids, tissues, and cells require detection methods insensitive to aggregation. Here, we have demonstrated that a significant MO activity may be observed at room temperature in aqueous solutions of dot-like and rod-like NMPs at magnetic fields as low as 0.5 T. The MCD signal is strictly associated with plasmonic bands in NMPs of different shapes and sizes and in their aggregates. The magnitude of the MCD signal is roughly proportional to the molar absorption coefficient of Au and Ag dots. Pyridine-assisted controlled aggregation of Ag MPs resulted in a double-band MCD signal, which is proposed to be used for differential optical detection of various analytes in muddy aqueous solutions.

ACKNOWLEDGMENTS

This study was supported by the Ministry of Higher Education and Science of the Russian Federation (grant nos. 11.G34.31.0050 and 11.519.11.2005) and in part by the European Commission through the FP7 Cooperation Program (grant no. NMP-2009-4.0-3-246479 NAMDIATREAM) and the CHEMREAGENTS program (Belarus).

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