

## Spectrophotometric Observations of the Adsorption of Organosulfur Compounds on Colloidal Silver Nanoparticles

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A silver colloid (mean particle size 6 nm) is prepared via photochemical reduction of  $\text{Ag}^+$  ions. After total silver ion reduction, the colloid exhibits an extraordinarily intense surface plasmon absorption band. The absorption band is strongly damped by small concentrations of carbon disulfide, thiophenol, and diethyl disulfide. Carbon disulfide is irreversibly adsorbed, and so is diethyl disulfide. The irreversible adsorption is attributed to the high reactivity of the nanoparticles due to their low Fermi level potential. It is proposed that this in turn leads to dissociative adsorption of the disulfides onto the silver particles. Weaker damping is observed for thiophene, thiourea, and diethyl sulfide. The damping of the plasmon absorption band is attributed to the electronic distortion of a thin layer within the particle by the adsorbate–particle interaction.

### Introduction

Chemisorption of thiols on metallic nanoparticles has often been used during the past few years to modify the properties of nanomaterials. For example, colloidal gold particles that carry long-aliphatic-chain thiols form a crystal lattice, where the lattice constant is determined by the length of the chain.<sup>1</sup> Highly oriented silver-thiol particles have also been reported.<sup>2</sup> Gold particles that carry thiols can even be analyzed in a mass spectrometer.<sup>3</sup> The binding of gold particles to sulfur-containing sites on modified DNA<sup>4</sup> and in sulfur-group-containing silicon–organic glasses<sup>5</sup> are other aspects of the interaction of metal particles with thiols. The nature of the interaction is not known in all cases: binding could occur by the formation of a truly covalent bond between the thiol sulfur and the surface (homolysis of the S–H bond), or chemisorption by donation of electron density from the thiolate group into the metal particle (heterolysis).

In the present paper, the interaction of silver particles with various organosulfur compounds is investigated to obtain information about nanoparticle–adsorbate interactions. Silver was chosen, as the adsorption of compounds on this metal can readily be detected spectrophotometrically. Nanoparticles of silver have an intense surface plasmon absorption band close to 380 nm in water, the shape of which changes upon the adsorption of substances.<sup>6,7,8</sup> For example, adsorbed thiophenol strongly dampens this band.<sup>6c</sup> It is shown here that carbon disulfide and diethyl disulfide affect the plasmon band of silver particles to a comparable extent and that thiophene, thiourea, and diethyl sulfide are less effective.

### Experimental Section

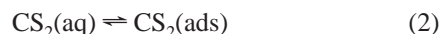
The colloid was made and substances added to it under strict exclusion of air as reported previously.<sup>8</sup> Fifty milliliters of an aqueous solution containing  $2.0 \times 10^{-4}$  M  $\text{AgClO}_4$ , 1 M 2-propanol, 0.02 M acetone, and  $6.0 \times 10^{-4}$  M polyethyleneimine (from Janssen) were exposed in a 140 mL quartz vessel

to the UV light of a 150 W xenon lamp at a distance of 50 cm. The vessel carried a sidearm with 0.5 cm optical cuvette; the spectrum of the solution could thus be recorded without exposing the solution to air. The vessel also carried a septum; substances could be injected using a syringe. The vessel was flushed with argon for 15 min and then closed prior to illumination. The solution acquires a yellow color after a few seconds of illumination, as the plasmon band of silver develops. The band becomes more intense with time and is rather narrow toward the end of a 25 min period of illumination, i.e., when the last traces of  $\text{Ag}^+$  ions have been reduced. The colloidal solution contains particles of about 6 nm mean diameter.<sup>8</sup>

The organosulfur compounds were added to the colloidal solution in 5–200  $\mu\text{L}$  amounts of a  $10^{-2}$  M solution in 2-propanol. Special attention had to be paid to  $\text{CS}_2$ , which is very volatile (bp 46.2 °C). At the micromolar quantities injected,  $\text{CS}_2$  distributes between the gaseous and the aqueous phase in the vessel according to Henry's law. The concentration in the solution was determined by recording the intensity of the 206.6 nm absorption band of  $\text{CS}_2$ ; the specific absorption at this wavelength was found to be  $7.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ . The equilibrium



was also investigated under the volume ratio described above. It was found that the amount of  $\text{CS}_2$  in the gas phase was 1.77 times higher than in the liquid phase. Thus, the total concentration of  $\text{CS}_2$  in the two phases,  $[\text{CS}_2(\text{tot})]$ , is 2.77 times the  $\text{CS}_2$  concentration in the liquid. When  $\text{CS}_2$  is reversibly adsorbed on the colloidal particles, a second equilibrium



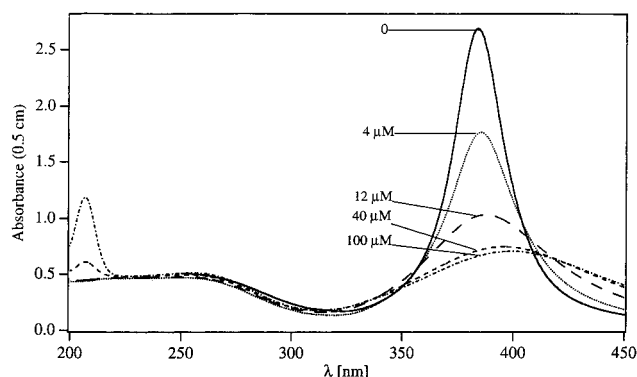
is established. From eqs 1 and 2 one derives

$$[\text{CS}_2(\text{ads})] = [\text{CS}_2(\text{tot})] - 2.77 [\text{CS}_2(\text{aq})] \quad (3)$$

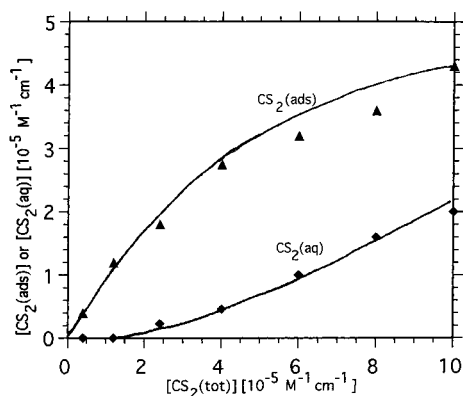
where  $[\text{CS}_2(\text{tot})]$  is now the total concentration in all three

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**Figure 1.** Absorption spectrum of the silver colloid before and after the addition of various concentrations of  $\text{CS}_2$ .



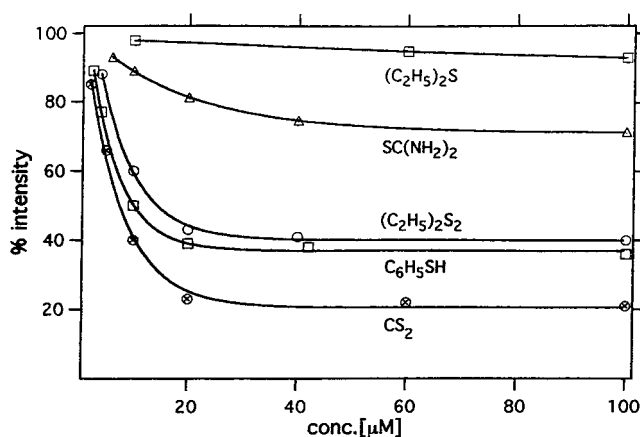
**Figure 2.** Concentrations of aqueous and adsorbed  $\text{CS}_2$  as functions of the total concentration of added carbon disulfide.

phases. As is discussed below, complications arise when the adsorption is irreversible.

## Results

Figure 1 shows the absorption spectrum of the silver colloid before and after the addition of various concentrations of carbon disulfide. The spectrum 0 of the silver particles contains a narrow plasmon band close to 380 nm and a broad band below 300 nm, which is caused by  $4d \rightarrow 5s, p$  interband transitions. It can be seen that the plasmon band is strongly damped at small concentrations of  $\text{CS}_2$  and that the band slightly shifts toward longer wavelengths, whereas the UV band is practically unaffected. Above 40  $\mu\text{M}$  of  $\text{CS}_2$ , the plasmon absorption band undergoes almost no more changes. The 206.6 nm band of  $\text{CS}_2$  is not present at low concentrations (below 12  $\mu\text{M}$ ). This indicates that the optical transition responsible for this band is affected upon the adsorption of carbon disulfide and that practically all the added  $\text{CS}_2$  is adsorbed at the very low concentrations. However, the 206.6 nm band appears at higher  $\text{CS}_2$  concentrations, although not as strong as in the absence of silver particles. Solutions containing up to 40  $\mu\text{M}$  of  $\text{CS}_2$  were stable for many days. At the higher concentrations, the solutions became slightly opalescent upon aging.

First, knowing  $[\text{CS}_2(\text{tot})]$ , and measuring  $[\text{CS}_2(\text{aq})]$  from the absorbance at 206.6 nm, the concentration of adsorbed  $\text{CS}_2$  was calculated using eq 3. In Figure 2, the concentrations of  $\text{CS}_2$  in the aqueous phase and in the adsorbed state are plotted as functions of the total  $\text{CS}_2$  concentration. At very low concentrations (below 12  $\mu\text{M}$ ), practically all the  $\text{CS}_2$  is adsorbed; i.e., the equilibrium of eq 2 is shifted very strongly to the right side. At higher concentrations,  $[\text{CS}_2(\text{aq})]$  increases with an upward curvature, whereas  $[\text{CS}_2(\text{ads})]$  tends to reach a limiting value



**Figure 3.** Percent intensity of the plasmon absorption band as a function of the concentration of various sulfur-containing compounds.

of about 50  $\mu\text{M}$ . This is roughly the concentration expected for one adsorbed molecular monolayer. A simple geometric consideration shows that about 25% of the silver atoms are on the surface of the 6 nm particles, i.e., the concentration of surface atoms is about  $2.0 \times 10^{-4} \times 0.25 = 50 \mu\text{M}$ .

However, the adsorption of  $\text{CS}_2$  on the silver particles is irreversible, as has to be concluded from the following observation: When colloidal solutions containing  $[\text{CS}_2(\text{tot})] = 4$  or 24  $\mu\text{M}$  were vigorously bubbled with argon to remove the volatile carbon disulfide, the dampened plasmon band did not recover. The adsorption would be irreversible if  $\text{CS}_2$  underwent a chemical transformation on the surface of the silver particles, and the damping then would be due to an adsorbed product of this transformation. Thus,  $[\text{CS}_2(\text{ads})]$  in Figure 2 represents the concentration of chemically modified  $\text{CS}_2$ .

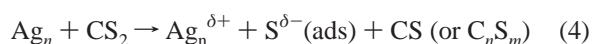
In the case of the other compounds, similar effects were observed, although to varying extent. This can be seen from Figure 3, where the relative intensity of the plasmon absorption band is plotted versus the concentration of various adsorbates in solution. The case of thiophenol has previously been discussed. The 260 nm charge-transfer-to-solvent band of this compound is absent when it is adsorbed on the silver particles. However, it reappears upon desorption under the influence of excess  $\text{SH}^-$ , which indicates that the adsorption is reversible.<sup>6c</sup> Other thiols (not shown in Figure 3), such as 3-mercaptopropionic acid,  $\text{HSCH}_2\text{CH}_2\text{COOH}$ , and mercaptoacetic acid,  $\text{HSCH}_2\text{COOH}$ , exert an effect comparable to thiophenol. The effects of the thiols, which have  $\text{pK}_a$  values around 10, were the same at pH = 7 and 10.5. Diethyl disulfide also strongly dampens the plasmon band; in this case, the damping is accompanied by a particularly strong red-shift of the band. Thiourea and diethyl sulfide are rather inefficient. Thiophene (not shown in Figure 3) is about as inefficient as diethyl sulfide.

## Discussion

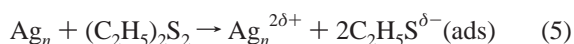
All sulfur-containing compounds investigated so far affect the intensity of the plasmon band of the silver particles. In the cases of  $\text{CS}_2$ ,  $\text{C}_6\text{H}_5\text{SH}$ , and  $(\text{C}_2\text{H}_5)_2\text{S}_2$ , the adsorption equilibrium lies strongly on the adsorption side at low concentrations, whereas it is shifted to the solution side for  $\text{SC}(\text{NH}_2)_2$ ,  $(\text{C}_2\text{H}_5)_2\text{S}$ , and  $\text{C}_4\text{H}_4\text{S}$ . In all cases, the interaction of the sulfur atom(s) in the adsorbate molecule is responsible for the interaction with the silver particles. One could argue that, in the case of thiourea, an interaction occurs via the amino groups of this molecule. However, amines in concentrations of less than 100  $\mu\text{M}$  practically do not affect the plasmon band. Both thiols and

dialkyl thioethers contain only one S atom. The much stronger adsorption of thiols is attributed to an interaction of the thiolate anion with the silver particles. As adsorption also occurs at pH values much lower than the  $pK_a$  of the thiol, it is concluded that the adsorption free energy of thiolate is substantially greater than the free energy of about 0.6 eV of the protolytic dissociation of the thiol. Thus, the heterolytic adsorption mentioned above is responsible for the interaction.

In the case of carbon disulfide, one encounters for the first time an irreversible adsorption. This observation suggests that the  $CS_2$  molecule may undergo a drastic change on the silver surface.  $CS_2$  is known to react with many metals at higher temperatures, with Raney-Ni even at room temperature.<sup>9</sup> In the absence of excess  $Ag^+$  ions, the Fermi level in the silver particles is positioned on a rather low potential, which favors particle-to-adsorbate charge-transfer interactions. In fact, the colloidal particles sometimes behave like a nonprecious metal. For example, carbon tetrachloride is decomposed via electron transfer.<sup>8</sup> Similarly, the reaction

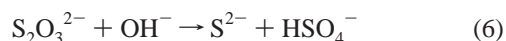


may occur. As discussed previously, reactions of this type are accompanied with a shift of the Fermi level to more positive potentials, until the reaction comes to a halt.<sup>8</sup> More detailed information about the nature of the adsorbed species upon the interaction of  $CS_2$  with silver might be obtained in a SERS experiment. The strong adsorption of diethyl disulfide is explained by the simultaneous binding of the two sulfur atoms to the silver surface. A chemical transformation may even take place, in which the S–S bond is broken

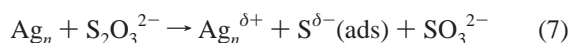


as it occurs in the adsorption of disulfide on nickel.<sup>10</sup>

The damping of the plasmon band by thiosulfate has been attributed to an ion exchange mechanism on the surface of the silver particles



the  $S^{2-}$  formed being adsorbed.<sup>7</sup> However, in analogy to the above organic cases, one may also think in terms of a redox mechanism



The examples reported here show once more the sensitivity of the optical plasmon excitation of silver particles to adsorbed substances. Although adsorbates of quite different kinds (such as  $I^-$ ,  $SH^-$ ,  $C_6H_5S^-$ ,<sup>6c</sup>  $PH_3$ ,<sup>6d</sup> and the presently studied organosulfur compounds) have been used, the effect always consists of the damping of the plasmon absorption band; no specific absorptions of adsorbate–particle complexes were ever seen. The only difference between the various adsorbates is the efficiency with which they bring about the damping (see Figure 3).

The damping of the plasmon band is not yet fully understood. In former reports, the electrochemical consequences that result from the electronic interaction of adsorbates with the nanoparticles have been emphasized. For example, nucleophilic adsorbates (such as anions) donate electron density into the silver particles: a chemical bond with a surface silver atom is preformed, the atom acquiring a small positive charge,  $\delta+$ , and a negative charge  $\delta-$  is shifted into the interior of the particle.<sup>6c</sup>

Thus, the electronic interaction between adsorbate and particle surface results in a change in the electron density of a thin layer of the silver particles. This change in the electronics of the surface layer is assumed to be the main reason for damping, as the resonance frequency of the oscillating electron gas in this layer is expected to be different from that in the interior of the particle. Another contribution may come from adsorbate-induced resonance states, as it has been formulated for the effects of adsorbed  $CO$ ,  $C_2H_4$ , which electronically interact much less with the silver particles than the presently investigated molecules<sup>11</sup> ( $CO$  and  $C_2H_4$  do not affect the plasmon band of silver in aqueous solution).

We have not yet discussed the wavelength shift that the plasmon band undergoes upon strong coverage of the surface by adsorbed substances. In all the above cases, a red-shift was observed. As has been shown by time-resolved measurements, the red-shift often does not necessarily occur simultaneously with the damping.<sup>6e</sup> For example, when  $I^-$  is adsorbed, one observes first the decrease in the intensity of the plasmon band and then a shift of the band to longer wavelengths. The effect was attributed to a loose agglomeration of the particles, whose stability is decreased by the adsorbate.<sup>6e</sup> Other effects, which are expected to shift the plasmon band, such as electron donation to<sup>6c,d</sup> or from<sup>8</sup> the silver particles, may be masked by the agglomeration effect.

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