Solvent Refractive Index and Core Charge Influences on the Surface Plasmon Absorbance of Alkanethiolate Monolayer-Protected Gold Clusters

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This report describes the effect of solvent refractive index and core charge on the surface plasmon absorbance of alkanethiolate monolayer-protected gold clusters (MPCs). Solution spectra of dodecanethiolate MPCs (5.2 nm average diameter) reveal an 8-nm shift in plasmon band position as the solvent refractive index is varied from $n_d^{20} = 1.33$ to 1.55. The spectral shift agrees with predictions of Mie theory when the alkanethiolate monolayer is accounted for in the calculations. Electronic charging of the MPC gold core by electrolysis, from its rest potential (−0.16 V) to +0.82 V vs a Ag quasi-reference electrode, causes a 9-nm (516 to 525 nm) shift in the surface plasmon band position. The shift in surface plasmon band position with core charge is compared to the predictions of the concentric sphere model for MPC capacitance and Mie theory, as a first step toward probing effects of quantized core charging on this important optical property.

Introduction

Research seeking access to the physical and electronic properties of nanometer-sized metallic particles has led to preparative routes[1] that expand on the well-established methods of gold colloid chemistry.[2] An important example is that of alkanethiolate monolayer-protected gold clusters (Au MPCs),[3] which exhibit excellent solubility in nonpolar organic solvents, good air and thermal stability, and a capacity to be repeatedly isolated in dry form—without aggregation—and redissolved in a range of solvents. Additionally, the mean core size of these nanomaterials can be manipulated by varying the Au:alkanethiolate ratio employed in the MPC synthesis, leading to modestly polydisperse Au MPCs with *average* core sizes ranging in diameter from 1.5 to 5.2 nm.[4]

The interesting colors observed in gold sols have led to extensive study of their optical spectroscopic properties.[5,6] Likewise, the optical properties of Au MPCs have been examined in several reports in an effort to correlate their behavior with gold colloids in terms of classical Mie theory.[7] The principal findings of these studies are: (a) The intensity of the surface plasmon (SP) band decreases sharply with decreasing core size for monodisperse Au MPCs with 1.4 to 3.2 nm core diameters, which is attributed to the onset of quantum size effects (QSEs).[7a] Assumptions regarding the interaction of the protecting alkanethiolate ligands with the underlying gold core were necessary to bring Mie theory into partial agreement with the experimental data. (b) Steplike spectral structures indicative of transitions to the discrete lowest unoccupied levels of the conduction band were observed in spectra of solutions of monodisperse Au MPCs with core diameters from 1.1 to 1.9 nm,[7b] and estimates of how the HOMO−LUMO "gap" energy changes with core size were derived.[7c] (c) Spectra of (modestly polydisperse) Au MPCs (4.4 nm av diameter) in solvents of

various refractive indices displayed distinct SP bands that did not detectably shift in energy.[4a]

In contrast to observation (c), the colors of noble metal sols of Cu, Ag, and Au have been found to be quite sensitive to the refractive index of the solvent medium,[8] and recent studies have shown that the effect of solvent refractive index on the color of polymer-stabilized gold sols was in agreement with Mie theory.[9] This apparent discrepancy prompted the present investigation, in which we demonstrate that the alkanethiolate monolayer used to protect Au MPCs drastically reduces the sensitivity of the SP band position to changes in solvent refractive index. Accounting in Mie theory calculations for the effect of the alkanethiolate monolayer shows the experimentally observed small shift in SP band position with refractive index to be in excellent agreement with theory.

A second variable in the electronic properties of metal nanoparticles in solutions is the state of their double layer charge. It is known[10] that addition or removal of some number of electrons (*n*) from colloidal particles produces a notable shift in SP band position, and efforts have been made to account for such SP band shifts using Mie theory.[11] Using recent results showing that MPC solutions can be electrolytically charged to controllable potentials,[12] we have explored and report here the effect of core charge state on the optical absorption spectra of MPC solutions. The SP band moves to lower energy as the core is electrolytically made more electron-deficient (charging −0.16 to +0.82 V), in qualitative agreement with Mie theory. These shifts in SP band position with core charge are analyzed using the concentric sphere model for MPC core capacitance,[13] in combination with Mie derivations.

Experimental Section

Gold MPCs with an average core diameter of 5.2 nm (∼2950 Au atoms) were prepared as described previously.[4a] Briefly, the reaction was based on combining dodecanethiol with $AuCl_4^-$ in a 1:6 mol ratio, with subsequent reduction at room temper-

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ature with an excess of BH_4^-. Purification of the MPC product was accomplished as before.[4a] These reaction conditions produce clusters with an *average* core diameter of 5.2 ± 0.2 nm estimated, from small angle X-ray scattering and based on an assumed *ideal* truncated octahedral shape,[14] to contain ca. 2951 gold atoms and ca. 371 protecting thiolate ligands. The MPCs were free of residual synthetic components as shown by proton NMR, and transmission electron microscopy results indicate a core diameter dispersity of $\sim \pm 10\%$. The MPC syntheses were not deaerated, but we have established[4a] that none of the MPC ligands are in an oxidized (sulfonate, etc.) state. The oxygen exposure aids dampening of reductive charging of the MPCs by the excess of borohydride used in their generation.

Electrochemical Measurements. Bulk electrolyses were performed on a Pine RDE4 bipotentiostat with a locally designed potential programmer. Electrolyses were based on a Pt mesh working electrode (rinsed with ethanol and acetone prior to each experiment), a Pt mesh counter electrode, and a Ag/Ag^+ nonaqueous reference electrode (Ag wire/$AgNO_3$(1 mM)/Bu_4-NPF_6 (0.1 M)/CH_3CN). For consistency with prior studies[12] of MPC charging, potentials are expressed vs a Ag quasi-reference electrode (AgQRE) that has a reference potential 220 mV negative of the Ag/Ag^+ reference electrode and 50 mV positive of SSCE. The working and reference electrodes and the counter electrodes were in opposite compartments of the electrochemical cell; the middle compartment contained a quiescent MPC solvent/electrolyte solution. A minor amount of working/middle electrode compartment mixing undoubtedly occurs. Solutions of charged MPCs generated by anodic bulk electrolysis were handled in air, while those generated at reducing potentials were handled under N_2.

Optical Measurements. All absorbance spectra were taken from 250 to 800 nm on an ATI−Unicam UV4 dual beam spectrophotometer in 0.1-cm path length quartz cuvettes (Starna). Approximately $2-5$ μM C12 MPC solutions in 0.1 M Bu_4-NPF_6/CH_2Cl_2 (exact concentrations are difficult to ascertain as some solvent evaporation during electrolysis was evident), either at their native open circuit potential or having been charged by bulk electrolysis, were employed.

Theory

Before presenting experimental data on solvent and core charge effects on the SP band position of MPCs, it is useful to summarize the predictions of classical optical theory for coated metal colloid particles and to develop the framework pertinent to the experiments. The factors known to influence the SP absorption band of small metal particles are:

Particle Size. The damping of the surface plasmon mode follows a $1/r$ ($r =$ radius) dependence due to, among other effects, surface scattering of the conduction electrons.[15,16]

Quantum Size Effects (QSEs). QSEs become important for particles with core sizes < 3 nm in diameter and cause a slight blue shift of the surface plasmon band.[16]

Stabilizing Ligand Shell. A dense shell of stabilizing surfactant, polymer, or alkanethiol will alter the refractive index at the particle surface and may cause either a red or blue shift in the peak position.[5c] Since some form of stabilizer is required to prevent particle aggregation, the band energy is rarely exactly where predicted by simple Mie theory, and in addition, because good stabilizers such as alkanethiolates form strong covalent bonds to surface gold atoms through back π-bonding from the sulfur, the SP band is also usually more damped than simple Mie theory predicts.

Solvent Refractive Index (n_d^{20}). The solvent refractive index alters the SP band position in a straightforward manner, as predicted by Mie theory (vide infra).[17]

Core Charge State. Core electronic charge state (i.e., core double layer charge) alters the SP band energy, with excess electronic charge and electron deficiency, with respect to the potential-of-zero charge (E_{PZC}) causing shifts to higher and lower energy, respectively.[11]

In the following theoretical construct, the alkanethiolate-protected gold clusters are treated as coated particles. The refractive index of the alkanethiolate monolayer depends on chain length; a refractive index value of 1.50 is assumed from literature precedent.[18] This value may be a slight overestimate; assuming a lower value has only a small effect on the results presented below. The monolayer-coated Au clusters under consideration can be accurately treated as dipole oscillators[5] and the extinction cross-section, Q_{ext}, calculated from electrostatics:

$$Q_{ext} = 4 \, x \, \text{Im}$$
$$\left\{ \frac{(\epsilon_s - \epsilon_m)(\epsilon_c + 2\epsilon_s) + (1 - g)(\epsilon_c - \epsilon_s)(\epsilon_m + 2\epsilon_s)}{(\epsilon_s + 2\epsilon_m)(\epsilon_c + 2\epsilon_s) + (1 - g)(2\epsilon_s - 2\epsilon_m)(\epsilon_c - \epsilon_s)} \right\} \quad (1)$$

where ϵ_s is the optical dielectric function of the shell layer, ϵ_c that of the gold core, and ϵ_m that of the medium. The volume fraction of the shell layer, g, is defined later. The size parameter, x, in eq 1 is described by

$$x = \frac{2\pi R \epsilon_m^{1/2}}{\lambda} \quad (2)$$

where R is the *coated* particle radius (radius of core with length of monolayer chain included) and λ is the wavelength of light. The actual extinction coefficient, EC, of the metal particle is described by

$$\text{EC}(M^{-1} \, cm^{-1}) = \frac{Q_{ext} \, (3 \times 10^{-3}) V_m}{4(2.303R)} \quad (3)$$

where V_m is the molar volume of gold ($\sim$10.4 cm^3/mol). The medium is assumed to be nonabsorbing so that ϵ_s is the dispersionless optical dielectric function of the shell, which, for the calculations here on alkanethiolate coatings, is taken to be $\epsilon_s = n_s^2 = 2.25$.[18]

The monolayer of the shell coating of the Au core modifies the condition for plasmon oscillations. Surface plasmon modes occur in the composite particle when the denominator in eq 1 is zero, i.e., when

$$\epsilon_c = -2\epsilon_s \frac{[\epsilon_s g + \epsilon_m (3 - g)]}{[\epsilon_s (3 - 2g) + 2\epsilon_m g]} \quad (4)$$

For monolayer shells that are thin relative to the core, $g \ll 1$, the condition for resonance becomes

$$\epsilon_c = - 2\epsilon_m - \frac{2g(\epsilon_s - \epsilon_{nt})}{3} \quad (5)$$

which reduces to the usual resonance condition for uncoated spheres as $g \rightarrow$ zero:

$$\epsilon_c = -2\epsilon_m \quad (6)$$

For simple metals, the real part of the dielectric function can be modeled approximately as

$$\epsilon_c' = \epsilon^\infty - \frac{\lambda^2}{\lambda_p^2} \tag{7}$$

where λ_p is the bulk metal plasmon wavelength, is given by

$$\lambda_p = \frac{2\pi c}{\omega_p} \tag{8}$$

where c is the speed of light in a vacuum and ω_p is the metal's bulk plasma frequency, given by

$$\omega_p = \left(\frac{Ne^2}{m\epsilon_0}\right)^{1/2} \tag{9}$$

where N is the free electron concentration and m the electron mass. This equation produces an excellent agreement with the measured values of the dielectric function of gold in the visible part of the spectrum,[19] using values of $\lambda_p = 131$ nm and $\epsilon^\infty = 12.2$.[20]

Combining the above, the surface plasmon peak position, λ_{peak}, is determined by

$$\frac{\lambda_{peak}^2}{\lambda_p^2} = \epsilon^\infty + 2\epsilon_m \text{ (uncoated)} \tag{10a}$$

$$\frac{\lambda_{peak}^2}{\lambda_p^2} = \epsilon^\infty + 2\epsilon_m +$$
$$\frac{2g(\epsilon_s - \epsilon_m)}{3} \text{ (alkanethiolate-protected)} \tag{10b}$$

Eq 10a,b shows clearly the differences between coated (alkanethiolate-protected) and uncoated particle optical properties. The equations first predict that, since g increases with chain length, longer-chain alkanethiolate ligands should shift the plasmon band position, λ_{peak}, to longer wavelengths. Second, if the refractive index of the monolayer, $n_s = \epsilon_s^{1/2}$, increases (e.g., through the use of longer, aromatic, or halogenated thiols), the band wavelength should increase. Likewise, an increase of the solvent refractive index should cause a lowering of SP band energy, but this shift will be less pronounced as g increases. For large g values, i.e., for small particles with thick alkanethiolate monolayers, the solvent refractive index effect will be quite small. Finally, eq 10a,b predicts that if the core charge state changes, causing a modulation of ω_p, the band position will be altered. Hence, the SP properties of small gold clusters are influenced by the nanoparticle size, the selection of solvent, and the state of core charge.

For naked particles, a plot of $\lambda_{peak}^2/\lambda_p^2$ vs ϵ_m has a slope of 2, but for an alkanethiolate-protected particle, a plot of $\lambda_{peak}^2/\lambda_p^2$ vs ϵ_m should have a slope of $2-(2g/3)$. This difference is due to the fact that the monolayer shell is also polarized by light and sets up a dipole that augments the core polarization charge.

For small core volume fractions, it is useful to rewrite the SP resonance condition as

$$\epsilon_c = -2\epsilon_s \frac{[\epsilon_s(1-f) + \epsilon_m(2+f)]}{[\epsilon_s(1+f) + 2\epsilon_m(1-f)]} \tag{11}$$

where $f = (1 - g)$ is the core volume fraction. For a small core
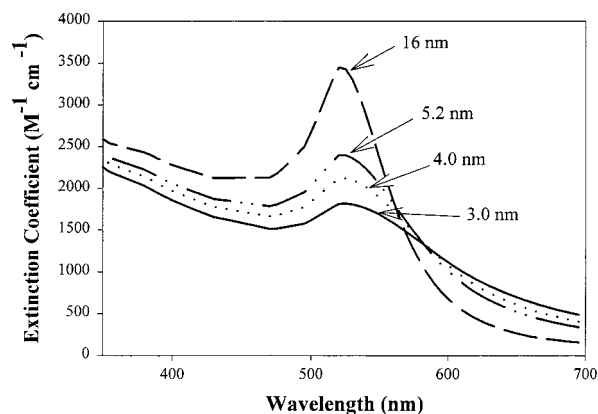
Figure 1. Calculated absorbance spectra of uncoated Au clusters, in water ($n_d^{20} = 1.3329$), as a function of nanoparticle diameter (as indicated on the figures). The peak position is almost constant at 522.5 ± 1 nm. The dielectric data for bulk gold were taken from ref 19, and damping was calculated using methods and parameters described in ref 7. Note that even with damping, a pronounced SP peak is predicted for nanoparticles with a 1.5 nm radius.

volume fraction, eq 11 reduces to

$$\epsilon_c = -2\epsilon_s \left[1 + \frac{f(\epsilon_m - \epsilon_s)}{(\epsilon_s + 2\epsilon_m)}\right] \tag{12}$$

As f goes to zero, the SP band shifts toward a limiting value of $\epsilon_c = -2\epsilon_s$, i.e., the core "sees" only the monolayer shell as the surrounding medium. Inserting eq 9 into eq 11, the peak position for small cores is given by

$$\frac{\lambda_{peak}^2}{\lambda_p^2} = \epsilon^\infty + 2\epsilon_s + \frac{2f\epsilon_s(\epsilon_m - \epsilon_s)}{\epsilon_s + 2\epsilon_m} \tag{13}$$

For typical values of $\epsilon_s = 2.25$, $\epsilon_m = 1.7$ to 3, and $f = (1 - g) = 0.05$, the above-mentioned slope will be less than 0.1, i.e., the surface plasmon mode is "frozen" at the value of $\epsilon_c = -2\epsilon_s$ and loses its sensitivity to solvent refractive index changes. This is the essential explanation of the prior[4a] MPC results.

For alkanethiolate Au MPCs, the shell volume fraction is large. Typically, MPC core size diameters are between 1.5 and 5.2 nm, with monolayer shell 1 to 1.5 nm in thickness. The values of g are given by

$$g = \frac{[(R_{core} + R_{shell})^3 - R_{core}^3]}{(R_{core} + R_{shell})^3} \tag{14}$$

and range from about 0.57 for a 1-nm layer around a core of diameter 6-nm, to 0.92 for a 1 nm coating around a cluster with 1.5 nm diameter. Even for larger, typical Turkevich sols,[6] a short chain-length thiolate coating such as $HSCH_2COOH$ will reduce surface plasmon sensitivity because, with $R_{core} = 8$ nm and $R_{shell} = 0.6$ nm, $g = 0.20$.

Results and Discussion

Solvent Refractive Index Effects on MPC SP Band Position. Figure 1 shows calculated absorbance spectra of uncoated gold particles as a function of core diameter in water ($n_d^{20} = 1.3329$). The surface scattering of conduction electrons causes strong broadening and damping in the SP band intensity (522.5 ± 1 nm) for these nanoparticles, and was accounted for in the calculated spectra using a previously reported procedure.[7] Additional contributions to SP band damping, such as core size

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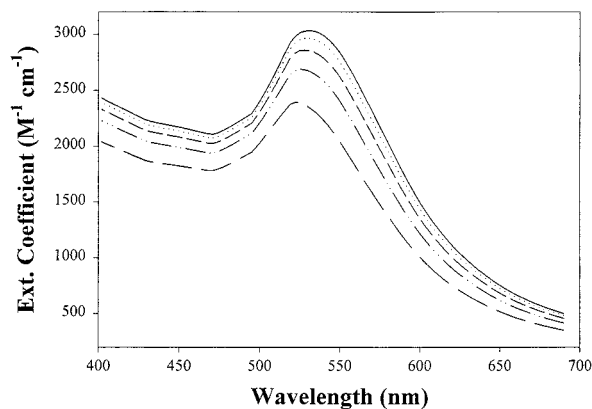
Figure 2. Calculated spectra of 5.2 nm Au clusters, in water (n_d^{20} = 1.3329), having monolayer shell thicknesses (from bottom to top) of 0.0 nm (— —, λ_{max} = 523 nm), 0.5 nm (—·, λ_{max} = 525.50 nm), 1.0 nm (— —, λ_{max} = 527 nm), 1.5 nm (···, λ_{max} = 528.70 nm), and 2.0 nm (—, λ_{max} = 530 nm). The calculated spectra show how alkanethiolate ligand chain-length alters the SP band position and intensity. The absolute values depend on the dielectric data used, but the shifts should be accurate.

polydispersity and the presence of an alkanethiolate monolayer, cannot be accounted for in the calculated spectra but may be manifest in the spectra of Au MPCs.[7a] Overall, the calculated spectra predict that the SP band should be pronounced for 5.2-nm diameter nanoparticles.

Figure 2 shows the effect of a monolayer shell on the calculated SP band of a 5.2-nm diameter particle. As the monolayer thickness increases, the band increasingly shifts to lower energy. With a 1.0-nm thick shell layer (λ_{max} = 527 nm), a red shift of 4 nm is predicted, relative to that of an uncoated particle (λ_{max} = 523 nm). A 2.0-nm thick monolayer shell (λ_{max} = 530 nm) likewise produces a lower-energy shift of 7 nm relative to the spectrum of an uncoated particle. The SP band additionally increases in intensity as the monolayer coating becomes thicker. The increase in plasmon band intensity with monolayer thickness is due to the attendant change in particle volume, because particle polarizability scales with particle volume.

Figure 3a shows experimental absorption spectra for as-prepared (unfractionated) dodecanethiolate MPCs with average core diameter of 5.2 nm, as a function of solvent refractive index (n_d^{20} = 1.33−1.55). Note that the SP band intensity compares well with that for the calculated spectra of uncoated particles of similar size (Figure 1). The SP band maximum (521 nm) is unchanged in hexane (n_d^{20} = 1.3750) and tetrahydrofuran (n_d^{20} = 1.4070) but shifts to 526 nm in benzene (n_d^{20} = 1.5010) and to 529 nm in o-dichlorobenzene (n_d^{20} = 1.5515). Previous studies[4a] with smaller diameter, unfractionated dodecanethiolate-protected Au clusters (4.4 nm av diam), over a more limited solvent refractive index range (n_d^{20} = 1.3750−1.5010), failed to detect a shift. In addition to using an expanded range of solvents, errors associated with selecting the SP band maximum (smoothing and differentiation) were minimized. While MPCs with larger core sizes would be expected to produce even more pronounced shifts in the SP band position, 5.2-nm diameter MPCs are the largest stable gold clusters prepared so far by the Brust reaction.[21] Exploration of the effect of solvent refractive index on the SP band position of larger gold clusters (>5 nm) will require procedures for the preparation of gold sols, their "capping" with an exclusive monolayer of alkanethiolate ligands, and their transfer to appropriate solvents.

For comparison to experimental results, Figure 3b maps out spectral shifts calculated for a 5.2-nm diameter Au cluster with
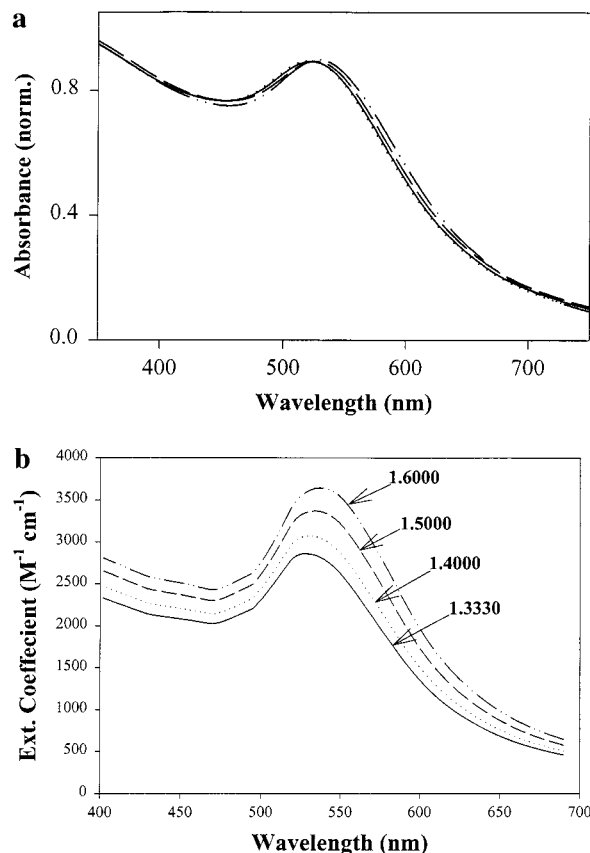

Figure 3. (a) Optical absorbance spectra of a 9.8×10^{-8} M (5.2 nm av diam) solution of Au MPCs,[13] in hexane (—, n_d^{20} = 1.3750, λ_{max} = 521 nm), tetrahydrofuran (···, n_d^{20} = 1.4070, λ_{max} = 521 nm), benzene (- - -, n_d^{20} = 1.5010, λ_{max} = 526 nm), and o-dichlorobenzene (—·, n_d^{20} = 1.5515, λ_{max} = 529 nm). The spectra are scaled to unity absorbance at 326 nm for comparison. (b) Calculated spectra of 5.2-nm Au clusters with a 1.0-nm thick monolayer shell, in media with refractive index values of n_d^{20} = 1.3330 (—, λ_{max} = 528.7 nm), n_d^{20} = 1.4000 (···, λ_{max} = 531.2 nm), n_d^{20} = 1.5000 (- - -, λ_{max} = 534.0 nm), and n_d^{20} = 1.6000 (—·, λ_{max} = 537.6 nm).

a 1.0-nm thick shell as a function of solvent refractive index. (The modeled length of a fully extended dodecanethiolate chain is 1.4 nm, but Figure 2 shows that the difference between calculated spectra with a difference in monolayer thickness of 0.4 nm is negligible.) The plot shows that the calculated SP band maximum shifts almost 10 nm going from water (n_d^{20} = 1.3329) to carbon disulfide (n_d^{20} =1.6319). While MPCs are not soluble over this same range of solvents, the shift in SP band position with solvent refractive index for the calculated spectra and experimental data agree well when considering the same range of refractive index values.

Figure 3a,b also allows comparison of the experimental and calculated SP band intensities. Using the idealized and average Au core atom number (vide supra) gives from Figure 3a a molar absorptivity of 8×10^6 M^{-1} cm^{-1}, using MPC molarity, and 2.8×10^3 M^{-1} cm^{-1}, using Au molarity.[22] The calculated molar absorptivity (extinction coefficient) in Figure 3b is somewhat larger, 3.4×10^3 M^{-1} cm^{-1}. The modest difference from the experimental results may arise from damping by the thiolate ligands.[20]

As a further comparison, Figure 4 shows calculated (♦) and experimental (●) MPC SP band positions, plotted vs solvent refractive index. The absolute values of the SP maxima for the calculated spectra are in slight error, in part because of uncertainties in the bulk gold dielectric data used in the calculations. (Errors in dielectric data for bulk gold come from
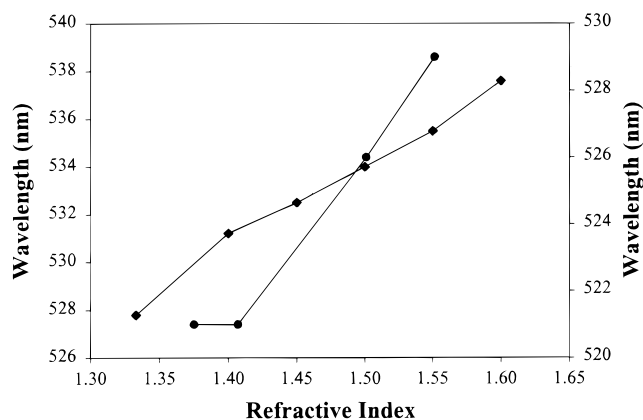
Figure 4. Plot of SP band maximum vs solvent refractive index for experimental data of Figure 3a (●, right axis) and calculated spectra of Figure 3b (♦, left axis). Over a similar solvent refractive index range, the experimentally observed SP band maximum shifts from 521 to 529 nm, whereas the calculated peak shifts from 528 to 536 nm. In both cases, the shift is on the order of 8 nm.

fitting the measured reflectivity of gold at each wavelength using Kramers−Kronig equations.[19]) The dielectric constant for small clusters could, of course, be substantially different from bulk values, and chemical interface damping[16] (that is, damping of the surface plasmon band by ligands) has been proposed as one of the manners to model intrinsic core size effects. The *absolute shifts* in position should, however, be accurate. Figure 4 shows that, over a similar range of solvent refractive index values and core sizes ($n_d^{20} = 1.33-1.55$), the 8-nm shift in experimental SP band position (Figure 3a) agrees well with that predicted from the calculated spectra of coated particles of similar size and coating thickness (Figure 3b).

We conclude this section by observing that the shift in surface plasmon band for alkanethiolate-protected gold clusters depends on the core-to-shell volume ratio (g). In the absence of this dense dielectric layer, Mie theory predicts significantly larger shifts than observed here,[9] and this supports our contention that knowledge of the core volume fraction parameter g (determined from eq 14) is essential for quantitative calculation of SP band shifts.

Core Charging Effects on MPC SP Band Position. We have recently shown[12] that MPC solutions can be electrolytically charged to produce solutions with stable, Nernstian potentials. The charged MPCs can be isolated in dried form, and retain most of their charge upon redissolution. Interestingly, the electronic charge on the MPC cores can be employed as a chemical reagent in redox reactions with electron acceptor/donor molecules, such as ethylferrocene and TCNQ. Charged MPCs also undergo electron transfer reactions when mixed with solutions of differently charged MPCs, and the potentials of the resulting solutions are consistent with Nernstian predictions.

Figure 5 shows optical absorption spectra of dodecanethiolate MPC (5.2 nm av diam) solutions as a function of their electrolytically established core potentials (i.e., core charge states). As with the solvent refractive index studies, large core radius MPCs were chosen for these studies because the SP bands are more readily observable in their absorption spectra. The spectrum in Figure 5 (−−, lower) shows that uncharged (open circuit potential −0.16 V) MPCs have an SP band maximum at 516 nm. (We have observed that open circuit, as-prepared MPC solution potentials can show some small dependence on concentration, so the value reported here must be considered in the context of the concentrations used in these experiments.) As the upper two Figure 5 spectra show, charging the MPCs to
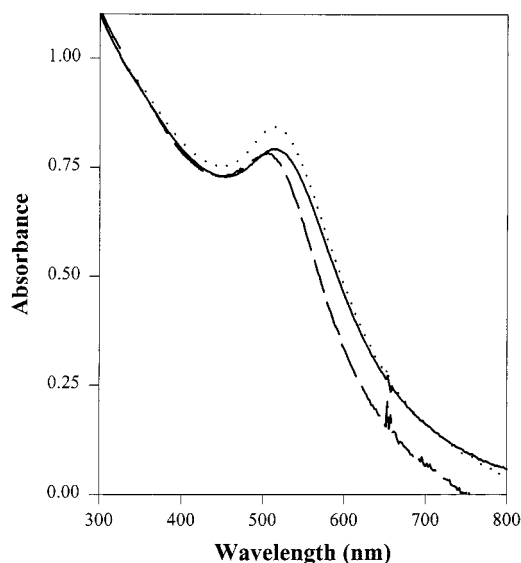
Figure 5. Optical absorbance spectra of ∼ 2 to 5 μM solutions of 5.2-nm avg diam. Au MPCs,[13] in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$, in a 0.1-cm path-length quartz cuvette, electrolyzed at 0.82 V (upper curve, ···) and 0.60 V (middle curve, —), and open circuit, as-prepared 0.16 V (lower curve, − − −), vs AgQRE.
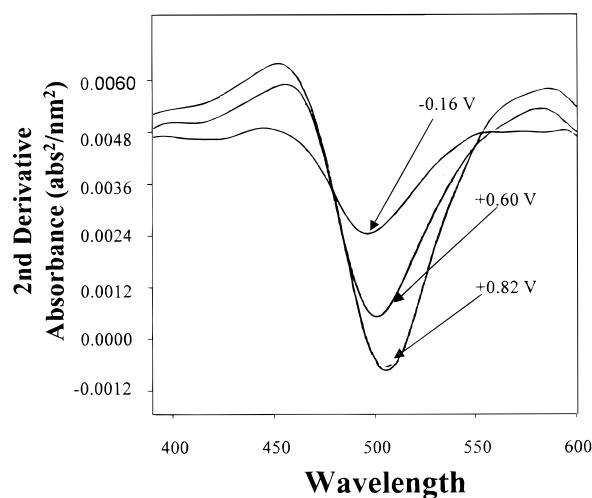
Figure 6. Second derivative of Figure 5 absorbance spectra of ∼ 2−5 μM MPC solutions, at the indicated potentials.

+0.60 V (−) and +0.82 V (···) shifts the SP band maximum to lower energy, at 520 and 525 nm, respectively.

Figure 6 shows a second derivative spectra of Figure 5, to further highlight the lower energy shift in SP band position with core charge. Both the SP peak position and intensity change as the MPC core change is made increasingly more positive. While intensity changes may result from concentration or data smoothing uncertainties, the observed shift to lower energy with increasingly electron-deficient core charge states, seen in the absorbance spectra of electrolytically charged MPC samples, is in qualitative agreement with theory developed for conduction band transitions in colloidal metals. Moreover, the direction of change in SP band position with core charge is anticipated by eqs 8, 9, and 10b. Examination of these relations shows that, other factors being held constant, a decrease in N (the free electron concentration in the metal, i.e., electrolysis at more positive potentials) serves to decrease ω_p, the bulk plasma frequency for the metal, and to increase λ_p and λ_{peak}, the bulk plasmon wavelength and the SP band wavelength, respectively. The observed red shift in SP band position (Figure 6) with

positive core charging is qualitatively consistent with this model.

An estimate of the predicted shift in SP band position with core charge can be based on the following analysis. We have found in other studies[13] that the MPC double-layer capacitance in electrolyte solution is well-described by the simple concentric sphere model:

$$C_{CLU} = 4\pi\epsilon\epsilon_0 r \frac{(r+d)}{d} \qquad (15)$$

where C_{CLU} is the capacitance of an individual MPC, ϵ is the static dielectric constant of the protecting monolayer, r is the metal core radius, and d is the thickness of the monolayer. Assuming values[13] for ϵ of 3.0, core radius (r) of 2.6 nm, and monolayer thickness (d) of 1.4 nm gives a value of 3.1 aF per MPC for the cluster dimensions used in the present study. On an area-normalized basis, this value is consistent[13,23] with double layer capacitances of flat Au surfaces bearing dodecanethiolate monolayers. For clusters charged to +0.82 V vs AgQRE, which is +0.98 V vs E_{PZC} (taken as the open circuit potential −0.16 V), a capacitance of 3.1 aF corresponds, by $\Delta V = e/C_{CLU}$, to removal of 19 electrons per particle.

Examination of eq 13 leads to a convenient expression for calculating the effect of changes in free electron concentration on the SP band energy:

$$\left[\frac{\lambda_{peak}^{final}}{\lambda_{peak}^{init}}\right] = \left[\frac{N_{init}}{N_{final}}\right]^{1/2} \qquad (16)$$

From this relation, assuming one free electron per Au atom in the idealized MPC core (e.g., N_{init} = 2951 free electrons per MPC core, and N_{final} is 19 electrons less), the predicted SP band redshift between MPC charge states at −0.16 and +0.82 V is just 1.7 nm. This estimate is much smaller than observed experimentally (9 nm, 516 to 525 nm). Conversely, the number of free electrons that must be removed from the core in order to produce a 9-nm redshift, calculated according to eq 16, is 100 electrons. This change in the free electron value seems far too large inasmuch as it would require an MPC double layer capacitance of some 16 aF, about 5-fold larger than would be consistent with flat Au electrode self-assembled monolayers (vide supra).

The reason(s) for the above difference between the capacity- and eq 15-predicted changes in free electron population in the Au MPC core are not clear at this time. One possible uncertainty is the use of the average, idealized 2951 Au atom core. However, it is the *ratio* of initial and final free electron numbers that affects the SP band position. The 9-nm shift can be reconciled with eq 16 only by assuming a free electron population as low as 560 electrons, which cannot be accommodated just by uncertainty in the experimental numbers of Au atoms per core. Either the free electron population indeed is lowered to such an extent, or somehow the thiolate ligands amplify the magnitude of SP shift with free electron changes, compared to eq 16. This is a topic that needs further measurements.

Summary

This report has compared theory with experiment for the effect of solvent refractive index and core charge on the surface plasmon absorption of solutions of alkanethiolate monolayer-protected gold clusters (MPCs). Spectra of dodecanethiolate-protected MPCs (5.2 nm average diameter) reveal an 8-nm red shift as the solvent refractive index is varied from n_d^{20} = 1.33 to 1.55; that is in accord with the predictions of Mie theory when the alkanethiolate monolayer is accounted for in the calculations. Spectra of electrolytically charged dodecanethiolate MPC solutions reveal a 9-nm (516 to 525 nm) shift in surface plasmon band position as the MPCs are made electron-deficient by charging from the rest potential (−0.16 V) to +0.82 V vs AgQRE. This shift in surface plasmon band position with core charge was compared to predictions of a concentric sphere model for cluster capacitance and of Mie theory. In other work,[7c,23] with smaller MPC cores, we have found it possible to observe their double layer charging, electron-by-electron, through voltammetric measurements. The sensitivity of SP band positions to MPC charge raises an exciting possibility that quantized changes of the optical property might be observable as well.

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(21) Syntheses with Au:dodecanethiol ratios of 1:16 and 1:20 were found to produce unstable materials which irreversibly aggregate in solution.

Materials from a preparation with a Au:butanethiol ratio of 1:12 were also found to consist of cluster aggregates.

(22) Analogous results[4a] obtained for a range of MPC core sizes average to $2.3 \pm 0.3 \times 10^3$ M^{-1} cm^{-1}, using Au molarity.

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