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ORIGINAL CONTRIBUTION

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Effect of a surface charge on the halfwidth and peak position of cluster plasmons in colloidal metal particles

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Abstract The optical response of colloidal particles depends on a variety of properties of the cluster, e.g., shape, size, size distribution and particle material. Since particles often are charged, also the surface charge may be a parameter which influences their optical properties. In this paper the effect of a surface charge on optical properties of spherical colloidal particles is studied and its magnitude is estimated by extended computations for silver clusters with surface plasmon in aqueous suspension. Two models are presented and discussed. The first model is based on the electrodynamic solution by Bohren and Hunt (Can. J. Phys. 55, 1930 (1977)), where a surface conductivity σ_s for a free surface charge yield an additional contribution ε_s to the dielectric constant of the particle material. In the second model, the surface charge contributes to the number density of free electrons in the cluster. Both models lead to a shift of the cluster plasmon peak, while an increase of the plasmon halfwidth could not be derived. The effect is quite small and limited on very small clusters.

Key words Surface charge – colloidal particles – charged clusters – cluster plasmon – blue shift – red shift

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Introduction

Since charging of small particles can be induced by friction, photoemission, adhesion of molecules or ion bombardment (sputtering), charged particles are often observed. In some applications, for instance in diffusion mobility analyzer or mass spectrometer, the charging is even utilized to determine the size of particles and clusters. An example where electrostatic charges play an important role for the stability of the whole system is colloidal suspensions. Surfactants or adsorbed molecules on the surface of the suspended particles lead to a Yukawa potential among the particles, preventing them from coming into contact. For high volume fractions, this potential even leads to formation of liquid crystals [1].

In this paper, the influence of a surface charge on the optical properties of small spherical particles and clusters in theoretically discussed using two different models.

Bohren and Hunt [2] already in 1977 derived an electrodynamic solution in which the scattering coefficients of a spherical particle were calculated under the presence of a surface charge. The main problem is the definition of a proper surface charge density, as already mentioned by the authors. We will use the model of free surface charges in the next section and present and discuss optical extinction spectra of charged silver clusters in aqueous suspension which exhibit a surface plasmon. The model yields a blue shift of the cluster plasmon resonance compared to the neutral cluster. Similar computations for other metals, e.g., sodium, gold and copper clusters, also show a blue shift of the corresponding surface plasmon.

As a surface charge on the surface of metal particles may contribute to the number density of free electrons in the cluster, in a second model the influence on the plasma frequency is discussed in the third section. For electrons as excess charge also a blue shift of the surface plasmon peak is obtained, while for a positive excess charge the plasmon is red shifted.

Compared to the uncharged cluster, however, the effect of the charge is quite small in both models and decreases rapidly with increasing cluster size. The shift is unaffected from particle size distribution. However, the proof of the charge-induced plasmon shift is restricted on experiments with monodisperse very small clusters, and is rendered more difficult due to size effects and quantum size effects in the particles, which are excluded in the presented models.

Free charges on the surface of metal clusters

In this section the model of free surface charges is used to determine the optical properties of charged spherical particles.

According to Mie's theory [3] the extinction and scattering cross-sections for a sphere with diameter 2a are determined from the scattering coefficients a_n and b_n

$$C_{ext} = \frac{\lambda^2}{2\pi\varepsilon_M(\lambda)} \sum_{n=1}^{\infty} (2n+1)\,\mathrm{Re}(a_n + b_n) \tag{1}$$

$$C_{sca} = \frac{\lambda^2}{2\pi\varepsilon_M(\lambda)} \sum_{n=1}^{\infty} (2n+1)\,(|a_n|^2 + |b_n|^2)\,. \tag{2}$$

$\varepsilon_M(\lambda)$ is the real dielectric constant of the surrounding matrix material at vacuum wavelength λ and Re means the real part. The scattering coefficients are obtained from Maxwell's boundary conditions for the electromagnetic fields of the incident and scattered wave outside and the electromagnetic fields inside the particle at the surface of the spherical particle. Under the presence of a surface charge, however, the boundary conditions are changed and now read [2]

$$(\mathbf{E}_{inc} + \mathbf{E}_{sca} - \mathbf{E}_p) \times \mathbf{n}|_{surface} = 0\,, \tag{3}$$

$$(\mathbf{H}_{inc} + \mathbf{H}_{sca} - \mathbf{H}_p) \times \mathbf{n}|_{surface} = \mathbf{K}\,, \tag{4}$$

where $\mathbf{n}$ is the vector normal to the surface and $\mathbf{K}$ is a surface current density parallel to the surface, caused by the surface charge. $\mathbf{K}$ solely affects the magnetic fields because of Maxwell's equation

$$\mathrm{rot}\,\mathbf{H} = \mathbf{K}\,. \tag{5}$$

As the surface current density is assumed to be limited to an infinitesimally thin layer at the particle surface, it is

$$\mathbf{K} = \sigma_s \mathbf{E}_t\,. \tag{6}$$

σ_s is the corresponding surface conductivity and $\mathbf{E}_t$ is the tangential component of the electric field. Using this relation in Maxwell's boundary conditions, the scattering coefficients a_n and b_n finally follow as [2]:

$$a_n = \frac{\psi_n(x)\psi_n'(mx) - m\psi_n'(x)\psi_n(mx) - i\sigma_s\sqrt{\frac{\mu_0}{\varepsilon_0\varepsilon_M}}\,\psi_n'(x)\psi_n'(mx)}{\xi_n(x)\psi_n'(mx) - m\xi_n'(x)\psi_n(mx) - i\sigma_s\sqrt{\frac{\mu_0}{\varepsilon_0\varepsilon_M}}\,\xi_n'(x)\,\psi_n'(mx)}\,, \tag{7}$$

$$b_n = \frac{m\psi_n(x)\psi_n'(mx) - \psi_n'(x)\psi_n(mx) - i\sigma_s\sqrt{\frac{\mu_0}{\varepsilon_0\varepsilon_M}}\,\psi_n(x)\psi_n(mx)}{m\xi_n(x)\psi_n'(mx) - \xi_n'(x)\,\psi_n(mx) - i\sigma_s\sqrt{\frac{\mu_0}{\varepsilon_0\varepsilon_M}}\,\xi_n(x)\,\psi_n(mx)}\,. \tag{8}$$

In these equations, x is the size parameter with $x = (2\pi/\lambda)\,a\sqrt{\varepsilon_M(\lambda)}$ and m is the relative refractive index with $m = \sqrt{\varepsilon(\lambda)/\varepsilon_M(\lambda)}$. $\varepsilon(\lambda)$ is the complex dielectric constant of the cluster material. ψ_n and ξ_n are the Riccati–Bessel and Riccati–Hankel functions of order n. The prime denotes the derivation with respect to the argument.

Compared to an uncharged particle, the surface charge contributes to the scattering coefficients by the terms containing the surface conductivity σ_s. Yet, for a more comprehensive discussion of the contribution to extinction and scattering, an appropriate model for σ_s is needed.

As it is our aim to discuss the problem for clusters, it seems useful to restrict the following considerations on the Rayleigh approximation, i.e., for particles as small as solely a dipole is induced in the particle by the incident field. Then, the functions ψ_n and ξ_n in Eqs. (7) and (8) can be approximated by the first term of their series expansions, finally leading to simpler expressions for the cross-sections:

$$C_{ext}(\lambda, a) = \frac{8\pi^2 a^3}{3\lambda}\,\varepsilon_M(\lambda)^{1/2}\,\mathrm{Im}\left(\frac{\varepsilon(\lambda) - \varepsilon_M(\lambda) + \varepsilon_s(\lambda)}{\varepsilon(\lambda) + 2\varepsilon_M(\lambda) + \varepsilon_s(\lambda)}\right), \tag{9}$$

$$C_{sca}(\lambda, a) = \frac{128\pi^5 a^6}{9\lambda^4}\,\varepsilon_M(\lambda)^2\left|\frac{\varepsilon(\lambda) - \varepsilon_M(\lambda) + \varepsilon_s(\lambda)}{\varepsilon(\lambda) + 2\varepsilon_M(\lambda) + \varepsilon_s(\lambda)}\right|^2, \tag{10}$$

with

$$\varepsilon_s(\lambda) = \frac{i\sigma_s(\lambda)\,\lambda}{\pi a}\sqrt{\frac{\varepsilon_0}{\mu_0}}\,. \tag{11}$$

Im means the imaginary part. Generally, the surface conductivity $\sigma_s(\lambda) = \sigma_{s1}(\lambda) + i\sigma_{s2}(\lambda)$ is a complex number. Apparently, σ_s results in an additional contribution ε_s to the total dielectric constant of the particle, meaning that the processes which lead to the surface charge are independent from those which lead to the bulk dielectric constant. An excess charge on the surface of a metal particle, however,

may also contribute to the charge density of free electrons. This model will be considered later in the next section.

The model of a free surface charge will be discussed for metal clusters, because only for metals the dielectric constants can be negative at wavelengths in the visible, leading to a resonance in scattering and extinction at wavelength λ_0, where $C_{ext}(\lambda)$ and $C_{sca}(\lambda)$ of Eqs. (9) and (10) take their maxima. Particularly for a charged cluster, λ_0 is obtained from the resonance condition

$$|(\varepsilon_1(\lambda_0) + \varepsilon_{s,1}(\lambda_0) + 2\varepsilon_M(\lambda_0)) + i(\varepsilon_2(\lambda_0) + \varepsilon_{s,2}(\lambda_0))|^2 = \text{minimum} . \quad (12)$$

The resonance in small metal clusters is the collective excitation of all free electrons in the cluster by the incident electromagnetic wave. It is called surface plasmon. The wavelength λ_0 at which the extinction is peaked and the halfwidth Γ depend on $\varepsilon(\lambda)$ (cluster material) and $\varepsilon_M(\lambda)$ (host medium). In fact, only a few metals (Au, Cu, Ag, alkali metals, Al) exhibit this plasmon because the imaginary part of ε is sufficiently small for these metals to fulfill Eq. (12). The narrowest resonances are found for alkali metals and silver. Therefore, silver was chosen in the following discussion.

It is evident from Eq. (12) that for a charged cluster a generally complex surface conductivity influences via ε_s the position of the surface plasmon as well as the halfwidth. For a more quantitative prediction, $\sigma_s(\lambda)$ is determined with the assumption of free surface charges, as caused for instance by adhesion of charged ions or by electron showering.

In a classical approach, when applying an electric field, the surface charge q_s with mass m moves along the surface with a drift velocity $\mathbf{u}_t$ tangential to the surface, forced by the tangential component $\mathbf{E}_t$ of the applied electric field. From the force balance

$$m\frac{\partial \mathbf{u}_t}{\partial t} + \gamma_s m \mathbf{u}_t = q_s \mathbf{E}_t \quad (13)$$

the velocity $\mathbf{u}_t$ is obtained as

$$\mathbf{u}_t = \frac{q_s}{m(\gamma_s - i\omega)} \mathbf{E}_t \quad (14)$$

presuming an oscillating electric field proportional to $\exp(-i\omega t)$ and a damping constant γ_s for the sur face charges. Then the surface charge density $\sigma_s(\omega)$ is given by

$$\sigma_s(\omega) = \frac{Nq_s}{4\pi a^2} u_t \quad (15)$$

and the additional dielectric constant $\varepsilon_s(\omega)$

$$\varepsilon_s(\omega) = \frac{Nq_s^2}{2\pi a^3 m\varepsilon_0 \omega} \frac{-\omega + i\gamma_s}{\omega^2 + \gamma_s^2} = \frac{-\omega_s^2}{\omega^2 + \gamma_s^2} + i\frac{\gamma_s}{\omega}\frac{\omega_s^2}{\omega^2 + \gamma_s^2} . \quad (16)$$

This is the Drude-model for N free excess surface charges q_s with damping constant γ_s and plasma frequency ω_s. The damping constant γ_s is a free parameter which is assumed to be much lower than the frequencies in the visible spectral region. The sign of q_s is unimportant because q_s^2 enters the calculation. The wavelength dependence of ε_s is simply obtained using the identity $\omega = 2\pi c/\lambda$ which is valid for the vacuum wavelength λ, c being the light velocity in vacuum.

In the following, we give an estimation for the number N of excess charges on silver clusters in colloidal suspensions. It can be estimated from the concepts of the classical DLVO-theory [4] and modern concepts of the jellium model [5] for metal clusters. When preparing colloidal metal particles by chemical reduction of the metal from a corresponding salt solution, it is observed that the particles are charged, e.g., Pt particles are positively charged, Ag and Au particles are negatively charged. This excess charge q_s on the surface of a metal particle in an electrolyte is compensated by a countercharge $-q_s$ from ions in the electrolyte, leading to a capacitor with capacitance C. While q_s is concentrated in a surface layer, $-q_s$ is randomly distributed in the solution as a diffuse ion cloud around the particle [4]. From various experimental results in the electrochemistry [6] it is known that the capacitance C consists of two parts

$$\frac{1}{C} = \frac{1}{C_{el}} + \frac{1}{C_{met}} \quad (17)$$

from the electrolyte and the metal. The capacitance C_{el} follows from DLVO-theory [4] as

$$C_{el} = \varepsilon_0 \varepsilon_{el}/\kappa , \quad (18)$$

with $1/\kappa$ being the Debye–Hückel screening length, defined via

$$\kappa = \frac{e_0^2}{\varepsilon_0 \varepsilon_{el} kT} \sum_i n_i z_i^2 . \quad (19)$$

ε_{el} is the static dielectric constant of the electrolyte, n_i and z_i are the density and valence of ions of kind i and e_0 is the elementary charge. The capacitance C_{met} results from the jellium model [5]. Typically, the values for C_{met} range from 30 μF to 50 μF per cm^2 of the metal surface. For a 1-1 electrolyte (e.g. NaCl-solution), $C_{met} = 30\ \mu\text{F/cm}^2$ and a

surface potential of $U = 100\,\mathrm{mV/cm^2}$, one obtains the number N in dependence on particle size $2a$ as:

$$N(a) = 2.8764 \cdot 10^9 \mathrm{m}^{-1} \cdot a + 0.48604 \cdot 10^{18} \mathrm{m}^{-2} \cdot a^2 \,. \quad (20)$$

We use this dependence for various cluster materials, to obtain the maximum effect of the excess charge. According to Eq. (1), extinction cross-section spectra were computed for silver clusters of various sizes in water in a narrow wavelength range around the resonance. For better comparison, they were normalized to the geometrical cross-section πa^2, i.e., the extinction efficiencies were computed. As an example, Fig. 1 shows computed extinction efficiency spectra for four cluster sizes. The number N of maximum excess charge is obtained from Eq. (20) and is given in the plots. For computation, the optical constants from Johnson and Christy [7] were used for silver and ε_s was calculated according to Eq. (16). The relaxation frequency γ_s was chosen as $\gamma_s = 10^{13}\,\mathrm{s}^{-1}$, which is in the same order as the relaxation frequency of free electrons in bulk. Therefore, this value is an upper limit, yielding the strongest effect in ε_s. For free charges on the particle surface much lower frequencies are possible without affecting the presented results. In each plot of Fig. 1, the dashed line is the extinction efficiency spectrum of the corresponding uncharged cluster.

It is seen that the plasmon peak position is shifted towards shorter wavelengths for the charged clusters, i.e., the cluster plasmon resonance is blue-shifted. The maximum shift occurs for the smallest particles, amounting to 3 nm. Although the number N increases with the surface area $4\pi a^2$ of the cluster, this shift rapidly vanishes with increasing cluster size and already for $2a = 10$ nm it has completely vanished. The peak height is scarcely decreased. It is hard to recognize from the plots that the peak halfwidth has changed. Actually, from evaluation of the curves, it follows that the halfwidth is slightly increased for the smallest clusters. For the larger clusters the halfwidth has not changed.

For discussion of the blue shift and the influence of particle material, particle size and surrounding medium it is assumed that the dielectric constant of the metal cluster can be described by a Drude dielectric constant $\varepsilon_{\mathrm{Drude}}$. Furthermore, the damping rates γ_D of the free electrons in the cluster and γ_s of the free charges on the surface are assumed to be very small compared to frequencies in the visible spectral region. Then,

$$\varepsilon_{\mathrm{Drude}} \approx 1 - \frac{\omega_p^2}{\omega^2}\,, \quad (21)$$

ω_p being the plasma frequency of bulk metal, and

$$\varepsilon_s \approx -\frac{\omega_s^2}{\omega^2}\,. \quad (22)$$

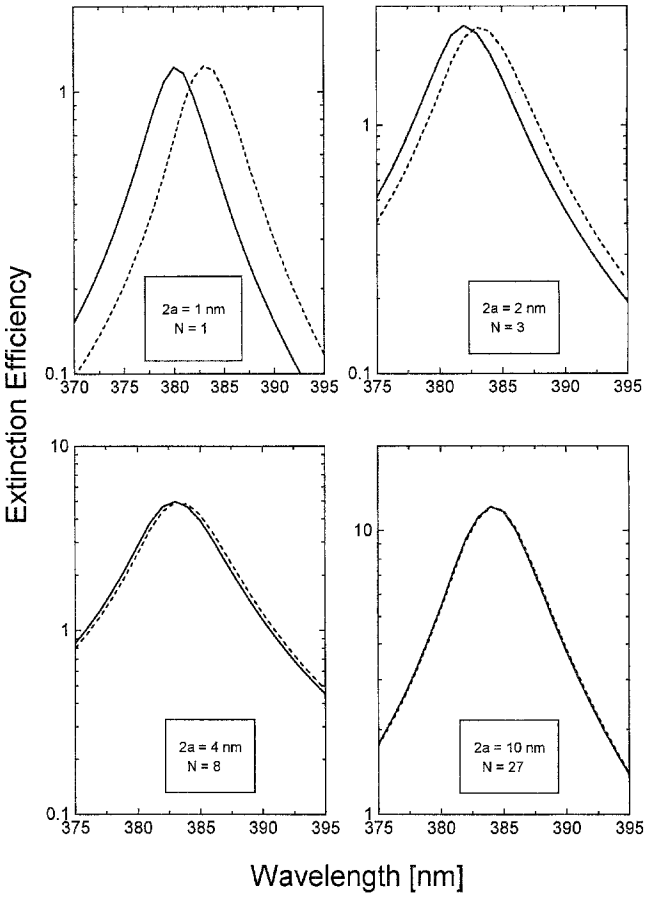

Fig. 1 Optical extinction efficiency spectra of charged silver clusters (solid lines) and uncharged silver clusters (dashed lines) with diameters $2a = 1$ nm, 2 nm, 4 nm and 10 nm. The maximum number N of elementary charges is given in the plots

The resonance condition Eq. (12) then yields

$$\omega^2 = \frac{\omega_p^2}{1 + 2\varepsilon_M} \quad (23)$$

for uncharged clusters, and

$$\omega^2 = \frac{\omega_p^2 + \omega_s^2}{1 + 2\varepsilon_M} \quad (24)$$

for charged clusters. It is evident that for a charged particle the resonance occurs at higher frequency (shorter wavelength) with respect to the uncharged particle, i.e., the resonance is blue-shifted. For other metal clusters, e.g. Na, Au or Cu, the corresponding resonances occur at different frequencies, depending on the plasma frequency ω_p of the metal.

The influence of the surrounding with dielectric constant ε_M is identical for charged and uncharged clusters: the resonance shifts towards lower frequencies (longer

wavelengths), i.e., the resonances are red-shifted for increasing ε_M. For increasing particle size, ω_s becomes smaller according to Eq. (16), although the number of excess charges increases with size (Eq. (20)). Therefore, for sufficiently large clusters Eq. (24) approaches Eq. (23) and the surface charge induced blue shift vanishes. These results are unaffected when interband transitions contribute to the dielectric constant of the metal. Finally, a particle size distribution which is normal or log-normal, does not strongly affect the blue shift. The halfwidth is unaffected by size distribution, only the magnitude of the cluster plasmon decreases slightly for very small clusters.

We point out that the model of free surface charges can also be applied on dielectric particles. However, since nanometer sized dielectric particles do not show any resonance in the visible spectral region, the effect of a surface charge is significantly smaller than for particles which exhibit a resonance like the cluster plasmon.

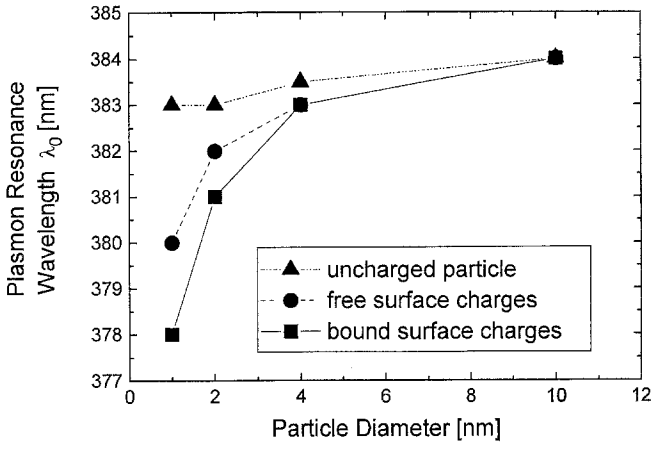

Fig. 2 Resonance wavelength λ_0 of charged silver clusters with diameters $2a = 1$ nm, 2 nm, 4 nm and 10 nm in the model of bound charges (full squares). For comparison, the results from the model of free surface charges (full circles) and for uncharged clusters (full triangles) are also plotted

Bound charges on the surface of metal clusters

In contrast to dielectric particles, an excess charge on the surface of a metal particle may also contribute to the density of free electrons in the cluster volume. In consequence, in this model the plasma frequency ω_p must be affected, rather than that an additional dielectric constant ε_s is created. This will be discussed in the following.

For this purpose, consider a spherical silver cluster with diameter $2a$. For an estimation of the effect, it is assumed that the half next neighbor distance a_0 in metals and the electron density n in the cluster are the same as in the bulk. In the bulk, the number of free electrons per atom is approximately 1 for silver. Then, a spherical cluster having $N_0 = 0.7405(a/a_0)^3$ atoms, has also N_0 free electrons. An excess charge $Q = -Ne_0$, corresponding to N excess electrons, then modifies the plasma frequency according to

$$\omega_p(N) = \omega_p(0)\sqrt{\frac{N_0 + N}{N_0}}\,. \tag{25}$$

That means that the plasma frequency is increased by a negative surface charge with respect to the uncharged cluster. In consequence, the corresponding surface plasmon as well as the bulk plasmon must be blue shifted. Vice versa, a positive excess charge $Q = +Ne_0$ lessen ω_p, leading to a red shift of the plasmons.

For a quantitative discussion, again numerical computations were performed for monodisperse Ag clusters. The number N of excess charges was taken from Eq. (20) to obtain the maximum effect. The optical constants of the silver cluster were modified according to

$$\varepsilon_1(\omega) = \varepsilon_{1,\mathrm{JC}}(\omega) - \varepsilon_{1,\mathrm{Drude}}(\omega_p(0)) + \varepsilon_{1,\mathrm{Drude}}(\omega_p(N))\,, \tag{26}$$

$$\varepsilon_2(\omega) = \varepsilon_{2,\mathrm{JC}}(\omega) - \varepsilon_{2,\mathrm{Drude}}(\omega_p(0)) + \varepsilon_{2,\mathrm{Drude}}(\omega_p(N))\,, \tag{27}$$

for each frequency ω. The subscript JC indicates the use of optical constants of Johnson and Christy [7]. Size and quantum size effects, which are known to change also the dielectric constant of the cluster material with respect to the bulk, are not considered here.

In Fig. 2 the wavelength λ_0 where the cluster plasmon is peaked is plotted for four different cluster sizes (full squares) in comparison to the uncharged cluster (full triangles) and the model of free surface charges (full circles). The blue shift is stronger than in the model of free surface charges. In fact, however, the magnitude of the shift is also quite small, amounting to maximum 5 nm for the smallest clusters. Further computations for other cluster materials, e.g., Na, Au and Cu, yielded similar results.

If the excess charge is not created from electrons but from adsorbed cationic or anionic molecules (e.g., in colloidal systems) the situation may be different. As the excess charge then is more located at the ion sites, its contribution to the number density of free electrons is expected to be strongly reduced to a much smaller number N^* of effective excess charges. The difference $N - N^*$ will then contribute as described earlier in the second section.

Summary

The optical response of charged spherical clusters exhibiting surface plasmon excitation was examined numerically. Two models were presented and discussed which take into account surface charges in different ways.

In the first, electrodynamical model, the surface charge q_s contributes by an additional dielectric constant ε_s to the total dielectric constant of the particle. This contribution yields a blue shift of the plasmon resonance, independently of the sign of the charge because q_s^2 enters the calculation. However, the effect rapidly decreases with increasing cluster size and vanishes for $2a = 10$ nm. A change in the halfwidth of the plasmon resonance could not be observed in the numerical spectra.

In the second model, the surface charge contributes directly to the dielectric constant of free electrons in the cluster. In this model, the sign of the charge enters the calculation. A negative (electronic) surface charge yields a blue shift of the cluster plasmon, which is largest for the smallest clusters. Nevertheless, as in the first model, the effect decreases rapidly with increasing size. A change in the cluster plasmon halfwidth was not recognized.

Although the blue shift is clearly seen in computations, the observation in experiments may be rendered more difficult because size effects and quantum size effects in small clusters change the dielectric constant with respect to the bulk. This fact has not been considered in the computations. A particle size distribution does not affect the influence of a surface charge on the optical properties of clusters. The final proof of this influence therefore requires more information about the optical constants of clusters.

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