

The size dependent shift of the surface plasmon absorption band of small spherical metal particles

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It has been previously established that the surface plasmon of small spherical silver particles, which are embedded in a noble gas matrix, shifts to higher energies (blue shift) as the mean diameter D of the particles decreases ($100 \text{ \AA} > D > 20 \text{ \AA}$). This blue shift has also been found for supported silver particles, and quite recently we observed it by elastic light scattering in the gas phase. This latter experiment proves unambiguously that the blue shift in small silver particles is not induced by interactions with the environment, the presence of which is clearly recognized in less inert matrices such as O_2 or CO . From self-consistent calculations of the surface response of planar jellium surfaces one would expect a red shift, which is also directly confirmed by a few calculations for selected jellium spheres. The contradiction between the observed blue shift for small particles and the predicted red shift for jellium spheres disappears, if one accounts for the d -electrons of silver in a very simple approximation.

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Introduction

The size dependence of the surface plasmon of small metal particles is usually investigated by measuring the absorption of colloids of such particles. If the fillfactor of the colloid is sufficiently low (ratio of metal volume to colloid volume smaller than 10^{-3}) and if the particles are spherical and small enough ($R \leq 100 \text{ \AA}$), one observes a distinct absorption band due to surface plasmon or dipole resonance absorption. A calculation of the dipole resonance of metal particles within the framework of classical optics [1] shows that the position of the absorption band is determined by the classical resonance condition for spherical particles

$$\text{Re } \varepsilon(\omega) + 2\varepsilon_{Ma} = 0 \quad (1)$$

where $\varepsilon(\omega)$ is the dielectric function of the bulk metal and ε_{Ma} is the dielectric constant of the (transparent) matrix, in which the particles are embedded. It should

be noticed that the classical resonance condition (1) predicts a size independence of the surface plasmon for small particles. In order to prove, whether this prediction is correct, one has to prepare colloids of spherical metal particles with a well defined mean diameter D , i.e., the size distribution of the particles has to be sufficiently narrow. The gas aggregation technique (GAT) [2, 3] is ideally suited for this purpose, because it yields almost Gaussian size distributions with a dispersion σ/D of about 0.2 and mean diameter D below 100 \AA . The colloids are then generated by condensing the metal particles grown in the gas phase together with the matrix gas on a cooled substrate (sapphire, 10 K). Figure 1 shows the absorption spectrum of Ag/Ar colloids with the mean diameter D of the Ag particles decreasing from bottom to top. In the upper two spectra the absorption by the Ag monomer dominates, and the particles are too small ($D < 20 \text{ \AA}$) for a size determination by electron microscopy [3]. The next to top spectrum contains already a slight indication of the surface plasmon absorption band,

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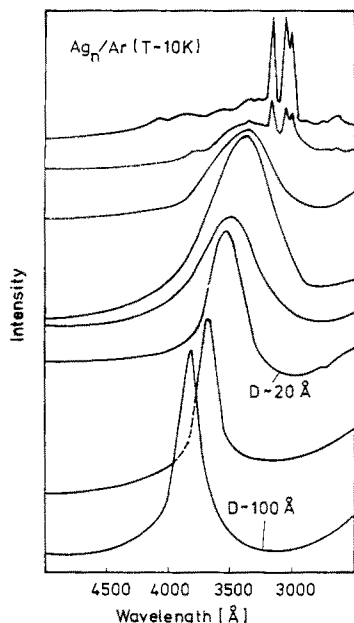


Fig. 1. Absorption spectra for Ag/Ar colloids. The mean diameter D of the spherical Ag particles decreases from bottom to top

which dominates the other spectra. For $D \cong 100 \text{ \AA}$ (bottom) the position of the resonance agrees almost perfectly with the classical prediction (1). The same holds for the calculated full width at half maximum (FWHM) of the band [4]. However, as D gets smaller, the surface plasmon absorption band obviously shifts to the blue, and the FWHM increases. This size dependent shift and damping of the surface plasmon of small metal particles ($D < 100 \text{ \AA}$), which is not predicted by classical optics [1], is a general phenomenon commonly called 'the size effect'. The size effect as such has been observed in Ag colloids before [5–7]. The point of the results for Ag/Ar colloids shown in Fig. 1 is that they are radically different: First a blue shift was observed for the first time [2]. In [7] practically no shift was observed and in [5, 6] a red shift was found. Second, the FWHM increases significantly more slowly (about 1/3) with decreasing diameter than was observed in [5–7].

Experimental

Results

Since the theoretical predictions for the size effect were confusing as well, an attempt was made to clarify the situation experimentally. A natural starting point was the question, whether the observed differences are due to different matrices (glass [5, 7], silica gel [6]) and probably also due to different preparation techniques.

Therefore the influence of the embedding matrix on the size effect was studied [8]. The preparation technique described above (GAT plus subsequent embedding) is perfectly suitable for such an investigation, because the Ag particles can be embedded in different matrices within the same experimental run. This way matrices can be directly compared with each other as shown in Fig. 2 (drawn out part of the curves), where CO, which is known to interact strongly with Ag, is compared with the inert Ar. In Ag/CO the blue shift disappears and the FWHM increases about 3 times faster than in Ag/Ar. Thus, the size effect in Ag/CO is very similar to that in Ag/glass [7]. The same kind of matrix influence has also been observed in Ag/NaCl and Ag/KCl (unpublished). On the other hand, in most matrices like the noble gases and N_2 the size effect is almost independent of the matrix. (In Ne there is a small quantitative change [8]). Even in the more reactive matrices O_2 and C_2H_4 , where the expected matrix influence is revealed by a stronger increase of the FWHM, the peak shift is the same as in Ar. These observations demonstrate clearly that the blue shift is a property of the Ag particles, whereas a red shift or no shift and a stronger increase of the FWHM is a matrix effect. This conclusion is confirmed at least qualitatively by reflectance measurements for Ag particles on an alumina support [9] and by preliminary results for Rayleigh-Scattering in the gas phase, where any matrix or support is absent.

Another novel and remarkable result is the observation that the peak shift for Ag in inert and weakly interacting matrices (O_2 , C_2H_4) depends linearly on the reciprocal mean diameter at least for $D \geq 20 \text{ \AA}$, where the size distribution of the Ag particles could be

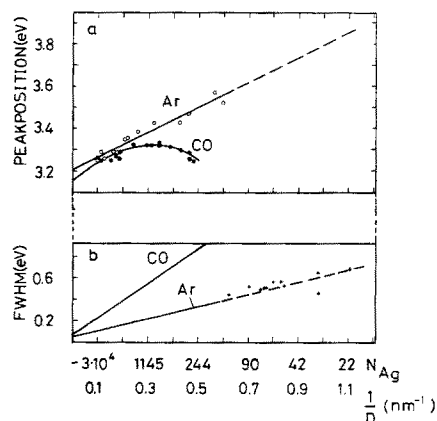


Fig. 2a and b. The position of the maximum (a) and the FWHM of the surface plasmon absorption band (b) in dependence of the reciprocal mean diameter of the particles for Ag/Ar and Ag/CO colloids. The number of atoms per particle is also indicated. For the dashed part of the curves and the crosses in b see text

determined in-situ with sufficient accuracy. As an example the linear shift is shown for Ag/Ar in Fig. 2a, drawn out part of the curve 'Ar'. The dashed part of this curve represents a conjecture for $D < 20 \text{ \AA}$, which was used the other way round to estimate the mean diameter from the peak position in cases such as represented by the upper spectra in Fig. 1. The crosses in Fig. 2b show that the measured FWHM coincide with the corresponding extrapolated FWHM curve. Admittedly, this proves only that the peak shift and the broadening of the absorption band both depend in the same way on the reciprocal mean diameter of the particles. Nevertheless, these results suggest strongly that clusters of a few ten Ag atoms still have a well defined surface plasmon. An investigation of this interesting question is underway.

The by now experimentally well established blue shift of the surface plasmon of Ag particles seems to be a serious problem for theory, which predicts a red shift for jellium (see below), the only tractable working model, which is free of questionable assumptions. In the discussion it will be shown that there is neither a qualitative contradiction nor a substantial quantitative disagreement between the measured shift of the surface plasmon frequency $\omega_{sp}(D)$ of spherical Ag particles and the jellium model, which is a good one for the conduction electrons in Ag. The theoretical background for the following treatment of the experimental data is the theory of the electromagnetic surface response of metals [10, 11] as developed by Feibelman for planar surfaces. For a spherical geometry this theory was subsequently formulated in [12, 13]. The result of interest in the present context is the new resonance condition

$$\begin{aligned} & \text{Re}[\varepsilon(\omega)] + 2\varepsilon_{Ma} + 2/R \\ & \times \text{Re}[(\varepsilon(\omega) - \varepsilon_{Ma})d(\omega; 1/R)] = 0 \end{aligned} \quad (2a)$$

for a sphere with radius R . The generally complex quantity d , which has the dimension of a length, is given by

$$d = d_{\perp} - d_{\parallel} \quad (3)$$

with d_{\perp} , d_{\parallel} being the surface response functions for electric fields normal and parallel to the surface. These surface response functions account essentially for the non-locality of the electromagnetic response of metals, which cannot be neglected in strongly inhomogeneous regions such as interfaces, especially not for normal fields.

Since the $\text{Im}[\varepsilon(\omega)]$ of Ag is very small compared to $|\text{Re}[\varepsilon(\omega)]|$ and ε_{Ma} in the spectral region of interest ($3.0 \text{ eV} \leq \hbar\omega \leq 3.7 \text{ eV}$) the somewhat simpler version

$$\varepsilon_1(\omega) + 2\varepsilon_{Ma} + 2/R[(\varepsilon_1(\omega) - \varepsilon_{Ma})\delta(\omega; 1/R)] = 0 \quad (2b)$$

with $\text{Re}[\varepsilon(\omega)] = \varepsilon_1(\omega)$ and $\text{Re}[d] = \delta$ is sufficiently accurate for an experimental determination of δ . It is emphasized that for this evaluation the actual $\varepsilon_1(\omega)$ for Ag [14] is used and not some free-electron surrogate, as is often done. In the results (symbols in Fig. 4 below) no statistically significant influence of the matrix (ε_{Ma}) and of the particle size (D) is found. Especially, there is no systematic trend (see below) for different ε_{Ma} . Therefore the experimental result in the frequency range $3.0 \text{ eV} \leq \hbar\omega \leq 3.6 \text{ eV}$ can be represented with sufficient accuracy by

$$\delta(\omega) = 0.5 r_s^{1/2} (1 - \omega^2/\omega_p^2)^{-1/2} \text{ \AA} \quad (4)$$

with $\hbar\omega_p = 3.78 \text{ eV}$ being the experimental bulk plasmon energy of Ag [14] and $r_s = 3.04$ being the density parameter for the conduction electrons.

Discussion

Since the experimentally determined real part of the surface response of Ag particles turns out to be independent of the particle diameter within experimental error, it must be the same as for planar surfaces [13]. Indeed, the surface response functions d_{\perp} , d_{\parallel} describe deviations from classical optics in a narrow range (a few \AA) around the interface, where classically a jump of local dielectric properties is presumed. Therefore one has in the limit of large spheres or vanishing curvature $1/R$ of the surface:

$$\lim_{R \rightarrow \infty} d_{\text{sphere}} = d_{\text{plane}} \quad (5)$$

This relation can be directly verified (unpublished) at least within the framework of the semiclassical infinite barrier (SCIB) model and the hydrodynamic approximation (HA) for the non-local response of the conduction electrons as applied to spheres in [15]. For a detailed discussion of SCIB and HA and their application to a plane the reader is referred to [10, 11]. In Fig. 3 the experimental result (4) for Ag particles (dotted line) is compared with $\text{Re}[d_{\perp}(\omega/\omega_p) - d_{\parallel}(\omega/\omega_p)]$ as calculated for planar jellium surfaces. The dashed curve is the SCIB + HA result

$$\text{Re}[d_{\perp} - d_{\parallel}] = 0.45 r_s^{1/2} (1 - \omega^2/\omega_p^2)^{-1/2} \text{ \AA} \quad (6)$$

where damping in the HA has been neglected, and the full curve is the result of the self consistent calculation of Feibelman [10] for $r_s = 3$. Note that the bulk plasmon frequency

$$\omega_p^2 = 4\pi n e^2/m \quad (7)$$

($\hbar\omega_p = 9.0 \text{ eV}$ for Ag) of jellium is used for these two curves, whereas for the experimental fit the actual plasmon frequency of Ag (see above) is used.

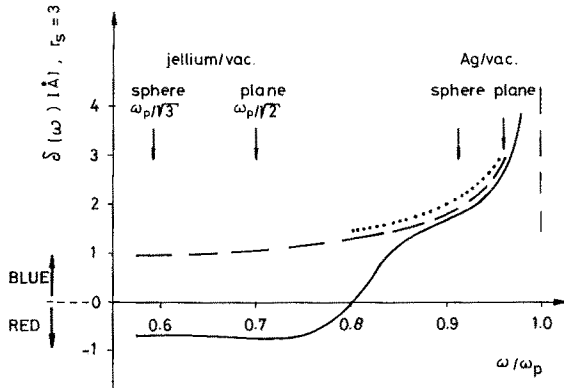


Fig. 3. Frequency dependence of the real part of the surface response, which is responsible for the shift of the surface plasmon frequency. The dotted curve is deduced from the experimental results for Ag particles in various matrices. Compare (4) in the text. *Dashed curve:* Theoretical result for a planar jellium/vacuum interface in the SCIB approximation plus HA (damping neglected). *Drawn out curve:* Result of a self consistent calculation for the same system redrawn from [10]

As Fig. 3 shows, such a rescaled jellium approach, which has been suggested in [9, 13] for Ag, explains the observed blue shift very nicely. It reveals very clearly that the reason is the contribution $\varepsilon_0(\omega)$ of the d electrons to the real part of the dielectric function $\varepsilon(\omega)$, due to which the surface plasmon for both a sphere and a plane are very close to the bulk plasmon (arrows on the right). If the d electrons can be neglected like in the alkali metals, the surface plasmons are more separated from the bulk plasmon (arrows on the left), and one expects a red shift, which is predicted from the self consistent calculation [10]. This qualitative prediction is confirmed by corresponding calculations for jellium spheres ($r_s = 4$; [16]) and recent experiments on Na clusters [17] in the gas phase.

Although the scaled jellium approach [9, 13] gives a correct hint for the observed size effect in Ag particles, the good agreement between (4) and the rescaled formula (6) is fortuitous, because the latter is not correct. This can be shown by a SCIB calculation of $\text{Re}(d_{\perp} - d_{\parallel})$ for an Ag/dielectric interface, either along the lines described in [11, 10] for a plane or as described in [15] for a spherical interface. The Fourier-Transform of the non-local longitudinal bulk dielectric function of Ag is in the HA given by [11, 15]

$$\varepsilon_l(\omega, k) = \varepsilon_0(\omega) - (\omega_p^0)^2 (\omega(\omega + i\gamma) - \beta^2 k^2)^{-1} \quad (8)$$

with $\beta^2 = 0.6 v_F^2$ (v_F being the Fermi velocity). The local contribution $\varepsilon_0(\omega)$ of the d electrons is determined from experimental data, which are described by the corresponding transversal function

$$\varepsilon_t(\omega) = \varepsilon_l(\omega, 0) \quad (9)$$

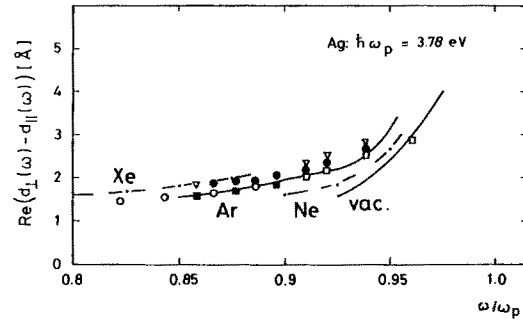


Fig. 4. Real part of the surface response of various Ag/dielectric interfaces. The symbols represent experimental results: *Open squares:* Ne, *filled circles:* Ar, *filled squares:* Kr, *open circles:* Xe, *open triangles:* O₂. The curves are calculated with the SCIB approximation plus HA (damping neglected)

using $\hbar\omega_p^0 = 9.2$ eV and damping is neglected ($\gamma = 0$) as before. The result depends now explicitly on $\varepsilon_0(\omega)$, which is frequency dependent, and on the dielectric constant of the matrix. Relevant examples for Xe ($\varepsilon_{Ma} = 2.3$), Ar ($\varepsilon_{Ma} = 1.75$), Ne ($\varepsilon_{Ma} = 1.25$) and vacuum are shown in Fig. 4 together with detailed experimental results for various matrices, which were summarized above in (4) or the dotted curve in Fig. 3. The rescaled jellium curve (dashed curve in Fig. 3) is very close to the curve for Ar in Fig. 4. Though the slight trend predicted by the correct calculations is not reproduced by the experimental results, the quantitative agreement is still satisfactory. In summary, it has been substantiated that the observed blue shift of the surface plasmon of spherical Ag particles ($D > 20$ Å) is essentially due to the peculiar bulk optical properties of silver, which are caused by its d electrons.

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