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Size-dependent surface-plasmon resonances of bare silver particles

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Surface-plasmon resonances of silver microparticle aerosols have been measured as a function of average particle size. Resonance line shapes are modeled as a function of particle size and complex refractive index. The surface-plasmon frequency is found to exhibit a red shift from 3.8 to 3.4 eV as the average particle diameter is decreased by approximately a factor of 3, in contrast to the blue shift observed for matrix-isolated silver particles.

The study of surface-plasmon resonances (SPR's) of bare silver particles has generated considerable theoretical and experimental interest over the past twenty years. This work has addressed the dependence of the frequency and width of the SPR on the size of the particles. On these issues there has been little agreement. In the experimental studies this has largely been due to the fact that almost all studies of SPR behavior have been on size-selected silver clusters supported in cryogenic or glass matrices.[1-4] Separating intrinsic cluster size effects from matrix effects is not possible. Indeed, the behavior of the SPR appears to be strongly matrix dependent. In rare-gas matrices the peak position blue shifts as cluster size decreases, in CO matrices the SPR shows an initial blue shift, then a red shift for smaller clusters, and in glass matrices it does neither. Recently, Huffman[5] has measured SPR's of silver-particle aerosols generated from a silver "smoke" source in which a flow of inert gas through an oven quenches a silver vapor and creates an aerosol. He reports a very slight blue shift as the distance between the extinction measurement and the oven is decreased. This is attributed to a blue shift with decreasing particle size, although the size range studied appears to be quite limited. Theoretically the situation is even less satisfying. Kreibig and Genzel,[6] in a recent review, have tabulated the predictions of seventeen different theoretical approaches to the problem. Of these seventeen, eight predict a red shift, six predict a blue shift, and three are inconclusive. Predictions concerning dependence of the resonance width with respect to particle size are similarly ambiguous. Clearly, a measurement of the SPR behavior of bare gas-phase silver particles over a large size range is essential to definitively address this question. In this paper we report such measurements. Bare silver-particle aerosols have been created by laser vaporizing a silver rod into an inert buffer gas. The average particle size may be controlled to some degree by variation of buffer gas pressure and composition to affect the cooling rate of the vaporized plasma. Absolute particle sizes have not been determined, but the SPR line shape exhibits a strong dependence on the diameters of the silver particles over the size range studied. Thus the SPR peak shapes and positions yield information concerning relative particle sizes and resonance frequencies. We observe a red shift with decreasing particle size. The largest particles made in our experiment have an SPR of 3.79 eV. As the average particle diameter is decreased by a factor of 3 the SPR linearly shifts red to approximately 3.45 eV.

EXPERIMENT

Cluster aerosols are generated by laser vaporization of an ultrahigh-purity silver rod (99.999%; Johnson Matthey batch W07040) mounted in a 3-in. vacuum-chamber cube. The chamber was evacuated to 10^{-6} torr and flushed twice with either high-purity helium or argon (99.999%). Prior to vaporization of the rod, the chamber was filled with between 50–800 torr of inert gas. The silver rod was then vaporized with 100–1000 shots of a focused excimer laser (308 nm, 40 mJ/pulse, 80 Hz). The chamber was placed in the beam path of a diode-array absorption spectrometer and the extinction spectrum from 200 to 800 nm was measured in 15 to 30 s. The chamber was then evacuated and a second (background) spectrum was taken and subtracted from the first. None of the background spectra exhibited evidence of a silver film on the optics. All spectra were taken within 60 s of vaporization. The lifetime of the aerosol is limited by diffusion of the clusters to the chamber walls, a process which can take many minutes, depending on the background pressure, temperature, and particle mass. For a sample with 400-torr He background pressure it takes 5–10 min before enough silver condenses onto the chamber windows to interfere with the gas-phase spectrum.

The mean particle size is controlled by changing the rate at which the vaporized silver plasma is quenched. This is most easily done by changing the buffer gas pressure. In general, low pressures appear to favor large clusters and helium favors larger clusters than argon. Variations in vaporization laser spot size, power, and buffer gas temperature also have an effect. Total number of laser shots, however, do not appear important. More detailed studies into thermal and pressure control of the mean cluster size are currently under way. Broida and coworkers[7] and Hecht[8] have measured the SPR's of alkali-metal particle aerosols using smoke sources and they found apparent size specificity which depended on buffer gas flow through the oven.

RESULTS

Typical SPR spectra for three different particle size distributions are shown in Fig. 1. The shape of the absorption peaks are dramatically different from one another. This variation in absorption profiles may be understood in terms of classical scattering theory for particles with a refractive index near 1 [Ag is such a material near the SPR (Ref. 7)]. In general one can consider these absorption profiles as passing from the near molecular to the bulk limit. For smaller clusters the absorption profile near the plasmon resonance is characterized by the extinction of light at wavelengths close to the resonance. For larger particles, however, the resonance peak somewhat resembles that of a dielectric film, where the extinction of light away from the resonance is greater than the on-resonance absorption. The mathematical argument for this transition from molecular to bulk behavior is outlined by van de Hulst[9] in some detail. Only those parts critical to the analysis of this data will be presented here.

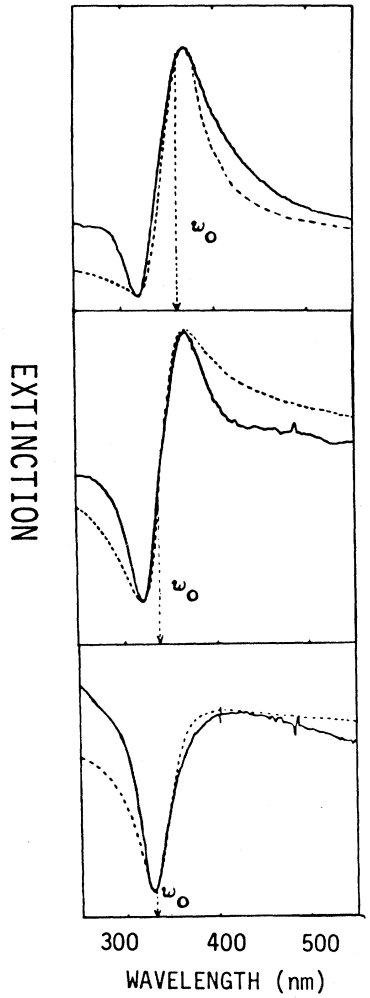

FIG. 1. Observed and calculated (dashed lines) extinctions for three different size distributions of silver particles with size increasing from top to bottom. These three spectra show the transition from molecular (absorption) to bulk (reflection) behavior at the surface-plasmon resonance. The position of the calculated resonance positions are indicated by the arrows. The only independent parameter varied to fit the shape of the observed extinction curves is the particle diameter.

The object of this exercise is to plot the extinction coefficient of a particular cluster size with a particular complex refractive index and a resonance (at w_0) as a function of wavelength. The final result is a modification of the dispersion equation based on the extinction (scattering plus absorption) cross section of a spherical particle. First it is instructive to consider nonresonant light scattering by a particle with a complex refractive index. It is necessary to define a few terms. The parameter β is defined by

$$\eta'/(\eta-1)=\tan\beta . \tag{1}$$

Here η and η' are the real and imaginary parts of the complex refractive index $m=\eta-i\eta'$. A second term is

$$\rho=2\chi(\eta-1) . \tag{2}$$

Here $\chi=2\pi a/\lambda$, a is the cluster radius, and λ is the wavelength of the incident radiation. The phase shift of a ray passing through the center of the cluster is due to the real part of

$$\rho^*=2\chi(m-1)=\rho(1-i\tan\beta) . \tag{3}$$

The damping of the incident wave is due to the imaginary part of the above equation. The extinction cross section is

$$Q_{\text{ext}}=4\,\text{Re}\{\kappa[\rho(1-i\tan\beta)]\} , \tag{4}$$

κ is the incident wave vector. This reduces to

$$\begin{aligned} Q_{\text{ext}} &= 2-4\exp(-\rho\tan\beta)\cos(\beta)\rho^{-1}\sin(\rho-\beta) \\ &\quad -4\exp(-\rho\tan\beta)[\cos(\beta)/\rho]^2\cos(\rho-2\beta) \\ &\quad +4[\cos(\beta)/\rho]^2\cos 2\beta . \end{aligned} \tag{5}$$

For classical dispersion theory the refractivity of a material with resonances at w_j is described by the well-known dispersion equation

$$F=3(m^2-1)/(m^2+2)=4\pi e^2/m_e\sum_j \frac{N_j f_j}{w_j^2-w^2+i\gamma_j w} . \tag{6}$$

Here γ is the damping constant, f is the oscillator strength, e and m_e are the charge and mass of an electron, and N is the density of species which can give rise to the absorption line. For particles of diameter not $\ll\lambda$ and with $m-1$ small, Eq. (6) may be approximated by separating it into real and imaginary components: $F=F_c+F_a/(i-v)$. Here $v=2(w-w_0)/\gamma$ and F_a and F_c are real constants. F_c corresponds to the constant off-resonant part of (6). This reduction of (6) comes from the approximation that near the resonance $(w+w_0)(w-w_0)=2w(w-w_0)$. If $m=1$ is close to 0 then the first equality in (6) reduces to

$$F=2(m-1)=F_c+F_a/(i-v) . \tag{7}$$

This assumption of m close to 1 for silver is certainly an approximation but its validity increases near the SPR.[10]

This reduction of F allows us to reintroduce the parameter $\rho = 2\chi(m-1)$. This parameter is equal to $\rho = \chi F_c$ outside the line and inside the line it is equal to

$$\rho^* = \rho\{1 + F_a/[F_c(i-\nu)]\} . \quad (8)$$

Resonance line shapes are calculated from the above formula by setting the ratio F_a/F_c to some constant. Changing this ratio affects, to a very good approximation, only the amplitude of the absorption profile, not the shape, width, or frequency position. The real and imaginary parts of (8) are separated algebraically so that it reduces to

$$\rho^* = a(1 - i\tan\beta) . \quad (9)$$

Thus for each wavelength increment a new ρ^* and a new β are calculated and put into Eq. (5) for Q_{ext}, the extinction coefficient. Q_{ext} is then plotted with respect to frequency to give the calculated line shape.

For extinction profiles calculated in this manner there are three variables to be determined: the damping constant γ, the resonance frequency w_0, and ρ. To a large degree, each of these corresponds to three different observables: the linewidth, the line position, and the line shape, respectively. This model was used to generate the calculated line shapes shown in Fig. 1 and ρ, γ, and w_0 were extracted from the fit. The parameter ρ is a linear function of both the refractive index and the cluster radius. The refractive index, in turn, is a function of the free-electron density within the particle. Studies on size-selected one-electron metals (Na, Cu, Ag) by both Knight's and Smalley's groups indicate that these clusters behave in the limit of one free electron and one core positive charge per atom.[11-13] Thus the change of ρ across the various SPR line-shape fits is dominated by a change in particle diameter.

Observed and calculated absorption spectra for three different cluster size distributions are shown in Fig. 1. The correlation between the size sensitive function ρ and w_0 is plotted in Fig. 2, showing the red shift with decreasing particle size. Disagreement between the calculated and observed spectra arise from a couple of sources. The first is that, away from the SPR, the assumption that $m-1$ is small breaks down. The second is that these calculations assume a single-particle size. This is obviously not a good assumption, but the size-sensitive line shapes and the good fit of ρ vs w_0 argue that it is not fatal either. The functional fit of the data is a Lorentzian and variation of the damping constant γ, which determines the calculated linewidth, changes the linewidth homogeneously. Particle size distributions, on the other hand, add to the inhomogeneous linewidth. There was no obvious correlation between the absorption linewidths with either w_0 or ρ, and this is undoubtedly due to fluctuating widths of particle size distributions. The observed surface-plasma red shift with decreasing cluster size is a very real and reproducible phenomenon, however. The SPR line shapes, especially those at the small or large particle extrema, are quite unique to their respective particle sizes. At resonance the small particles are dominated by the imaginary part of the refractive index (positive going peak) and the large particles are dominated by the real part of the refractive index (negative going peak). The fact that this model fits the observed line shapes quite well, coupled with SPR line shapes observed by other groups,[1-6] indicates that the particles studied here are probably in the 10–100-nm size range.

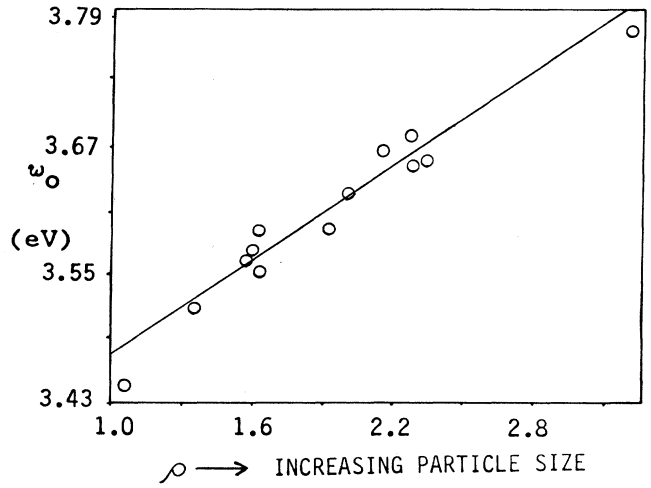

FIG. 2. Plot of the particle-size-dependent function ρ (obtained from the line-shape fit) vs the observed surface-plasmon resonance frequency. The straight line has the function $0.147\rho + 3.325 = y(\text{eV})$. The correlation coefficient for the linear regression is 0.97. The data indicate a red shift of the surface-plasmon resonance with decreasing particle size, in contrast to a blue shift observed for matrix-supported silver particles.

SUMMARY

Surface-plasmon resonances have been measured for a large size range of bare silver particles for the first time. The shape of the resonance is observed to evolve from the molecular (absorption) to the bulk (reflection) limit. A red shift of the SPR with decreasing cluster size is observed—in contrast to results taken from matrix isolated silver clusters. This red shift is similar to that observed in small size-selected sodium clusters by Knight and coworkers[12,13] and discussed by Kresin.[14] It is consistent with a decrease in the free-electron density within the cluster as the surface-to-volume ratio of the cluster increases—by spillout of conduction-band electrons outside the hard-sphere radius of the cluster.

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