

Blue shift of the Mie plasma frequency in Ag clusters and particles

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Photodepletion spectroscopy is used to measure the optical activity of sputtered Ag ionic clusters with up to 70 atoms. With decreasing cluster size the giant resonance caused by collective excitation of the valence electrons shifts to higher frequencies. This blue shift is qualitatively explained in terms of a reduced s - d screening interaction in the surface region of the particles.

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The possibility of measuring the optical spectra of free metal particles has recently greatly intensified the interest in understanding the physics of these systems, which can be regarded as intermediates between molecules and solids. The most systematic experimental and theoretical studies so far have been carried out for alkali-metal-atom clusters [1–16]. The main absorption feature in this case is related to the well-known Mie resonance [17], which, however, is typically red-shifted by a few percent compared to the frequency expected in the classical limit. Although it is by now well established that this red shift is caused by the spilling of the valence electrons beyond the nominal particle radius and by surface scattering processes, the quantitative prediction of the resonance frequencies and their variation with particle size remains very difficult.

In striking contrast to the alkali-metal-atom clusters, small Ag particles have long been known to exhibit a blue shift of the main resonance peak as a function of decreasing particle radius [18–21]. All of these spectra were, however, taken for Ag clusters embedded in various matrices where the resonance shifts induced by the surrounding medium were actually of the same order or larger than the shifts associated with the finite particle size. The matrix effect can in fact be so strong that it leads to a red shift of the resonance [22]. Only recently have we reported [23] gas-phase spectra of free Ag_N^+ clusters (up to 21 atoms) that indeed show a blue shift of the Mie resonance compared to the classical limit. These particles are, however, too small to test the behavior of the electronic properties as the particles approach bulk Ag.

The aim of this paper is twofold: First, we present experimental photodepletion spectra of larger Ag_N^+ clusters of up to 70 atoms. The molecular nature of the electronic properties of these particles should be much less pronounced than in the clusters investigated previously [23]. Thus, the present spectra provide a more reliable

link between the molecular and solid-state limits. Our results, combined with the earlier ones for smaller clusters, now give a rather systematic trend for the blue shift of the frequency of the Ag Mie resonance with decreasing size, and they allow a realistic extrapolation to the large particle limit. Second, we discuss a theoretical model for the dynamical response of the two-component s - d electron system [24]. The key feature of this model is the reduced s - d screening interaction in the outer regions of the particle where the s electrons spill into the vacuum. Since the s electrons in this region oscillate with the unscreened plasma frequency and since this region becomes relatively more important at smaller radii, this mechanism leads to a blue shift of the effective s - d resonance frequency.

In contrast to previous work on decay channels of photodissociated Ag cluster ions [25], we investigate the integral photodestruction as a function of the exciting photon energy. The experimental setup for the photofragmentation spectroscopy has been described elsewhere [23]. In short, a beam of positively charged Ag clusters is extracted from a sputtering source. Due to the production process, mainly odd clusters are obtained with sufficient intensity. After mass selection in a Wien filter the monodisperse beam enters the interaction zone (10 cm long) where it is collinearly irradiated by pulsed laser light ($\hbar\omega = 2.2$ – 5.6 eV, $\rho = 50$ – 1500 $\mu\text{J}/\text{cm}^2$). The light fluence is measured before and after each run by a pyroelectrical detector and averaged in a boxcar integrator. Particular precautions have to be taken to achieve an optimal overlap of the cluster and laser beam. A combination of a quadrupole ion deflector and a retarding field analyzer separates the photofragments from the parent clusters. Laser fluence studies show that the measured beam depletion is caused by single-photon absorption. This method yields absolute photofragmentation cross sections that represent lower limits of the photoabsorption cross sections. Due to uncertainties in the laser

fluence, absolute values are accurate to within 50%. These relative errors will be presented with the results discussed below.

In Fig. 1 the photofragmentation cross sections of several Ag_N^+ clusters are shown as a function of energy. All spectra are dominated by a main absorption feature around or below 4 eV whose intensity is approximately proportional to the number of s electrons and whose position exhibits a weak blue shift with decreasing particle size. At frequencies above 4 eV, a broad spectral background is observed, which is presumably caused by single-particle transitions from the occupied $4d$ states to the unfilled s - p orbitals. The Ag_9^+ and Ag_{21}^+ clusters in Fig. 1 involve $5s$ valence electronic structures that consist of filled shells. Thus their spectra exhibit a single collective resonance corresponding to that of a spherical electron system. Clusters with partly filled shells show a splitting of the Mie resonance into several components [23,26]. Their average frequency may be derived from the expression $\omega_0 = \sum_i \omega_i \sigma_i \Gamma_i / \sum_i \sigma_i \Gamma_i$, where ω_i , σ_i , and Γ_i are the positions, maxima, and widths, respectively, of the Lorentzian fits to these components.

Table I summarizes the average frequencies for all of the small Ag clusters measured so far and also gives the mean position of the $\text{Ag}_{50\pm 3}^+$ and $\text{Ag}_{70\pm 5}^+$ resonances shown in Fig. 1. These frequencies are plotted in Fig. 2 as a function of the inverse of the mean particle radius R , which is defined as $R = a_0 r_s N^{1/3}$ where $a_0 = 0.529 \text{ \AA}$ and

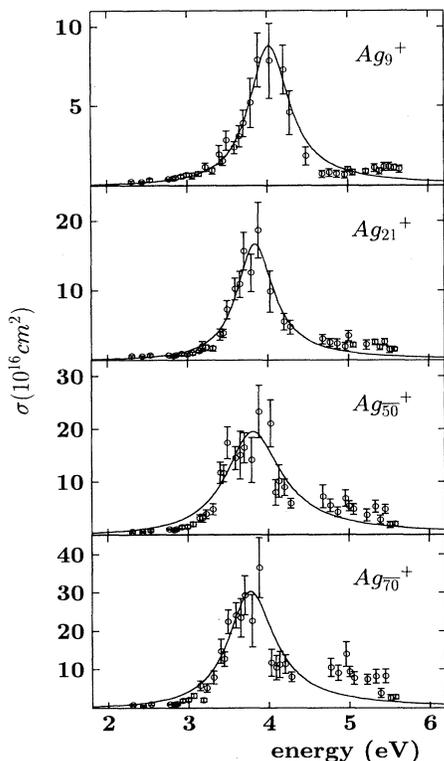


FIG. 1. Photofragmentation spectra of sputtered Ag clusters Ag_9^+ , Ag_{21}^+ , $\text{Ag}_{50\pm 3}^+$, and $\text{Ag}_{70\pm 5}^+$, using collinear ion beam depletion spectroscopy. The solid curves correspond to Lorentzian fits.

TABLE I. Experimental average resonance energies of free silver clusters.

N	$\hbar\omega_0$ (eV)
5	4.35 ± 0.03
7	4.17 ± 0.03
8	3.97 ± 0.03
9	4.02 ± 0.03
11	3.98 ± 0.03
13	3.95 ± 0.03
15	4.00 ± 0.03
17	3.96 ± 0.03
19	3.97 ± 0.03
21	3.84 ± 0.03
50	3.80 ± 0.05
70	3.77 ± 0.03

$r_s = 3.02$ is the electron density parameter of bulk Ag. The resonance frequencies are seen to converge reasonably well with increasing radius towards the classical limit at 3.5 eV, which is obtained from the condition $\text{Re} \epsilon(\omega) = -2$, where $\epsilon(\omega)$ is the bulk dielectric function of Ag. This trend is qualitatively consistent with the blue shift observed for large Ag particles ($10 \text{ \AA} \leq R \leq 50 \text{ \AA}$) in Ar [20]. Nevertheless, the slope of the resonance frequencies versus $1/R$ in the latter case is about twice as large as the one found in the present work. The average frequencies of small Ag clusters (5–11 atoms) in solid argon [21] also agree qualitatively with our results.

Before discussing the theoretical model for the observed blue shift of the Ag Mie resonance frequency with decreasing particle size, let us briefly recall the physical mechanism responsible for the red shift in the case of alkali-metal-atom particles [6–11]. This red shift is now commonly interpreted in terms of the so-called spill-out effect: Since the electronic density profile extends beyond the nominal radius R of the particle, the polarizability is enhanced and the resonance frequency is decreased. It should be noted, however, that the red shift is intrinsically a dynamical effect. Thus, additional contributions to it arise from scattering against electron-hole pairs at the

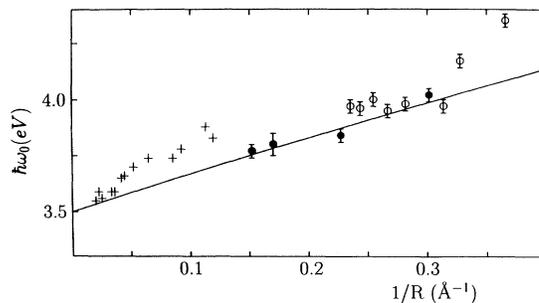


FIG. 2. Average resonance frequencies ω_0 of Ag clusters as a function of the inverse particle radius. The symbols denote the following cases: \circ and \bullet , free Ag clusters in the gas phase (present work and [23,26]); linear fit through data of the spherical clusters (filled symbols) and the classical Mie resonance at 3.5 eV in the limit of large R ; +, Ag particles ($10 \text{ \AA} \leq R \leq 50 \text{ \AA}$) in Ar matrix [20] after correction for the dielectric constant of the matrix.

surface and from the nonlocal nature of the response to the incident radiation. These processes become relatively more important as the particle size decreases.

For sufficiently large particles, these effects can be described in terms of a complex self-energy $\Sigma(R, \omega)$ that modifies the dielectric function of the particle [24,27]:

$$\epsilon(R, \omega) = 1 - \omega_p^2 / [\omega^2 + \Sigma(R, \omega)] , \quad (1)$$

where ω_p is the volume plasma frequency. The effective particle polarizability can then be written as

$$\alpha(R, \omega) = R^3 \frac{\epsilon(R, \omega) - 1}{\epsilon(R, \omega) + 2} = R^3 \frac{\omega_M^2}{\omega_M^2 - \omega^2 - \Sigma(R, \omega)} , \quad (2)$$

where $\omega_M = \omega_p / \sqrt{3}$. If we assume that, in the limit of large R , these self-energy processes are similar to those at a flat simple metal surface, we obtain the expression [24]

$$\Sigma(R, \omega) = R^{-1} d(\omega) (\omega_p^2 - \omega^2) , \quad (3)$$

where $d(\omega)$ is the centroid of the induced surface charge in the long-wavelength limit. In Ref. [24] it was shown that the overall frequency dependence of the cross section given by Eqs. (2) and (3) agrees very well with that obtained in full quantum-mechanical calculations [6]. Thus the size dependence of the Mie resonance in the limit of large R is given by

$$\omega_M(R) = \omega_M [1 - R^{-1} \text{Re} d(\omega_M) + O(R^{-2})] . \quad (4)$$

This dispersion agrees with that derived by Apell and Ljungbert [28] using a different approach. Because of the efficient screening in the simple metals, the induced charge is located outside the metal surface, i.e., $\text{Re} d(\omega_M) > 0$ [29]. Thus the Mie resonance is red shifted with decreasing particle radius. This red shift therefore has the same physical origin as the initial negative slope of the surface plasmon dispersion for simple metals [30].

The blue shift of the Ag Mie resonance can only be understood by taking into account the influence of the $4d$ electrons [31]. Since a quantum-mechanical calculation of the dynamical response of real Ag particles would be exceedingly difficult, we adopt here an approximate approach in order to describe the essential physical role played by the $4d$ electrons. In the bulk, their effect on the dielectric properties can be qualitatively accounted for by adding a term $\Delta(\omega)$ to the Drude dielectric function. $\Delta(\omega)$ is primarily related to the onset of the interband transitions from the $4d$ band to the nearly free electron bands at the Fermi energy. As a result of the s - d interaction the bulk plasma frequency is reduced from its unscreened value $\omega_p = 9.2$ eV/ \hbar to $\omega_p^* \approx \omega_p / \sqrt{1 + \text{Re}\Delta} \approx 3.76$ eV/ \hbar .

The important feature of our model is now that, like in the case of a flat Ag surface [24], this s - d interaction is absent in the surface region where the $5s$ electrons spill out into the vacuum. Since part of the density fluctuation associated with the Mie resonance oscillates with the unscreened plasma frequency, this mechanism leads to a blue shift. Moreover, this effect becomes more pronounced with decreasing particle radius because of the larger surface-to-volume ratio. In order to account for

this mechanism we write the effective dielectric function as

$$\epsilon(R, \omega) = 1 - \omega_p^2 / [\omega^2 + \Sigma(R, \omega)] + \Delta(\omega) , \quad (5)$$

where $\Delta(\omega)$ is taken to be the same bound term as in bulk Ag since we are only concerned with the limit of large R . Furthermore, we assume, as above for the alkali-metal-atom particles, that the self-energy processes at the surface of an Ag particle are similar to those at a flat Ag surface. We have recently calculated [24] the Ag surface excitation spectra within the model outlined above using the time-dependent density-functional approach [32]. The nonlocal dynamical response of the $5s$ electrons is described within the jellium model and the influence of the filled $4d$ bands is treated in terms of a homogeneous polarizable medium with its dielectric function $\Delta(\omega)$ extending up to a fixed distance from the surface. The position of this boundary is located between the jellium edge and the first plane of Ag nuclei.

On the basis of these results, the particle self-energy may be written in the form $\Sigma(R, \omega) \approx R^{-1} D(\omega) \omega_s^{*2}$, where $\omega_s^* \approx \omega_p / \sqrt{2 + \text{Re}\Delta} \approx 3.70$ eV/ \hbar . The experimental data [33] for the initial slope of the surface plasmon dispersion on the various crystal faces of Ag yield $D_s \equiv \text{Re} D(\omega_s^*) \approx -0.4$ to -0.8 Å. With this self-energy, the size dependence of the Ag Mie resonance at large R is given by

$$\omega_0 = \omega_M^* [1 - 0.5 R^{-1} D_M(\omega_s^* / \omega_M^*)^2 + O(R^{-2})] , \quad (6)$$

where $\omega_M^* \approx \omega_p / \sqrt{3 + \text{Re}\Delta} \approx 3.5$ eV/ \hbar and $D_M = \text{Re} D(\omega_M^*)$. Because of the closeness of the frequencies ω_s^* and ω_M^* this result shows that the linear coefficient for the Mie resonance should be nearly the same as that of the surface plasmon. The solid line in Fig. 2 corresponds to $D_M \approx -0.85$ Å, which agrees reasonably well with the slope expected from the dispersion of the Ag surface plasmon.

The above considerations apply to neutral Ag surfaces and particles. For the positively charged clusters studied in the present experiments, the effective centroid of the induced s - d surface density should be located somewhat farther inside the metal, leading to an enhancement of the blue shift. Conversely, the centroids of negatively charged Ag clusters are presumably located outside the surface, which should cause a red shift of the Mie resonance with decreasing radius. Such a reversal of the shift upon negative charging has indeed been observed [26].

Slight frequency shifts could also result from the rather high temperature of the sputtered clusters (2000–3000 K [34]). In the bulk, raising the temperature from 300 K to about 700 K leads to a red shift of the volume plasma frequency of about 0.1 eV [35]. At higher temperatures, the plasmon loss feature broadens considerably and its main position shifts to higher frequencies. Nevertheless, the resonance frequencies of the small clusters studied here agree quite well with those of Ag clusters in solid Ar at 10 K [21]. It should also be emphasized that, in particular, in small Ag clusters, the interatomic spacing might not be the same as in the bulk. Such differences could also lead to shifts of the resonance frequency.

In summary, giant resonances in the photofragmentation cross sections of sputtered Ag cluster ions have been measured using photodepletion spectroscopy. These data now establish a clear trend for the size dependence of the Mie resonance frequency unaffected by any interactions with surrounding media or by interactions between particles. The observed blue shift of the resonance with decreasing Ag cluster radius can be qualitatively understood in terms of a reduced s - d screening interaction in the outer regions of the Ag particles. Since the unscreened portion of the charge fluctuation associated with

the resonance increases with decreasing size this effect produces a shift towards higher frequencies. Thus we suggest that the blue shift of the Ag Mie resonance is caused by the same mechanism that leads to the positive dispersion of the Ag surface plasmon.

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