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Plasmon resonances in large noble-metal clusters

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Abstract. We investigate the optical properties of spherical gold and silver clusters with diameters of 20 nm and larger. The light scattering spectra of individual clusters are measured using dark-field microscopy, thus avoiding inhomogeneous broadening effects. The dipolar plasmon resonances of the clusters are found to have nearly Lorentzian line shapes. With increasing size we observe polaritonic red-shifts of the plasmon line and increased radiation damping for both gold and silver clusters. Apart from some cluster-to-cluster variations of the plasmon lines, agreement with Mie theory is reasonably good for the gold clusters. However, it is less satisfactory for the silver clusters, possibly due to cluster faceting or chemical effects.

1. Introduction

The optical spectra of noble-metal clusters show pronounced resonance lines caused by collective excitations of conduction electrons. These excitations are known as particle plasmons, Mie plasmons or surface plasmons. Their spectral properties have attracted a lot of interest, both for fundamental reasons and with a view to applications [1, 2]. These properties are known to be controlled by a variety of effects. In particular, the spectral position of the particle plasmon depends on the dielectric properties of the cluster metal; for instance, silver clusters generally have higher particle-plasmon energies than gold clusters. The spectral position also depends on the size and shape of the clusters; for example, it experiences a polaritonic red-shift with increasing cluster size for sizes greater than approximately 10 nm, due to electromagnetic retardation [1]. In

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addition, resonances of higher multipolar order appear besides the usual dipolar resonance when the cluster size is increased such that the optical field becomes non-uniform across the cluster [1]. In clusters of non-spherical shape, the single dipolar resonance of the spherical case splits into two or more non-degenerate plasmon modes that differ by their oscillation directions [2, 3]. Another important influence is that of the surrounding medium; the resonance energy generally shifts to the red with increased refractive index of the surrounding medium, due to screening of the Coulomb attraction between the oscillating electrons and the positively charged cluster ions [4], and may also be influenced by chemical interactions with the environment [5].

The linewidth of the particle-plasmon resonance is controlled by lifetime broadening due to various decay processes. Part of this lifetime broadening results from nonradiative decay of the particle plasmon into electron–hole excitations in the metal; if the excitations occur within the conduction (s–p) band, the decay process is termed intraband damping; conversely, it is called interband damping if the excitations are between d bands and the conduction band [6]. One matter of current debate is to what extent the decay into electron–hole excitations is influenced by the scattering of individual electrons. For instance, scattering of conduction electrons off the cluster surface and interaction with adsorbates may result in contributions to the decay called interface damping [7]. These processes are expected to become more important with decreasing cluster size, i.e., with increasing ratio of surface area and cluster volume. Another effect contributing to the lifetime broadening is radiation damping, i.e., the transformation of particle plasmons into photons; this contribution becomes more important with increased particle size due to increased coupling to the radiation field [6, 8, 9]. Spectroscopically, the lifetime broadening is characterized by the homogeneous linewidth $\Gamma_{\text{hom}} = 2\hbar/T_2$, which is connected to the dephasing time $T_2$, i.e., the decay time of the coherent polarization associated with the collective electron oscillation.

The spectral properties of the particle plasmon thus reflect a large variety of physical and chemical effects, and therefore have attracted much interest. However, experimental investigations of these spectral properties are usually performed on cluster ensembles, where inevitable variations in cluster size, shape and surface properties lead to cluster-to-cluster fluctuations of the particle-plasmon line position. These inhomogeneous broadening effects tend to mask the spectral properties of the individual clusters, and make it difficult to determine linewidths and line positions with the precision required for a direct comparison with theory. This problem has recently been circumvented by performing microscopic experiments on single noble-metal clusters [6, 10, 11, 12]. In [6], we have used a dark-field microscopy technique to measure light-scattering spectra of individual gold clusters of various sizes and shapes, and to determine the particle-plasmon damping mechanisms. Here, we apply the same technique to compare the particle-plasmon lines in large spherical gold and silver clusters. With increasing size we observe polaritonic red-shifts of the plasmon line and increased radiation damping for both gold and silver clusters. Apart from some cluster-to-cluster variations of the plasmon lines, agreement with Mie theory is reasonably good for the gold clusters. However, it is less satisfactory for the silver clusters, possibly due to cluster faceting or chemical effects.

2. Experimental details

The clusters investigated here were produced chemically. Both gold and silver clusters were obtained commercially in various nominal sizes (diameters $d = 20, 40, 60, 80, 100$ and $150$ nm in the case of gold and $d = 20, 40, 60$ and $80$ nm in the case of silver clusters) and with relatively narrow size distributions (size deviation $< 15\%$) [13]. Transmission electron micrographs (not
shown here) reveal that the clusters usually show slight deviations from a perfectly spherical shape due to surface faceting. Some clusters have highly nonspherical shapes; this is more often the case with silver than with gold clusters. Both gold and silver clusters are stored in stable suspensions in water. We spin cast a dilute suspension onto cleaned glass slides. After drying, the slide is covered with index matching fluid to ensure a homogeneous refractive index of $n = 1.5$ around the clusters.

The clusters are investigated in a conventional microscope using a high-aperture dark-field condenser, an oil immersion objective, and a halogen lamp as the light source for measurements on gold clusters; a xenon lamp is used for silver clusters. Individual clusters that lie far enough apart from each other can be observed as separate bright spots due to light scattered by each cluster. For spectral investigations, the scattered light from a single cluster is focused with the microscope onto the entrance slit of a spectrometer coupled to a sensitive cooled CCD camera [6]. This dark-field spectroscopic technique allows us to record single-cluster spectra with little background light. The remaining background and the spectral characteristics of the illumination lamp and detection system are taken into account by subtracting from each cluster spectrum the background spectrum measured in an adjacent position on the sample and by normalizing with respect to the lamp spectrum. We make sure that each cluster is optically spherical by checking that its spectrum is independent of the polarization of the incident light. Clusters with strongly nonspherical shape are not used for evaluation. The optical experiments on the silver clusters are performed immediately after sample preparation, in order to avoid aging of the silver. This aging process, which is presumably due to chemical reactions, usually occurs within a few days after exposure of the clusters to air, and is observable in a reduction of the brightness of scattered light from the clusters. In the case of the gold clusters, this problem is not observed due to the greater chemical inertness of gold.

3. Results and discussion

Figure 1 shows, as black curves, typical single-cluster scattering spectra from a gold and a silver cluster with 60 nm diameter. The spectra show the particle-plasmon resonances of the gold cluster at 2.19 eV, and of the silver cluster at 2.72 eV. The red curves are Lorentz fits to the experimental spectra. Both experimental resonances have nearly Lorentzian lineshapes; the slight deviations in the case of the gold cluster may be caused by the well known deviations from quasi-free-electron behaviour of the gold dielectric function due to interband transitions above 1.8 eV.

Figure 2 shows the size dependence of the gold cluster spectra. The spectrum of the 20 nm cluster appears noisy since the scattered light intensity from small clusters is extremely low. Indeed, Rayleigh scattering theory predicts that the scattering cross section of a spherical cluster should drop as the sixth power of the diameter [1]. The spectra show a systematic dependence of peak position and linewidth on cluster size; the resonances shift to lower energies and become broader with increasing cluster diameter. These observations are explained with the polaritonic red shift and radiation damping of the dipolar plasmon resonance, which both increase with cluster size [6]. In addition, a quadrupolar plasmon peak appears near 2.25 eV, at the high-energy side of the dipolar resonance, for the largest cluster size studied here (150 nm). The emergence of this quadrupolar peak is expected for very large clusters where the optical field becomes non-uniform across the cluster [1]. For comparison, figure 2 also shows the results of a calculation based on Mie theory (which is essentially a formulation of Maxwell’s theory for
spherical boundary conditions) [1]. In this calculation, we use the bulk dielectric function of gold measured on gold films under high-vacuum conditions [14], $n = 1.5$ for the refractive index of the embedding material, and the nominal size of the clusters; no further parameters enter the calculation. In particular, we do not take into account surface effects such as electron–surface scattering. Good agreement with the experimental spectra in figure 2 is obtained with respect to line shape, peak energy and linewidth of the dipolar plasmon resonance. Only at a cluster size of 150 nm is there a significant deviation. This deviation looks as if the relative weights of dipolar and quadrupolar contributions were different in the calculation and the experiment. The reason for this difference is presently unclear.

Figure 3 shows the results of a systematic evaluation of measurements performed on many individual gold clusters. Here the single-cluster linewidth determined from the spectra is plotted versus the dipolar plasmon resonance energy. The right-hand scale shows the dephasing time $T_2$ deduced from the linewidth via $T_2 = 2\hbar/\Gamma_{\text{hom}}$. The results for each nominal cluster size are plotted in a separate colour. The data in figure 3 have been obtained from Lorentz fits of the plasmon peaks in the spectra. The error bars for the 100 nm clusters show the uncertainties involved in the fit procedure; the error bars for all other sizes have been omitted to avoid cluttering of the figure. In the case of the 150 nm clusters, the fit involves the separation of the dipolar and quadrupolar resonances by using separate Lorentzians for the two modes. Again, as in figure 2, we observe in figure 3 a large polaritonic red-shift with growing cluster size. Furthermore, a drastic increase in linewidth with growing cluster size is observed due to increased radiation damping. The size dependence of the linewidth appears less pronounced above a resonance energy of approximately 2.15 eV. This is a consequence of a linewidth contribution from interband damping, which increases with energy, as shown in [6]. Both red-shift and linewidth increase are reproduced by the Mie theory calculation shown as a grey curve. This curve predicts an unambiguous relation between polaritonic red-shift and radiation damping for each cluster size. The error bars for the 100 nm clusters show that the apparent scatter of the experimental data around the theoretical line cannot be explained by fit uncertainties but are due to real sample properties. Some distribution of experimental data along the theoretical line is expected due to the size distribution within each nominal size group. The deviations from the theoretical line are
Figure 2. Single-cluster scattering spectra for various cluster sizes (black curves). The cluster diameters are indicated. The blue curves show the results of Mie theory calculations using the dielectric function of gold from [14].

more difficult to understand. They are possibly caused by faceting of the cluster surfaces, small variations in the cluster environment due to contamination on a molecular scale, or charges in or on the clusters. It is interesting that most of the experimental data points lie above the theoretical curve. However, there are also some points within each size group that lie on or below it. At least for these particular data points, we can conclude that interface damping processes (which are not included in the Mie calculations) seem to give no significant contributions to the line broadening.

Figure 4 shows the results of a similar evaluation of the silver-cluster spectra. Qualitatively we observe the same polaritonic red-shift and increase in radiation damping with increased cluster size as for the gold clusters. Here, however, significant systematic deviations from theory occur. The grey curve shows the results of a Mie theory calculation using the dielectric function of silver from [14]. This calculation yields smaller linewidths than found experimentally for energies above 2.8 eV, and larger linewidths below. It is possible that the disagreement between calculation and experiment comes from chemical surface effects that may be present in our chemically prepared silver clusters while they should be absent in the high-vacuum measurements of the dielectric function performed in [14]. It is natural that the agreement is better in the case of the gold clusters where such chemical surface effects should play a lesser role due to the more inert character of gold. The agreement between calculation and experiment becomes better when a different dielectric function is used. The orange curve in figure 4 shows the results of a Mie theory calculation using the dielectric function of silver extracted from measurements on silver-
Figure 3. Measured linewidth of plasmon resonances in single gold clusters versus resonance energy (symbols). The nominal cluster diameters are indicated. The error bars for the 100 nm clusters show the uncertainties involved in the curve fit procedure; the error bars for all other sizes have been omitted to avoid cluttering of the figure. Grey curve: Mie theory using the dielectric function of gold from [14].

Figure 4. Measured linewidth of plasmon resonances in single silver clusters versus resonance energy (symbols). The nominal cluster diameters are indicated. Grey curve: Mie theory calculation using the dielectric function of silver from [14]. Orange curve: Mie theory calculation using the dielectric function of silver from [15].

Cluster ensembles prepared chemically [15]. The agreement is now reasonable at energies above 2.6 eV; however, the linewidth below 2.6 eV is underestimated in the calculation. We thus obtain only partial agreement of the calculation with experiment for the silver clusters. This incomplete agreement may originate from different chemical conditions in [15] and in the present work. It may also be caused by inhomogeneous broadening effects that may have been present in [15]. These points will require further investigation in the future.
Another interesting observation in figure 4 is that the experimental data for the silver clusters show much more scatter than those of the gold clusters in figure 3. If indeed cluster faceting, charges, or molecular contaminations are the reasons for the scatter of the gold data (as suggested earlier), then these explanations could also help to understand the even wider scatter of the silver data. It is possible that either the silver clusters tend more towards faceting than the gold clusters, or that they are more sensitive to charges or molecular contaminations. The latter explanation would be consistent with the less inert chemical character of silver. Again, these aspects will require further investigation in the future.

4. Summary

In summary, we have investigated the optical properties of large spherical gold and silver clusters. The light scattering spectra of individual clusters were measured using dark-field microscopy, thus avoiding inhomogeneous broadening effects. The dipolar plasmon resonances of the clusters were found to have nearly Lorentzian shapes. With increasing cluster size we have observed polaritonic red-shifts and radiation damping of the plasmon line for both gold and silver clusters. Apart from some cluster-to-cluster variations of the plasmon lines, agreement with Mie theory is reasonably good for the gold clusters. However, it is less satisfactory for the silver clusters, possibly due to cluster faceting or chemical effects. Remarkably, our silver clusters do not have narrower linewidths than the gold clusters, contrary to expectation based on the better free-electron character of bulk silver as compared to gold. The single-cluster spectroscopy used here is expected to help to elucidate these issues in the future, and to give valuable information also on other aspects of the optical properties of large metal clusters.

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