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Photoelectron spectroscopy of single-size Au clusters collected on a substrate

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We have successfully collected size-selected Au clusters from a liquid-metal ion source onto amorphous carbon substrates. The systematics of the photoemission spectra show that there was no significant fragmentation or coalescence of clusters with seven or more atoms. We estimate the transition from metallic to local screening of the photoemission core hole to occur at a cluster size of approximately 150 atoms.

Clusters of metal atoms bridge the gap between molecules and condensed matter,[1] provide insight into bulk surfaces, and are of practical importance in understanding catalysis. Photoemission is a useful probe of the electronic nature of clusters.[2,3] The clusters studied by photoemission are usually prepared by evaporating metal onto substrates, usually amorphous carbon. This allows *in situ* growth of clusters under ultrahigh vacuum (UHV), but data analysis is compromised by the wide distribution of cluster sizes. More recently cluster beams have allowed excellent mass resolution in vapor-phase studies, but clearly most applications will require clusters condensed on some kind of support. A question then is whether the clusters retain their identity on the support. In this paper we present x-ray photoelectron spectroscopy (XPS) data for size-selected Au clusters deposited onto amorphous carbon from a liquid-metal ion source (LMIS). The spectra show, at least for some cluster sizes, little or no fragmentation, and a smooth tendency towards atomic or molecular character with decreasing cluster size.

The LMIS has been described in detail elsewhere.[4] Briefly, a nominally 4.0-keV beam of Au ions and cluster ions is emitted from the source tip and focused into a parallel beam, which passes through a 60° sector magnet to select a well-defined cluster size. This beam was refocused through a 0.125-in aperture and decelerated through 2 mm onto a carbon substrate. The cluster ions reaching the substrate had energies between 0 and 2 eV per atom, and a mean energy of ~0.6 eV per atom.

The sample stub was withdrawn into a portable vacuum chamber ($p \approx 4 \times 10^{-8}$ Torr), which was transported 50 m and attached to our UHV system. The sample was then transferred under UHV into the ESCALAB II spectormeter ($p \approx 5 \times 10^{-11}$ Torr), which features a monochromated Al $K\alpha$ x-ray source ($h\nu \approx 1487$ eV). Data were collected continuously for approximately one week. The C 1s spectrum was monitored as a check of instrumental drift, which was no more than 0.05 eV. The Au spectra were not observed to change with time.

Figure 1 shows Au 4f spectra for Au$_n$ clusters ($n = 5,7,27,33$) and for a thick layer of evaporated gold. The energy scale was calibrated by the C 1s spectra. The data have not been otherwise manipulated in any way.

The Au 5d spectra are shown in Fig. 2. The carbon-valence emission has been eliminated by subtracting a bare-substrate spectrum, normalized by the respective C 1s intensities. The smoothed valence spectra were obtained by convolution of each difference spectrum with a Gaussian of width ~0.5 eV.

The first question in evaluating our success in collecting intact clusters is whether all the metal adheres to the carbon surface. For the two larger cluster sizes the Au

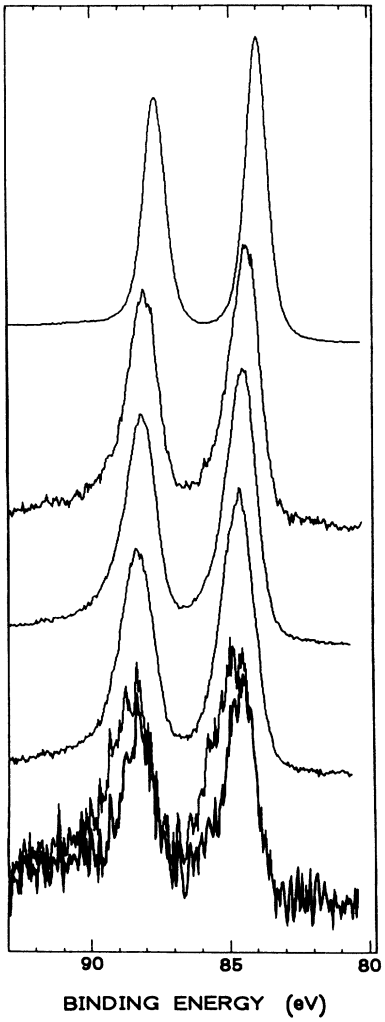

FIG. 1. Au 4$f_{7/2}$ spectra for mass-selected Au$_n$ clusters collected upon an amorphous carbon substrate. From top, bulk gold, $n = 33,27,7,5$. The Au$_5$ spectrum is shown both as taken and with the higher-energy component stripped out.

coverage, estimated from the Au 4f intensities, agrees with an order-of-magnitude estimate based on the LMIS operating conditions. Because the Au_5 and Au_7 beam intensities were so high that collection times were short, similar comparisons were not made.

A more important concern is that there may have been fragmentation or coalescence of the deposited clusters. This is easily ruled out for the heavier clusters. Such activity would cause a broad size distribution with a coverage-dependent mean. However, while the coverage of Au for the Au_{27} sample is similar to that for Au_7 and ~6 times as high as for Au_{33}, the Au_{27} and Au_{33} spectra are very similar, as we expect, and overall the properties of both the core and the valence spectra vary smoothly with n for $n \geq 7$. Had there been fragmentation and coalescence, the trends would have been disrupted, with the Au_{33} spectra, e.g., having the highest core-level energy and the smallest 5d splitting.[5] Thus while there may be loss or gain of a single atom, these deposited clusters are largely intact.

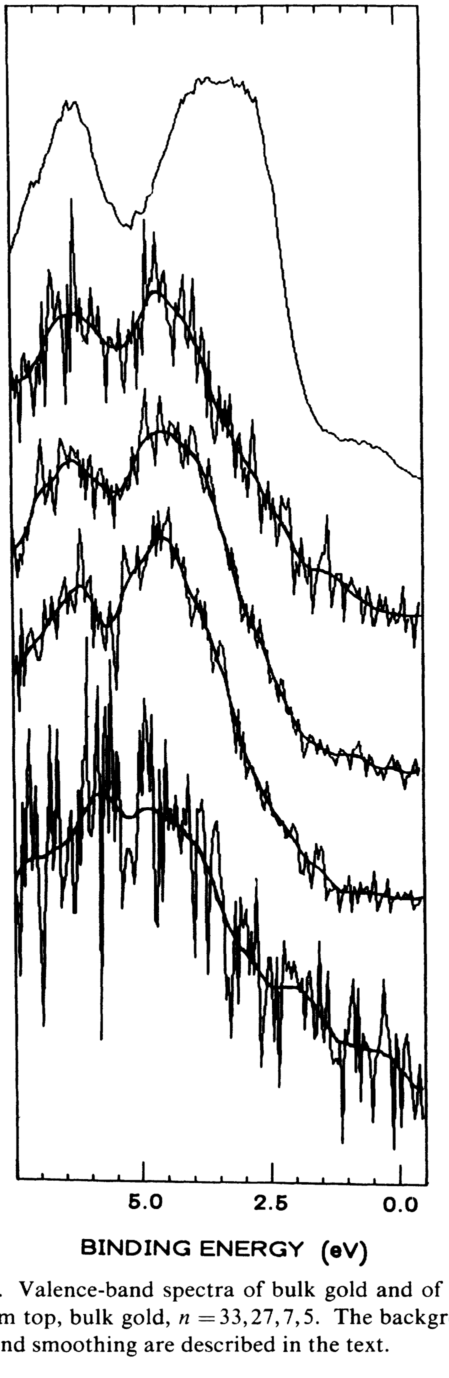

FIG. 2. Valence-band spectra of bulk gold and of Au_n clusters. From top, bulk gold, $n = 33,27,7,5$. The background subtraction and smoothing are described in the text.

With our smallest clusters, Au_5, there is evidence of possible fragmentation in the unusual high-energy shoulder on the Au 4f doublet. This is most likely in the smallest clusters, both because their lower average coordination reduces the cohesive energy for each atom and because the impact energy is dissipated in fewer internal modes. Atoms emitted by small clusters may remain monomers, trapped at the $\sim 3\times 10^{12}$ cm^{-2} nucleation sites that characterize cluster growth on amorphous carbon. Such monomers may be responsible for the shoulder in the (nominal) Au_5 4f spectrum, while the lower-energy component may or may not be due to Au_n clusters, where n is comparable with 5. Little can be inferred from the noisy Au_5 valence spectrum.

For the horizontal axes in Figs. 3 and 4, we have chosen $\langle n \rangle$, the average coordination number of atoms in each cluster. This physically significant parameter allows data for bulk Au on the same plot with data for clusters. Figure 3 shows the splitting between the two main components of the Au 5d bands, which in the smallest clusters approaches the atomic spin-orbit splitting of 1.5 eV. Our value for a thick gold layer is plotted at $\langle n \rangle \approx 11.7$, allowing for the importance of the (lower-coordinated) surface atoms in our spectrum. The open circle at $\langle n \rangle =$nine atoms, for the surface of bulk gold, is inferred from reference 6. As the uncertainty in these data is at least one channel (0.05 eV), the Au_{27} and Au_{33} values are indistinguishable, as expected for similar $\langle n \rangle$ values. Overall the splitting depends rather smoothly on

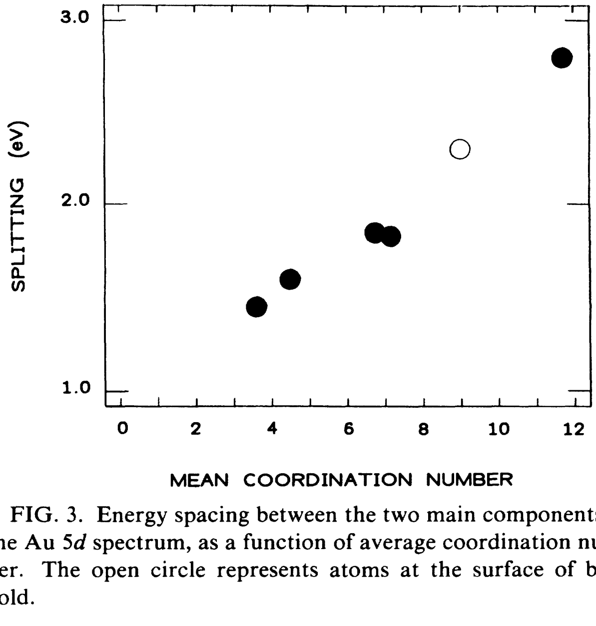

FIG. 3. Energy spacing between the two main components of the Au 5d spectrum, as a function of average coordination number. The open circle represents atoms at the surface of bulk gold.

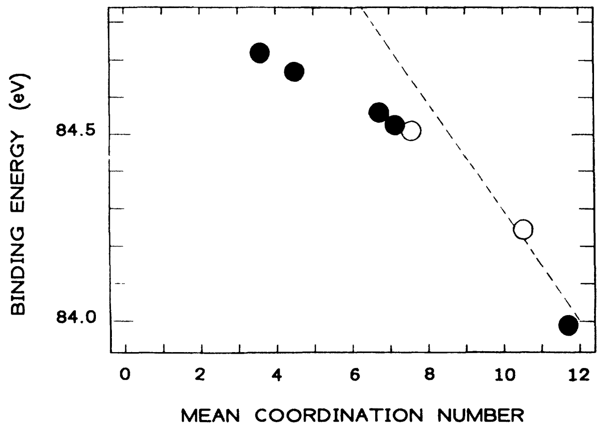

FIG. 4. Au $4f_{7/2}$ binding energy. The open circles are data for clusters obtained by vapor deposition on amorphous carbon; the average coordination numbers for these were determined from their Au 5d splitting using Fig. 3. The dashed line shows the binding energies expected for supported Au clusters allowing only for the Coulomb energy of the positively charged clusters in the photoemission final state.

$\langle n \rangle$, which is somewhat accidental given the inherent uncertainty of >0.05 eV.

Figure 4 shows the centroids of the Au $4f_{7/2}$ peaks as a function of $\langle n \rangle$. Here the low-binding-energy component of the Au_5 spectrum is assumed to represent Au_5 clusters. The thick-gold value is again plotted at 11.7 nearest neighbors, and an energy that is a weighted average of the bulk Au $4f_{7/2}$ energy of 84.0 eV and the surface-shifted component at 0.4 eV less. The open circles represent two coverages of evaporated gold, for which $\langle n \rangle$ was obtained from their 5d splittings using Fig. 3. The dashed curve will be discussed below. Again we note the systematic variation.

The narrowing of the valence d bands with decreasing cluster size has been previously observed in XPS of Au clusters,[5] and indeed of Ag and of Pd clusters.[7] The data in Fig. 3, then, are qualitatively what we expect to see as the decreasing cluster size (and hence $\langle n \rangle$) causes a transition from bulk-metal to atomic or molecular properties. The origins of the Au 4f shifts are more complicated, since the core-electron binding energy E_B is sensitive not only to the initial state changes that influence the valence-band spectra, but also to changes in final-state processes. These influences depend directly on an atom's coordination number, and hence on cluster size. For example, because atoms in a cluster have fewer neighbors than in the bulk, the repulsion between a core electron and the surrounding valence charge is reduced, resulting in a higher E_B, as we see in our Au_n data. There are also final-state effects that can increase E_B. In XPS from a bulk metal, the positive core hole is efficiently screened by conduction charge, lowering the final-state energy and thus reducing the measured E_B. In clusters so small as not to be metallic, this metallic screening is replaced by a less efficient local process (such as polarization of neighboring atoms), and the measured E_B increases. The importance of coordination number to local screening is obvious.

To determine at what size Au clusters change from metallic to nonmetallic behavior, we consider an effect less directly related to coordination number. Data for larger clusters on amorphous carbon show both a core-level shift proportional to $\Theta^{-1/3}$, where Θ is the metal coverage, and a simultaneous shift of the clusters' Fermi edge.[3,5,8] These phenomena result from the delay in neutralization of the photoionized cluster by the semimetal substrate, and the shifts are the Coulomb energy of the charged cluster in the photoemission final state. For an isolated, spherical cluster the Coulomb shift is $e^2/2R$, where R is the cluster's radius,[9] but in supported clusters the core hole and its associated screening charge evoke an image charge in the substrate, reducing the Coulomb shift by about one-half. This reduced shift is shown as the dashed curve in Fig. 4. For large clusters with bulklike electronic structure, this charging energy dominates the core-level shift. The core-level shift deviates significantly from the Coulomb shift in small clusters, when metallic screening is suppressed, either because the cluster becomes nonmetallic or because the Coulomb energy of the surface charge is greater than the difference between metallic- and local-screening processes. In Fig. 4 we see a significant deviation from the Coulomb shift for all of our smaller clusters, and thus infer that the suppression of metallic screening (and possibly the transition from metallic character) occurs from some $n>33$. By a linear extrapolation of our data in Fig. 4 we deduce that the transition occurs at $\langle n \rangle \approx 9.1$, or $n \approx 150$ atoms. This is consistent with the rough estimate one can make of the minimum number of atoms needed for metallic behavior, by requiring significant overlap of the Au s levels and assuming n evenly-spaced levels of width kT in the Au_n s band.

We now comment on the width of the Au 4f peaks. Besides being on average reduced from the bulk value, the coordination number of an atom varies strongly with position in a cluster. Since E_B depends on coordination number, this results in some broadening of the Au 4f peaks relative to bulk gold. However, the observed widths are much greater than we would estimate from the coordination dependence seen in Fig. 4. This extra broadening may be due to phonon excitations, which contribute a Gaussianlike broadening to core line shapes for all materials, especially nonmetals. Such broadening may be enhanced if, in these very small clusters, displacement of the atoms in the initial state requires little energy while in the final state the energy of the photoionized atom has a much stronger position dependence.

In conclusion, our XPS data show clearly that we have succeeded in collecting size-selected metal clusters on a substrate. This is important for future materials applications of cluster beams, and allows the study of fundamental electronic properties of clusters. We deduce that the small clusters are not metallic, and that the transition from metallic to local screening occurs at a cluster size of ~ 150 atoms. Although this transition can be observed for clusters prepared as usual by vapor deposition, our data for size-selected clusters establish the normalization for the size scale, which is otherwise uncertain by ~30%. The core-level spectra show broadening beyond that expected from the variation of coordination within a cluster, which broadening we suggest is a final-state effect.

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