Photoelectron spectroscopy of Al$_{32000}^-$: Observation of a "Coulomb staircase" in a free cluster

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Using a recently developed experimental setup we have measured UV ($h\nu = 6.42$ eV) photoelectron spectra of free size-selected cold aluminum cluster anions with up to 32 000 atoms. The spectra exhibit stairlike structures, which result from a superposition of the spectra of different charge states due to the detachment of several electrons from each cluster. The ionization potentials obtained this way allows one to determine the charging energy of the particle as well as the work function of the cluster material.

The charging energy of nanoparticles is of general interest as it is plays a crucial role, e.g., in single electron electronics. One experiment where this energy can be directly measured is tunneling spectroscopy of isolated supported nanoparticles using a scanning-tunneling microscope.[1] Here the different energies of different charge states of the small particle lead to a stepwise increment of the current as a function of the bias voltage, which is colloquially called a "Coulomb staircase." Comparison of the charging energies obtained with calculated values is, however, often not easy due to the strongly nonspherical shape of the particles studied and due to the influence of the surface.

It is therefore desirable to study free particles, and indeed a great number of experiments has been done on size-selected free clusters to study their ionization potentials and electron affinities (earlier reviews are given by de Heer[2] and Meiwes-Broer;[3] for a theoretical treatment see Seidl *et al.*,[4,5] and references therein). Two techniques have been mainly used: photoionization efficiency measurements on neutral particles and photoelectron spectroscopy on negatively charged ones. Size-selective photoionization studies have already been done on particles in the nanometer-size range.[6] The determination of ionization potentials, however, turned out not to be trivial in this case as detailed assumptions about the shape of the ionization cross section at the threshold are necessary in order to evaluate the data.[7] Photoelectron spectroscopy, in principle, allows a much more direct determination of ionization potentials; nevertheless up to now it has only been applied to rather small particles. Aluminum clusters, for example, have been studied in detail,[8–11] but only for sizes with 1–162 atoms. The largest cluster for which a photoelectron spectrum has been published to our knowledge is Cu$_{410}^-$.[12]

Here we present photoelectron spectra of much larger free metal particles. Such big particles are interesting for two reasons: first they should have a rather continuous, almost bulklike electronic density of states, which means that electronic shell effects can be neglected. This facilitates the study of the general size dependence of the properties in question. Second, and more importantly here, their charging energy is so small that the ionization potentials of several charge states can be determined simultaneously, as will be described below.

The experiments were made using an experimental setup which will be described in detail in a forthcoming publication. The clusters are produced in a standard gas aggregation source.[13] Aluminum atoms are sputtered by a magnetron discharge into a stream of liquid-nitrogen-cooled rare gas, which is a variable mixture of helium and argon. Positively and negatively charged clusters are formed, the average size of which can be varied between a few atoms and some hundred thousand atoms. After passing a variable iris aperture and a skimmer the negatively charged ions are accelerated into a tandem-reflectron time-of-flight mass spectrometer, in which a multiwire mass gate between the two reflectors allows one to select clusters of a certain mass with a selectivity of up to $m/dm = 2000$. In the case discussed here a relatively broad selection window of about 1% width has been chosen for intensity reasons; the actual cluster size selected therefore was, for example, $32\,000 \pm 150$. The selected clusters are irradiated by a laser pulse from an ArF-excimer laser (193 nm), and the kinetic energies of the detached electrons are measured with a magnetic bottle-type electron spectrometer. The energy scale is calibrated with the known photoelectron spectrum of Pt$^-$ ions.

Examples of the photoelectron spectra obtained are shown in Fig. 1. The upper graph shows the result for a negatively charged aluminum cluster with about 2000 atoms; the lower graph the result for one with about 32 000 atoms. In the spectrum of the smaller cluster one can see an onset at a binding energy of approximately 3.9 eV, which is the electron affinity of the cluster (at its finite temperature). At higher binding energies a series of steps appears, with a step width of roughly 0.7 eV. These steps can be explained as follows: at the laser fluence used here (about 1 mJ/cm^2) the clusters absorb several photons. After almost each absorption an electron is emitted, until a maximum charge state is reached for which the ionization potential is higher than the photon energy. The photoelectron spectra of all these ionization processes add up to the result as shown in Fig. 1. The upper spectrum for example is a superposition of the spectra of Al$_{2000}^-$, Al$_{2000}$, Al$_{2000}^+$, and Al$_{2000}^{2+}$. In the case of the larger cluster even seven different charge states contribute, from the singly negatively charged cluster up to the fivefold positively charged one. The height of the steps in the spectra is a measure for the total number of electrons emitted for each ionization process and therefore for the probability to reach a certain charge state. Equal step heights would mean that all clusters reach the maximum charge state. An increase of the step heights with increasing charge state as observed here
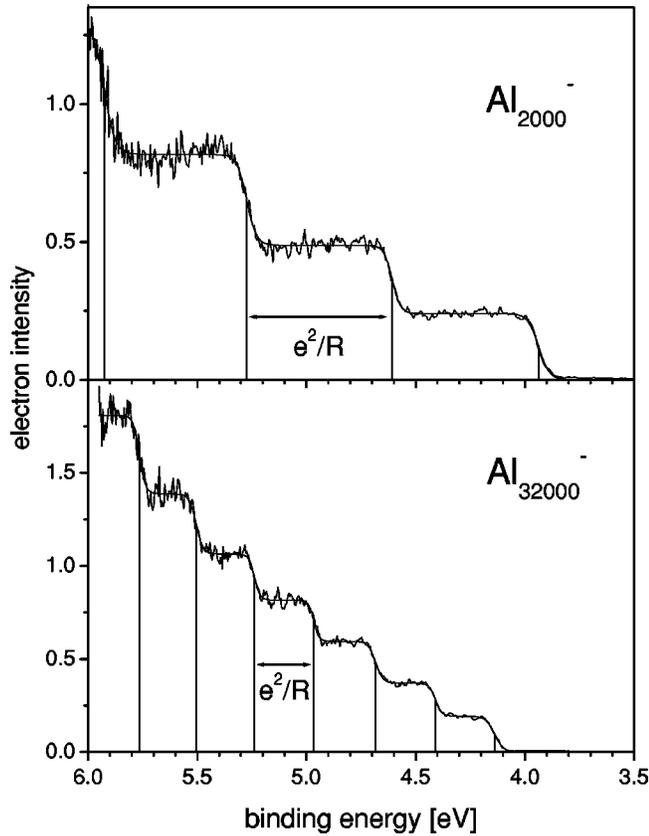
FIG. 1. Photoelectron spectrum of free size-selected $Al_{2000\pm10}^-$ and $Al_{32\,000\pm150}^-$ at a photon energy of $h\nu=6.42$ eV. Due to multiple electron emission the ionization thresholds of four different charge states of the smaller cluster can be observed (from Al_{2000}^- to Al_{2000}^{2+}), and of seven different charge states of the larger cluster (from $Al_{32\,000}^-$ to $Al_{32\,000}^{5+}$). The steps have been fitted with Fermi distributions corresponding to a temperature of 150 K, which have been broadened by the spectrometer resolution.

cannot be real. Indeed it is an experimental artifact: the collection efficiency of our magnetic bottle spectrometer is higher for electrons with low kinetic energies. Obviously at the laser intensity used the ionization probability is close to unity for all charge states. A decrease of the laser intensity leads to a decrease of the relative contribution of the higher charge states, as can be expected from the statistical nature of this multiphoton absorption process.

We will now discuss the step positions in detail. A common approximation for the ionization potentials (IP) of the different charge states of a spherical metal cluster is given by[5]

$$IP(Z)=W_\infty+(Z+\alpha)\frac{e^2}{R+\delta}. \qquad (1)$$

Here R is the radius of the cluster as calculated from its density and weight, Z its charge state, and W_∞ the work function of the bulk. δ is a correction of the cluster radius due to the electron "spillout" into the vacuum, and α incorporates the quantum corrections of the bulk work function for a spherical particle. Classical theory[5] gives $\delta=0$ and α
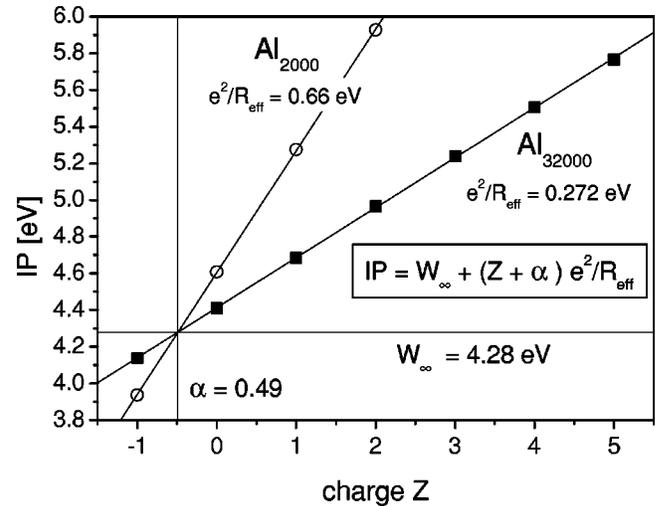

FIG. 2. Measured ionization potentials of Al_{2000} and $Al_{32\,000}$ as a function of their charge states. The linear fits of the data give the charging energy per elementary charge and thereby the effective radius of the clusters; the crossing point of the fit lines yields the bulk work function and the coefficient α. These latter values have to be taken as preliminary as the clusters exhibit densities more than 10% lower than the bulk. See text for details.

$=1/2$. Quantum calculations[5] for metal spheres having the same electron density as aluminum obtain values between $\alpha=0.42$ and $\alpha=0.45$. For δ calculated values strongly depend on the model used as well as on the surface structure. For aluminum, Kiejna,[14] e.g., obtains values between $\delta=0.54$ Å and $\delta=1.1$ Å.

In order to test Eq. (1) we have fitted the steps with Fermi distribution functions, which have been broadened by the spectrometer resolution (~60 meV at the position of the first step). One outcome of this fit is a value of about 150 K for the temperature of the clusters, which demonstrates that indeed very cold clusters are produced by the gas aggregation source. The main result of the fit is of course the step positions (that is, the turning points of the distributions), which have been plotted in Fig. 2 as a function of the cluster charge state. An almost perfect linear dependence can be seen for both cluster sizes, which shows that the charging energy per elementary charge is independent of the charge state. Linear fits of the data points allows one to determine several parameters:

(i) The slopes of the curves give the cluster charging energies. From these the cluster densities can be obtained, if an assumption about the unknown "spillout" parameter δ is made. In order to get an estimate for the range of the resulting densities we have inserted the two limiting values given above. Assuming a value of $\delta=0.54$ Å one obtains densities of 2.25 g/cm^3 and 2.38 g/cm^3 for Al_{2000} and $Al_{32\,000}$, respectively. For $\delta=1.1$ Å one obtains 2.43 g/cm^3 and 2.46 g/cm^3. These values are close to, but still significantly lower than, the bulk density of aluminum (2.70 g/cm^3).[15] This deviation could result because of several reasons. A trivial reason would be a wrong calibration of the mass selector, but this has been carefully checked and can be

excluded.[16] Second, the clusters could really have a lower density than bulk aluminum. This, however, would be in contradiction to the general observation that metal nanocrystals exhibit a contraction of the lattice.[17,18] A third reason could well be a strongly nonspherical shape of the particles, in which case Eq. (1) would have to be modified. This question will hopefully be clarified in the near future by electron microscopy on deposited clusters of the same type.

(ii) The crossing point of the two lines yields the bulk work function W_∞ as well as the coefficient α. A value of 4.28 (± 0.03) eV for the work function is obtained, which is exactly the value given in the literature for polycrystalline aluminum.[19] The work function of the cluster should be similar to that of the polycrystalline surface as in both cases it represents an average over several different crystal faces. Nevertheless this perfect agreement could just be a coincidence, as first the value we have obtained has to be taken as preliminary until the question of the cluster structure is clarified, and second as measured bulk work functions especially of reactive surfaces do have quite an experimental uncertainty. Although Eastment and Mee[19] estimate the error of the value given above to be only ± 0.01 eV, in the same publication a value of 4.20 ± 0.03 eV is given for Al(100), which deviates by 0.21 eV from the newer value of 4.41 ± 0.02 eV.[20,21]

This shows that it might be useful to have an alternative method to measure the bulk work function of reactive metals. As has been demonstrated here, photoelectron spectroscopy of very big clusters can, in principle, obtain precise values for the work functions of such materials. Because the production of clusters is often much easier than the preparation of a clean surface in ultrahigh vacuum, this represents an unexpected application of cluster spectroscopy. Indeed it has just recently been shown that photoionization efficiency studies of free, unselected nanoparticles can be used for this purpose.[22] The use of photoelectron spectroscopy on very large size-selected clusters might be even more promising, as no assumptions about the particle size distribution or the shape of the ionization cross section have to be made.

For α a value of 0.49 ± 0.04 is obtained. This is close to the predicted values; but again due to the unclear structure of the clusters this value has to be taken as preliminary. Nevertheless the results show that the experimental method in principle, is capable of yielding precise values for α, which hopefully will be achieved in the near future.

In summary, photoelectron spectra of free aluminum clusters with about 2000 and 32 000 atoms have been measured. A staircaselike structure has been observed in both cases, which reveals the stepwise increase of the charging energy per elementary charge. Evaluation of the data yields the ionization potentials of several different charge states of the clusters, which allows one to determine the work function of the cluster material as well as its quantum correction for a curved surface.

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[16] Up to size 2000 single cluster sizes can be resolved in the mass spectrum, which yields an unambiguous mass calibration. For the larger clusters this calibration has to be extrapolated. Here a problem can arise from the significant kinetic energies large clusters have due to their acceleration by the expanding gas at the exit of the aggregation source. In our setup the clusters are decelerated to energies of a few eV before being extracted into the mass spectrometer. It has been checked whether this remaining kinetic energy has a significant influence on the mass calibration; this is not the case.

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