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Photoelectron spectroscopy of sodium clusters: Direct observation of the electronic shell structure

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Size selected, positively charged sodium clusters (Na_n^+, $n=31$–500) have been studied by photoelectron spectroscopy using photons of 6.42 eV. The spectra clearly exhibit the expected shell-like electronic density of states that in this size range up to now has only been observed indirectly. The overall agreement of the measured structure with jellium model predictions is excellent. One prominent exception is Na_{55}^+ for which jellium models predict a prolate shape, while here strong evidence for an icosahedral structure has been found.

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I. INTRODUCTION

In 1984, Knight and co-workers [1] observed, by mass spectroscopy of sodium clusters, that some cluster sizes have a higher stability, which was the first experimental evidence for electronic shells in metal clusters. This shell structure has a simple origin: a metal cluster can be seen as a spherical box filled with free electrons. The electrons occupy orbitals that can be characterized by a radial quantum number and an angular momentum $(1s,1p,1d,2s,1f,\ldots)$. For each angular momentum l there are $(2l+1)$ degenerate orbitals, which together constitute a shell. With increasing cluster size more and more of the orbitals are occupied; completion of shells leads to clusters with particular properties as, for example, enhanced stability. This is most pronounced for clusters with a large gap between the completed and the next unoccupied shell, which are the so-called “magic sizes.” The validity of this concept has been demonstrated by a wealth of experiments on a broad range of metal clusters. In the case of sodium, electronic shell effects have been seen in cluster abundance [1], binding energies [2,3], ionization potentials [4], and photoabsorption cross sections [5–8].

An open question was, however, to what extent the overall electronic structure of sodium clusters exhibits shell-like modulation. Real clusters, even “magic” ones, never have the perfect spherical symmetry assumed above, but always an atomic structure that belongs to a lower symmetry group. This will lift the degeneracy of the angular-momentum states and, therefore, lead to a broadening or even blurring of the levels, depending on the strength of the coupling between electrons and ions. As sodium is the best representative of a free electron metal [9], it should exhibit the least perturbed electronic shell structure of all metal clusters. This is supported by a number of theoretical studies. Most calculations are based on the quasi-free-electron or jellium model [8,10]. This model neglects the atomic structure of the cluster and, therefore, inevitably leads to a shell-like density of states, which is only perturbed by cluster deformations. But also the models that take the atomic structure explicitly into account have obtained clearly shell-like density of states [11,12]. These predictions could not be compared to experiments so far, as photoelectron spectra, which (in principle) give a direct map of the electronic density of states, were not available for clusters big enough to contain several shells. Photoelectron spectra have been published only for Na_n^- with $n\leq 7$ [13,14], and in the kindred potassium case for clusters with $n\leq 19$ [15].

Clusters made of nonalkali metals have been studied by photoelectron spectroscopy much more intensively, but for these the interpretation turned out to be not so easy. For aluminum clusters, evidence for electronic shell closings could be obtained [16]; the observed density of states, however, does not really resemble the expected shell structure. This is probably due to the strong interaction of the electrons with the triply charged background ions [16]. In the case of noble-metal clusters, jellium-like electronic densities of states have been observed [17,18], but here the presence of the low-lying d bands leads to deviations from free-electron behavior [19]. This lack of a characterization of a “really” simple metal was the motivation for the photoelectron spectroscopy study of sodium clusters presented here.

II. EXPERIMENT

The clusters have been produced in a gas aggregation source such as the one used in earlier optical spectroscopy experiments [7,10]. Briefly, sodium is evaporated from a crucible into a liquid-nitrogen-cooled stream of helium having a pressure of about 0.5 mbar. The clusters are ionized by a gas discharge burning in the crucible, and thermalized afterwards by collisions with the cold He gas. They are mass selected and inserted into a magnetic bottle-type time-of-flight photoelectron spectrometer. Here they are decelerated by a high-voltage pulse, and irradiated by photons from an ArF-excimer laser ($h\nu=6.42$ eV). Due to the very low photoionization cross sections at this energy (about 0.2 Å^2 for Na_{100}^+) the relative contribution of background electrons was much stronger than for other cluster materials and amounted to values from 10% to 60% of the total electron intensity. Therefore, cluster and background photoelectron spectra (PES) were alternately acquired and subtracted. The resolution of the photoelectron spectrometer is roughly linear with the kinetic energy of the electrons; it is better than 100 meV at a kinetic electron energy of 2.4 eV (which corresponds to a binding energy of 4 eV). All spectra have been smoothed by convolution with a rectangle function of 60 meV width. The spectrometer has been calibrated by the known PES of Pt^-, which leads to an absolute error of the energy scale of less than 30 meV.

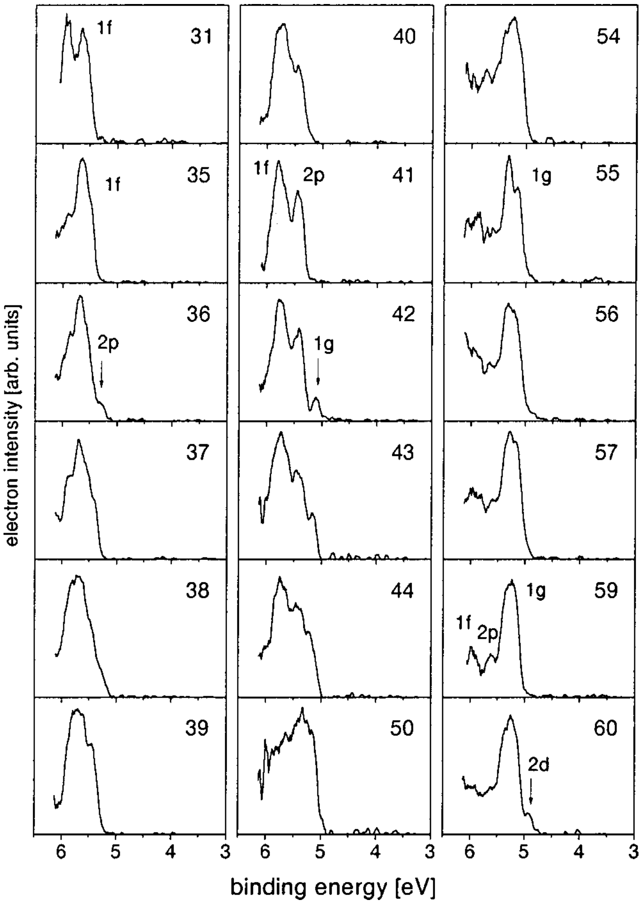

FIG. 1. Photoelectron spectra of Na_n^+ ($n=31$–60) at 6.42 eV photon energy. The peak labels give the quantum numbers of the corresponding electron shells. Shell closings with subsequent openings of additional shells can be seen for $n=35$ (34 electrons), $n=41$, and $n=59$. The exceptional sharpness of the Na_{55}^+ spectrum is an indication for a spherical symmetry of this cluster.

III. RESULTS AND DISCUSSION

The spectra obtained are shown in Figs. 1 and 2. We will first discuss their general structure in view of shell closings and subsequent appearances of additional shells, and then will discuss some spectra in more detail. The smallest cluster examined, Na_{31}^+, has a $1s^2$ $1p^6$ $1d^{10}$ $2s^2$ $1f^{10}$ electronic structure in the spherical jellium model [8], i.e., there are four electrons missing for a complete filling of the $1f$ shell. This shell is filled for Na_{35}^+. Therefore in Na_{36}^+ one electron has to occupy the higher $2p$ shell, which should lead to an additional peak in the PES. Indeed a small shoulder appears at the onset of the spectrum. The $2p$ shell gets filled up between Na_{36}^+ and Na_{41}^+. At Na_{42}^+ one electron has to occupy the higher $1g$ shell, which again leads to the appearance of a different peak in the spectrum. Here the gap between the additional shell and the one filled before is much more pronounced than in the case of Na_{36}^+; this is the reason why Na_{41}^+ is a so-called magic size (exhibiting a much higher binding energy than other cluster sizes), but Na_{35}^+ is not.

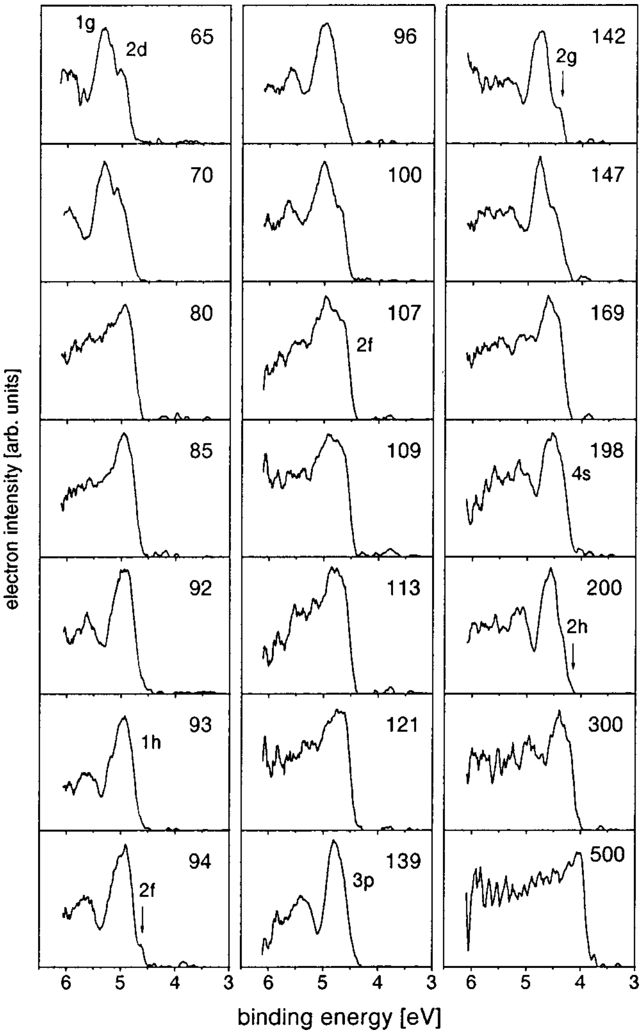

FIG. 2. Photoelectron spectra of Na_n^+ ($n=65$–500) at 6.42 eV photon energy. Shell closings with subsequent openings of additional shells can be seen for the "magic" sizes $n=93$ and $n=139$, and, to a lesser extent, around the "magic" size $n=199$. The broad and featureless spectra of the intermediate sizes indicate a deformation of these clusters.

The $1g$ shell is filled at Na_{59}^+; at Na_{60}^+ the $2d$ shell starts to be filled, and again a quite pronounced energy gap is visible, which is responsible for the high stability of Na_{59}^+. The filling of the $1g$ shell is accomplished for Na_{69}^+; at Na_{70}^+ the $3s/1h$ shell starts to be filled (the $3s$ and the $1h$ shells are almost degenerate according to calculations [20] and will probably overlap). No new peak is visible here, however, which means that the energy gap is small again; this could be expected, as Na_{69}^+ is not a magic number. The same applies for the predicted shell closings at atom numbers 107 ($2f$) and 133 ($1i$) (shell sequence taken from [20]). Shell closings with a visible gap can instead be observed for the two well-known magic sizes Na_{93}^+ ($3s/1h$) and Na_{139}^+ ($3p$). Even in the case of Na_{200}^+ a small shoulder is discernible at the onset that might be due to the closing of the $4s$ shell at Na_{199}^+ and the opening of the $2h$ shell. A shell-like modulation of the spec-

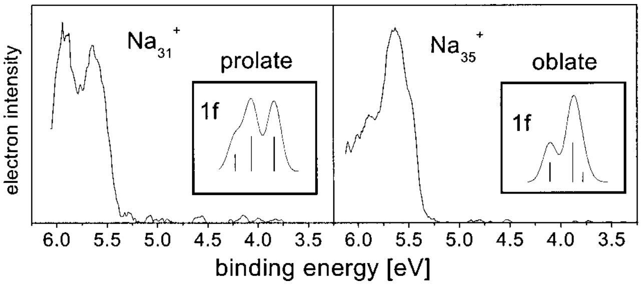

FIG. 3. Spectra of Na_{31}^+ and Na_{35}^+. In the insets the structure of the $1f$ band is given as predicted by the Clemenger-Nilsson model [21] for deformed sodium clusters with 30 and 34 electrons, respectively. The $1f$ sublevels have been broadened by Gaussians to make the comparison easier.

trum is still visible for Na_{300}^+; only in the case of Na_{500}^+ it is not clearly recognizable anymore.

We will now discuss some spectra in more detail. In Fig. 3 the spectra of Na_{31}^+ and Na_{35}^+ are shown again. Both exhibit a feature that, as explained above, can be identified as the $1f$ shell. In the case of Na_{31}^+, however, this is split into a double peak, while Na_{35}^+ only exhibits a narrow peak with a high-energy shoulder. The reason for this is simple: as is well known from calculations and from photoabsorption experiments [6,7], Na_{31}^+ has a prolate shape, while Na_{35}^+ is oblate.

These different deformations lead to different energies of the $1f$ sublevels. In the insets of Fig. 3 the shapes of the resulting $1f$ bands are indicated, as predicted by the Clemenger-Nilsson model [21]. The correspondence with the measured peak structures is very good, which is a remarkable confirmation of the free-electron model. The next example is shown in Fig. 4. Here the spectra of Na_{41}^+, Na_{42}^+, and Na_{59}^+ are compared to the most comprehensive calculation of the electron density of states of neutral Na_{40} [12], which is isoelectronic to Na_{41}^+. Only the results for a spherical Na_{40} are shown here; the results for an octupole deformed isomer, which the authors found to be energetically favorable, are practically identical.

The agreement of the Na_{41}^+ spectrum with the calculation is excellent. The two visible peaks can safely be identified with the $1f$ and the $2p$ shell obtained in the calculation. The same applies for the Na_{42}^+ spectrum, where both peaks appear again with almost identical position and width. The position of the additional $1g$ orbital, however, seems to disagree with the calculation: the gap between the $1g$ shell and the $2p$ shell is smaller than predicted. Even if one takes into account that the full $1g$ shell actually is a band of states occupied by 18 electrons, which means that the first electron in this shell will occupy a state located at the onset of the band, there remains a discrepancy. A reason for this could be that the $1g$ shell is either broader or lies closer to the $2p$ shell than predicted by the calculation. Inspection of the spectrum of Na_{59}^+ gives some evidence for the second point: if one identifies the two small peaks visible at 5.62 eV and 5.94 eV binding energy as the $1f$ and the $2p$ shell, the position of the now fully occupied $1g$ shell with respect to the $2p$ shell is only slightly shifted to higher energies, which means that the energy difference between the $1g$ shell and the $2p$ shell is still significantly smaller than in the calculation for Na_{40} (even if one takes into account that the $1g$ and the $2p$ shell move closer together by about 20% between Na_{40} and Na_{59}^+ due to the increase of the cluster diameter). A comparison of the spectra of Na_{42}^+ and Na_{59}^+ with the calculated electronic structure of a smaller cluster is, of course, not fully appropriate; a comparison with similar high quality results for the cluster sizes actually studied would be much more significant. Such calculations, however, are not available at the moment. This is unfortunate, as the measured spectra could serve as sensitive tests for this type of numerical results.

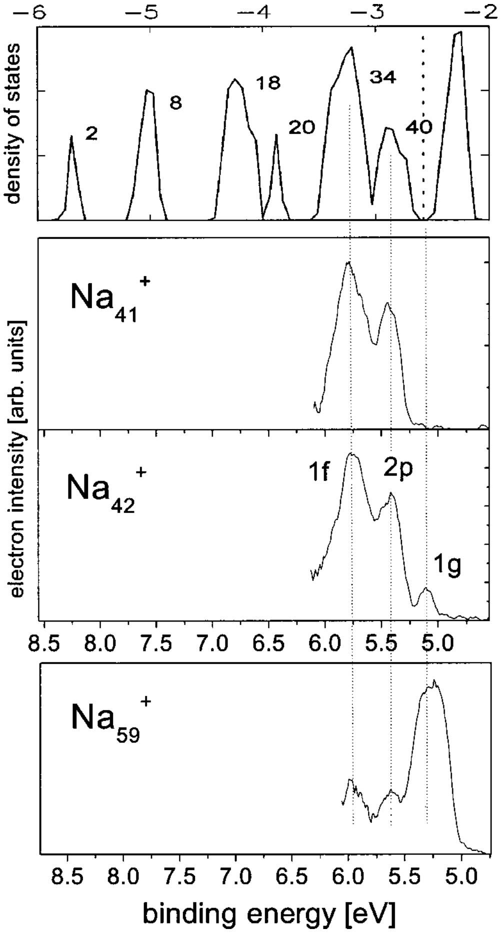

FIG. 4. Spectra of Na_{41}^+, Na_{42}^+, and Na_{59}^+ compared to a simulation of the electron density of states for a "spherical" neutral Na_{40} [12] (the peak at lowest binding energy indicates the unoccupied $1g$ shell). The energy scales of the spectra have been shifted in order to align the observed peaks. Excellent agreement is obtained for the calculated and measured splitting between $1f$ and $2p$ shell.

Another example of a clearly visible electron shell structure is shown in Fig. 5. Here the spectrum of Na_{93}^+ is compared to the shell energies obtained in a jellium model calculation of a neutral Na_{92} [20]. One can not only identify the $1h$ (the large peak) and the $1g$ shell (the smaller one), but even the $2d$ shell is visible as a shoulder of the large peak.

A straightforward identification of the electronic shells as in the case of Na_{93}^+ is, in general, only possible for the magic, spherical clusters. The nonmagic, deformed clusters exhibit

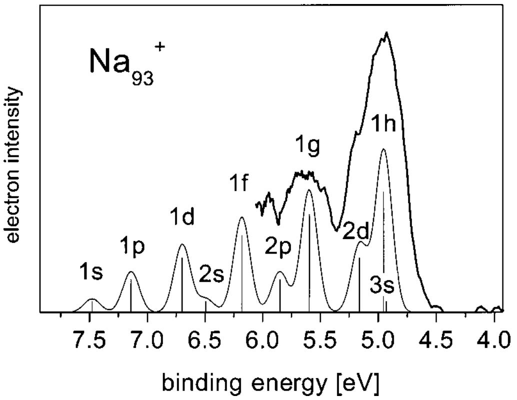

FIG. 5. Spectrum of Na_{93}^{+} compared to a jellium model calculation of the energy-level structure of a neutral Na_{92} [20]. The energy scale of the latter has been shifted and the energy levels have been broadened by Gaussians in order to facilitate the comparison. The $1h$, $2d$, and $1g$ shell can be clearly identified in the measurement.

much less structured spectra (extreme examples being Na_{80}^{+} and Na_{113}^{+}). Consequently the next cluster sizes with well structured spectra are the magic Na_{139}^{+} and, to a lesser extent, the almost magic Na_{198}^{+} and Na_{200}^{+}. Even Na_{300}^{+} still exhibits a shell-like electronic structure; one has to go as far up in size as to Na_{500}^{+} to obtain a more bulklike, almost smooth spectrum.

It is remarkable that sodium clusters with 300 atoms still exhibit structured spectra at all. One can expect that even within the jellium model at some size there will be so many levels that one obtains an almost continuous state density. For a cluster with 300 atoms, however, this is actually not yet the case. In Fig. 6 the density of states for a cluster with 306 electrons is shown as obtained from a simple spherical box potential model (infinite wall potential filled with 306 noninteracting electrons). This model, of course, cannot reproduce the exact level energies; nevertheless it should give a fairly good estimate for the level density. When comparing the results with the experiment one should keep in mind that such a hard wall potential overestimates the Fermi energy of the electrons, which means that the energy axis has to be scaled down to allow a quantitative comparison (the theoretical Fermi energy of bulk sodium is 3.24 eV [9]; the valence-band width as measured by photoelectron spectroscopy is 2.65 eV [22]). In the lower curve all levels have been broadened by Gaussians with a width of 50 meV, which allows to see details of the level structure; in the upper curve Gaussians with a width of 400 meV have been used, which corresponds to the width of the first peak visible in the spectrum of Na_{300}^{+}. Despite this relatively strong broadening the shell structure indeed remains clearly visible.

All this demonstrates the very weak coupling between the electrons and the ionic background in the sodium clusters, and represents a strong justification for the use of the jellium model.

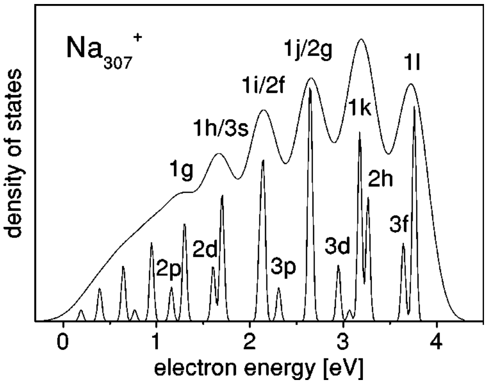

FIG. 6. Simple model calculation for a Na_{307}^{+}: level structure of a spherical box potential (radius 14 Å) filled with 306 noninteracting electrons. Note that this hard wall potential overestimates the Fermi energy (the bulk value of sodium is $E_f = 3.24$ eV [9]). The calculated levels have been broadened by Gaussians of 50 meV width (lower curve) and 400 meV width (upper curve). Despite this relatively strong broadening the electronic shell structure remains clearly discernible.

There is, however, one example where the jellium model fails. In this model Na_{55}^{+} is predicted to be nonspherical due to its partially filled $1g$ shell. Its photoabsorption cross section seems to give some evidence for such a deformation [6,7]. The PES of Na_{55}^{+}, however, exhibits very sharp features; in fact, the narrowest peaks of all examined clusters, which strongly hints towards a spherical geometry. Indeed calculations, which take the atom positions into account, obtain an icosahedral structure for this cluster [23,24]. In Fig. 7 we compare the measured spectrum of Na_{55}^{+} with that calculated for a neutral Na_{55} [24]. The agreement is excellent; the splitting of the $1g$ shell is well reproduced, and one could

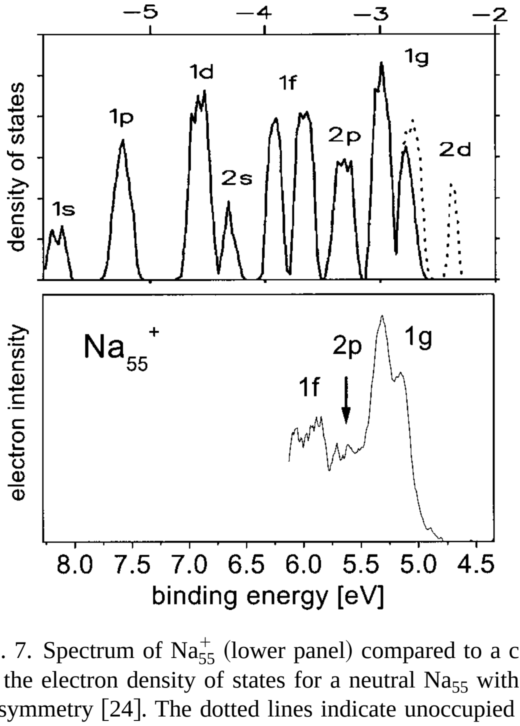

FIG. 7. Spectrum of Na_{55}^{+} (lower panel) compared to a calculation of the electron density of states for a neutral Na_{55} with icosahedral symmetry [24]. The dotted lines indicate unoccupied levels. In order to align the observed structures, the energy scales have been shifted. The excellent agreement between the calculated and the measured spectra represents strong evidence for an icosahedral structure of the Na_{55}^{+}.

even venture to claim the observation of the predicted $1f$ level splitting. Both the exceptional narrowness of the observed peaks and the agreement with the calculated spectrum, therefore, represent very strong evidence for the icosahedral structure of Na_{55}^{+}.

The fact that both neutral and positively charged Na_{55} have the same icosahedral structure represents an interesting exception: in general, the properties of sodium clusters are determined only by the number of electrons contained, but here it is obviously the number of atoms which matters.

IV. CONCLUSIONS

In summary, the electronic shell structure of sodium cluster ions has been directly observed by photoelectron spectroscopy. Shell closings and openings of additional shells can be clearly seen up to cluster sizes containing 200 atoms; the overall agreement with the jellium model is excellent. One exception to the jellium model has been found: Na_{55}^{+} has an icosahedral structure.

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