P H Y S I C A L   R E V I E W   L E T T E R S

# Structure Determination of Medium-Sized Sodium Clusters

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Sodium cluster anions $Na_n^-$ with $n = 39$–350 have been studied by low temperature photoelectron spectroscopy and density functional theory (DFT). The highly structured experimental spectra are in excellent agreement with the electronic density of states (DOS) of the DFT lowest energy structures. Even for the largest sizes, a pronounced sensitivity of the DOS on fine geometric details could be observed, allowing for a reliable identification of a specific icosahedral growth motif. The intermediate sizes between the closed-shell Mackay clusters with 55, 147, and 309 atoms form by growth of overlayers, which often exhibit a twist deformation with respect to regular (Mackay-type) ones.

Part of the great promise of nanotechnology is based on the fact that small particles can exhibit a very different behavior than the corresponding bulk material [1–4]. The properties of nanoparticles and clusters are dominated by electronic and geometric finite size effects, that is by the discretization of the electronic density of states and the surface induced tendency towards nonbulklike crystalline structures. Electronic and nuclear structure are strongly intertwined; a crucial first step for the understanding of small particle properties therefore is the determination of their geometrical structure. Consequently, an enormous effort, both experimental and theoretical, has been undertaken in the last two decades to unravel the building principles of clusters and nanoparticles. A variety of smaller clusters (with up to a few tens of atoms) have been characterized by the combination of high level (first principle) calculations with high resolution spectroscopy [4], and, very recently, with electron diffraction studies of trapped clusters [5,6]. For larger clusters with sizes up to the nanoparticle regime (where particles can be directly imaged by electron microscopy [7]), however, significant information is scarce. Practically no detailed experimental data are available, and in the huge number of theoretical studies global structure optimizations have only been done using lower level theory (e.g., using semiempirical classical potentials). Because of the computational cost high level theory was (and still is) restricted to the optimization of chosen structures or symmetries. The uncertainties connected to both approaches definitely require a validation of the structural predictions by experimental means.

Here we present a combined photoemission and density functional theory (DFT) study on sodium clusters, which is the first comprehensive determination of cluster structures in this intermediate size range. Sodium was chosen because it is the best representative of a free electron metal [8], making its smaller clusters close to ideal simple quantum systems [9–11]. It is an open question at what size sodium particles start to exhibit a more "classical" behav-

ior, where structures are rather determined by atomic packing schemes [12]. Furthermore there are many indications that the cluster geometries have a decisive influence on their melting behavior [13–18]; an unambiguous determination of these structures, however, has yet to be done.

Our experimental setup is the same as used in earlier studies [11,19,20]. Sodium clusters produced in a gas aggregation source get negatively charged by a pulsed gas discharge inside the aggregation tube and after expansion into the vacuum are inserted into a liquid nitrogen cooled rf octupole ion trap, where they are thermalized by background helium collisions to about 100 K. Note that in the uncooled front part of the trap the clusters get temporarily heated, which potentially induces some annealing of the cluster structures. After pulsed extraction from the trap the clusters are size selected in a reflectron time-of-flight mass spectrometer (with a selectivity of $m/dm = 2000$), decelerated and finally irradiated by a XeCl-excimer laser pulse ($h\nu = 4.02$ eV) in the interaction region of a magnetic bottle type time-of-flight photoelectron spectrometer.

In Fig. 1 examples of the measured sodium photoelectron spectra (PES) in the size range $n = 55$–350 are shown. We present here spectra of the sizes which exhibit the most prominent features (indicated by underlined numbers) and additionally spectra of neighboring or intermediate sizes for comparison.

Up to the largest size the spectra are highly structured and exhibit a strong size dependence. One well known feature of simple metal clusters, the electron shell structure, can be immediately observed. For $Na_{58}^-$, $Na_{92}^-$, and $Na_{138}^-$ an additional small peak appears at the threshold, which indicates the appearance of a new shell (of $2d$, $2f$, and $2g$, respectively). This has been discussed already for the kindred case of $Na_n^+$ clusters [11], so we will not go into detail here. We want to focus on the observation that some sizes exhibit much more structured spectra than neighboring sizes, as, for example, $Na_{71}^-$ or $Na_{178}^-$. Sharp peaks in the spectra indicate highly degenerate states, which in turn
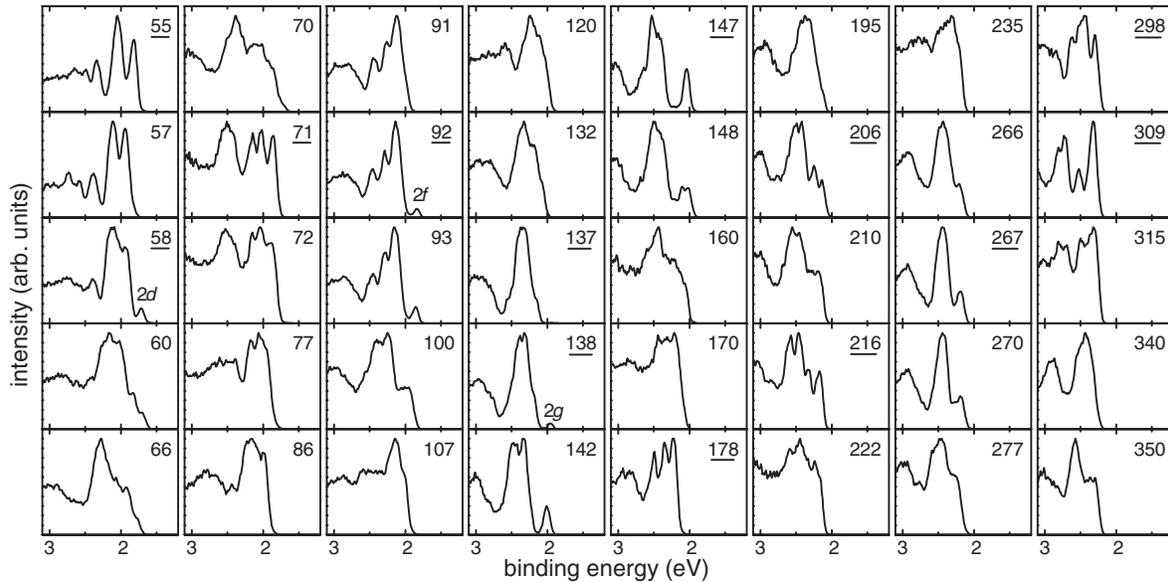
FIG. 1.    Photoelectron spectra of cold ($T \approx 100$ K) sodium cluster anions $Na_n^-$ ($n = 55$–350), measured at a photon energy of 4.02 eV. Underlined numbers indicate sizes with prominent features.

hints at a high symmetry of the cluster structure, as has recently been demonstrated for noble metal clusters [21]. So most probably all of the sizes in Fig. 1 exhibiting highly modulated spectra have some well-ordered geometric structure, and are therefore promising candidates for structure determination. To identify these structures, the photoelectron spectra were simulated with the help of density functional theory. We compare the measured spectra directly to the calculated DOS, which has become a standard method for small clusters [20,22], and turned out to work as well (if not better) for the larger sizes studied here.

We applied the Born-Oppenheimer molecular dynamics method [23] combined with norm-conserving nonlocal pseudopotentials [24] and including self-consistent gradient corrections (PBE-GGA) [25]. The ground state isomers were obtained by optimizing a huge variety of different initial configurations from the Cambridge cluster database [26], which lists the optimum structures for a large range of empirical model potentials. Additional trial structures were obtained by a global structural search employing our Na tight-binding model (similar to the Au model in [27]) and construction ''by hand.'' For each cluster the calculated DOS was shifted to align the binding energy of the highest occupied level with the calculated vertical detachment energy [20]. Finally, the calculated spectra were convoluted with Gaussians of 0.07 eV width in order to facilitate the comparison with the finite resolution experimental spectra.

The results are shown in Fig. 2. In the left and center column the measured spectra are plotted together with the DOS of the lowest energy (or in one case the best fitting) isomer; the structure of these isomers is indicated. In the right column, measured spectra are compared to the DOS

of other (wrong) candidate structures. Note that the comparison with the theoretical DOS is only meaningful down to a binding energy of about 3 eV, as lower lying states in the measured spectra are strongly broadened due to lifetime effects, and as additional features appear here due to two photon effects (electron emission from the neutralized cluster [28]) and inelastic electron scattering.

We will now discuss the structures of the clusters in detail. For $Na_{55}^-$, $Na_{147}^-$, and $Na_{309}^-$ the measured spectra are in very good agreement with the DOS calculated for Mackay icosahedrons with 3, 4, and 5 complete shells of atoms (Fig. 2), which is the ground state structure in the DFT as well as in most empirical potential calculations. Pronounced similarities in the photoemission spectra of the size range $Na_{137}^-$ to $Na_{147}^-$ (Fig. 1) and also $Na_{305}^-$ to $Na_{309}^-$ (not shown) suggest that the Mackay icosahedron geometry is generally maintained for sizes slightly below the closed shell ones. Indeed, for instance $Na_{137}^-$ and $Na_{138}^-$ turn out to be a icosahedral $Na_{147}$ with 10 and 9 vertex atoms missing, respectively (see Fig. 2 left column).

The next size we look at is the before mentioned $Na_{71}^-$. A 71 atom cluster can be produced from a 55-atom Mackay icosahedron by adding a 16-atom cap overlayer. There are two obvious ways in which an overlayer can grow on the surface of a Mackay icosahedron, which are termed Mackay (M) and anti-Mackay (AM) growth modes [29,30]. For both of these structures the calculated DOS is compared to the experimental spectrum in the right column of Fig. 2. Reasonable, but not perfect agreement is obtained. It was recently found that the global minimum structure for $Na_{71}^-$ modeled by Murrell-Mottram (MM) or Gupta potentials is none of these two structures, but an intermediate: the overlayer cap is twisted by 18° with
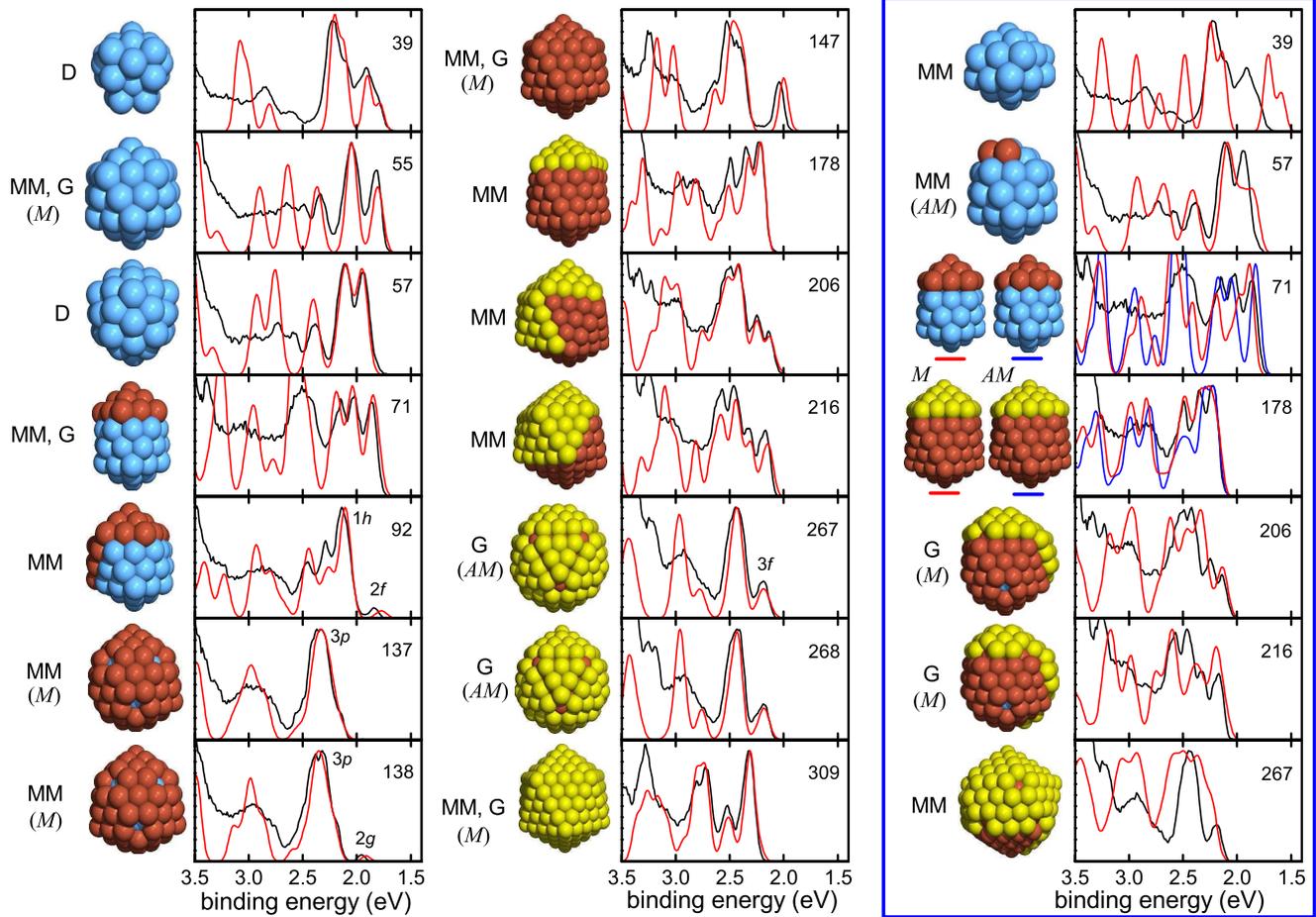
FIG. 2 (color online).    Comparison of photoelectron spectra (black lines) to calculated electron densities of states (colored or shaded lines). The Kohn-Sham levels as obtained by DFT have been broadened by 70 meV width Gaussians and shifted as to reproduce the calculated electron affinity. The structures used in the calculations are indicated (left and center column: assigned ground state structures; right column: wrong structure candidates). The letters give the origin of the structures (MM: ground state structure for Murrell-Mottram potential [26], G: ground state for Gupta potential [26], D: ground state only within DFT) and indicate the structural motif of closed and open shell icosahedral structures (M/AM: Mackay/anti-Mackay overlayer [29]).

respect to the ideal Mackay position (Fig. 2 left column), which increases the coordination number of some of the surface atoms and creates a structure which consists entirely of {111}-like faces [18]. It turns out that this geometry is favorable as well in the DFT calculation; it lies about 0.2 eV lower in energy than the two other candidates. Furthermore, its calculated DOS is in much better agreement with the measured spectra, which provides strong evidence that $Na_{71}^-$ indeed adopts this structure. This ability to detect a small rotation of a capping layer demonstrates that photoelectron spectroscopy is a powerful tool for structure determination even for rather large clusters.

As predicted by the MM calculation, a similar structure is adopted by $Na_{92}^-$. Here ten faces are covered by a Mackay overlayer, which then undergoes a twist distortion. Features in the photoelectron spectra of $Na_{178}^-$ and $Na_{216}^-$ can be explained accordingly. $Na_{178}^-$ is produced by the addition of a twisted 31 atom cap on a complete 147 atom

icosahedron. $Na_{216}^-$ like $Na_{92}^-$ has a twisted ten face overlayer. The DOS of both structures again is in much better agreement with the PES (Fig. 2 central column) than the DOS for the candidates shown in the right column of Fig. 2 (Mackay and anti-Mackay overlayers for $Na_{178}^-$; the Gupta potential ground state for $Na_{216}^-$, an incomplete Mackay icosahedron). The same twisted motif is found for $Na_{206}^-$, which corresponds to $Na_{178}^-$ plus four additional faces. So for the larger clusters empirical potential calculations obviously can predict correct cluster structures. The question arises up to what cluster size electron shell effects, which are neglected in such model potentials, influence the cluster structures. For small sodium clusters with less than 20 atoms it was shown that the ground state structures have moments of inertia almost identical to those predicted by liquid droplet models, with spherical symmetries for electronic closed shells and characteristic ellipsoidal deformations for intermediate sizes [20]; so here electronic

quantum size effects dominate the cluster structure. In our study we see similar effects for certain sizes. $Na_{57}^-$ with its 58 valence electrons, for example, is a closed-shell cluster. The putative global minima for $Na_{56}^-$ and $Na_{57}^-$ modeled by empirical potentials like MM, Sutton-Chen, or Gupta are clusters with a 55 atoms icosahedral core and additional atoms occupying places on the surface [26]. But due to the tendency of electronically closed-shell clusters to have a spherical shape in the DFT calculation the extra atoms are pushed into the surface of the icosahedron for $Na_{56}^-$ and $Na_{57}^-$, resulting in three almost equal radii of inertia and an energy gain of 0.1 eV with respect to the MM structure. Comparison of the calculated DOS and the measured PES shows that this is indeed what happens. The same is true for the closed-shell $Na_{39}^-$, which adopts a spherical ground state structure in contrast to empirical potential calculation predictions (see Fig. 2).

$Na_{267}^-$ is a special cluster. With 268 electrons it has a closed $3f$ electronic shell and therefore a tendency towards a spherical shape, which can be obtained by covering the 147-atom icosahedron with a closed anti-Mackay overlayer. This ''double magic'' structure is highly symmetric and has a simple, strongly discretized DOS, in excellent agreement with experiment (Fig. 2 central column). It represents the global minimum for the Gupta potential, while the global minimum for the MM potential is again a twisted Mackay icosahedron [18]. Surprisingly in the DFT calculation the MM structure lies 160 meV lower in energy than the Gupta structure, although only the DOS of the Gupta structure fits to the PES (Fig. 2). One possible explanation could be that this size ends up in a metastable state upon solidification of an initially liquid cluster, which should be more strongly influenced by electron shell effects. But note that for $Na_{268}^-$ neither in the calculation nor in the experiment a clear appearance of the new $4p$ shell can be seen (see Fig. 2), which indicates a small $3f$-$4p$ band gap and thus a not very pronounced electronic shell closing. It is a question whether this is strong enough to force a liquid cluster into the observed spherical anti-Mackay structure, or whether here we have a case where DFT prefers a wrong ground state.

We would like to end with the only cluster for which no structure could be found. $Na_{298}^-$ is definitely neither a regular icosahedron with 11 vertex atoms missing, nor any of the other icosahedron based structures (anti-Mackay and twisted overlayers) we tested. One could speculate that at this size for the first time a more bulklike, bcc or fcc based structure is adopted; but certainly the true structure has to be found before any conclusions can be drawn.

In summary, by comparing low temperature PES of sodium clusters anions with up to 350 atoms to the results of DFT calculation we were able to assign the geometrical structure of most of the principal sizes. Sodium clusters between 55 and 309 atoms per cluster clearly favor icosahedral geometries. Our study provides strong evidence that clusters between closed-shell icosahedral structures form twisted overlayers, leading to prominent subshell closings at sizes 71, 92, 178, 206, and 216.

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[30] While a Mackay overlayer continues the fcc stacking of each of the 20 tetrahedra forming an icosahedron, an anti-Mackay overlayer introduces a hexagonal stacking fault.