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Ultraviolet photoelectron spectroscopy of Nb_4^- to Nb_{200}^-

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Abstract. We present UV ($h\nu = 6.42$ eV) photoelectron spectra of niobium cluster anions Nb_n^- in the size range from $n = 4$ to $n = 200$. The spectra exhibit a variety of patterns, which can be related to the geometrical structures of the clusters. The charging energies of the larger clusters are in very good agreement with the metallic sphere model. Nevertheless a strong size dependence of the work function is observed, which underlines the special properties of this transition metal.

PACS. 33.60.Cv Ultraviolet and vacuum ultraviolet photoelectron spectra – 36.40.Cg Electronic and magnetic properties of clusters – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

The strong mixing of the partially filled d-band with the valence s-band leads to the fascinatingly complex properties of transition metal clusters, which range from unusual magnetic properties to the strong size dependence of the chemical reactivity. Niobium clusters have been studied especially for the latter reason. In a number of experiments the reactivity of neutral and charged clusters have been measured ([1], and references therein). A strongly varying reactivity has been observed. In the case of chemisorption of H_2 some sizes (namely $n = 8$, 10, 16) exhibit a reaction rate several orders of magnitude lower than that of the other clusters. In a number of studies it has been shown that this extremely low reactivity correlates with an enhanced ionization potential [2] of the neutral and quite a large bandgap of the negatively charged clusters [3,4]. The knowledge of the electronic as well as the intimately related geometrical structure is obviously crucial for the understanding of these clusters. Quite a few theoretical studies [5–8] have been done in the recent past for this purpose, which makes niobium one of the most intensively studied transition metal cluster material. The fact that the size range of the clusters for which the electronic density of states has been calculated meanwhile exceeds that of published photoelectron data has motivated the study presented here.

2 Experiment

The niobium clusters are produced by a magnetron sputter gas aggregation source [9]. Inside a liquid nitrogen cooled aggregation tube a magnetron sputter source injects niobium vapor into a mixture of helium and argon, which leads to cluster formation. Due to the magnetron discharge a large portion of these clusters is charged. After expansion into the vacuum the clusters enter a rf octupole ion guide. The octupole has a pulsed exit aperture and can therefore be used as a temporal trap for the cluster ions in order to bunch the continuous output of the cluster source. This enhances the cluster intensity in a bunch by a factor of 10−100. The cluster ion bunches are inserted into a high resolution double-reflectron time-of-flight mass spectrometer, where a multiwire mass gate positioned at the focus point of the first reflector can be used to select single cluster sizes with a selectivity of up to $m/\mathrm{d}m = 2000$. After passing the second reflector the size selected clusters are decelerated and inserted into a magnetic bottle photoelectron spectrometer, where they are irradiated by an ArF excimer laser ($h\nu = 6.42$ eV). The flight time distribution of the emitted electrons is measured and converted into a binding energy distribution. The spectrometer has an energy resolution of about $E/\mathrm{d}E = 40$. It has been calibrated by measuring the known spectrum of Pt^-, which for the highest energy electrons leads to an error of the energy axis of less than 50 meV, and for the lowest energy ones of less than 10 meV. In most cases the photoelectron spectra have been averaged over 30 000 laser shots at a repetition rate of 150 Hz.

3 Results

Figures 1 and 2 show the series of photoelectron spectra obtained. All spectra have been smoothed by convolution with a rectangle function of 20 meV width. The results

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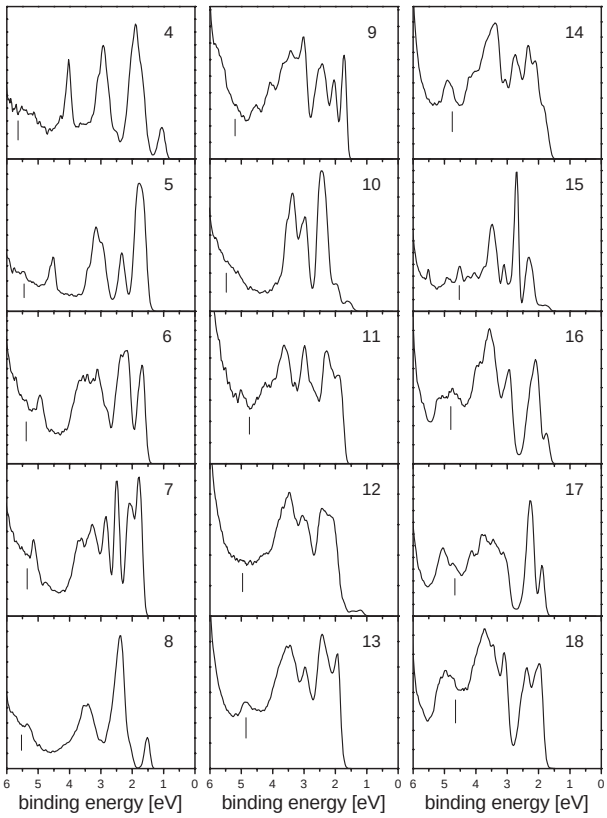

Fig. 1. Photoelectron spectra of Nb_n^- ($n = 4$ to 18) at a photon energy of 6.42 eV. The vertical lines indicate the ionization potentials of the corresponding neutral clusters [2].

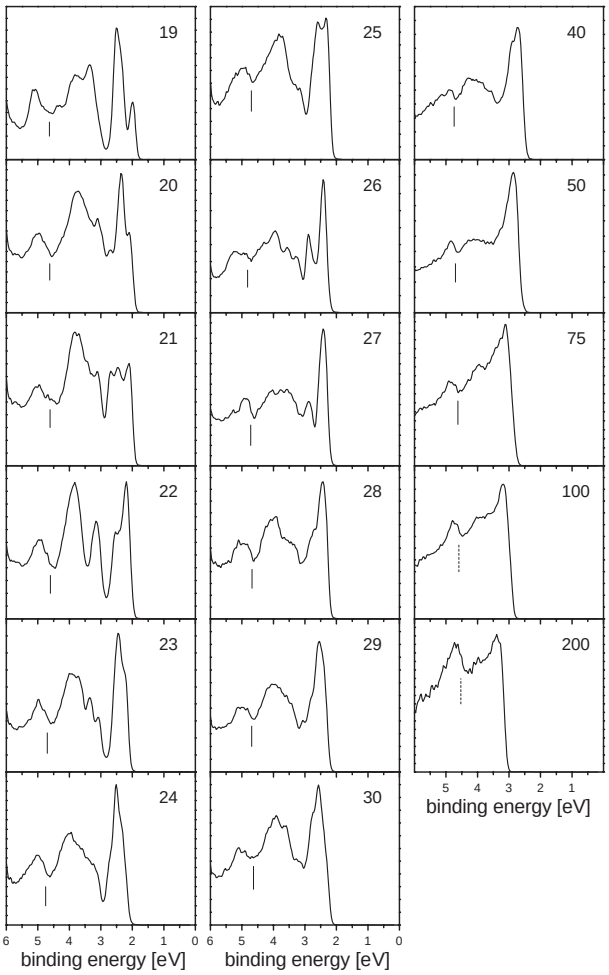

Fig. 2. Photoelectron spectra of Nb_n^- ($n = 19$ to 200) at a photon energy of 6.42 eV. The vertical lines indicate the ionization potentials of the corresponding neutral clusters [2]. The spectral patterns starting at these positions are obviously spectra of the neutral clusters, produced by sequential two-photon absorption.

for the smaller clusters ($n = 4$ to 20) are almost identical to the spectra of Kietzmann *et al.* [3,4]. Apart from the slightly better signal-to-noise ratio in our data one can observe some differences in the relative peak intensities, which is obviously due to the wavelength dependence of the related detachment cross-sections.

We will now first discuss the qualitative structures of the spectra, and then study the size dependence of the electron affinity. For the discussion of the patterns observed we will divide the spectra into three groups.

(i) $n = 4-15$. This size range is governed by a very strong size dependence of the spectra. Nb_4^- for example has a very simple spectrum. It exhibits a neat series of four peaks, in almost perfect quantitative agreement with the calculated density of states (shifted Kohn-Sham levels) in a recent work by Fournier *et al.* [7]. This is, however, a very intriguing result. As the authors show, and as has been demonstrated earlier for the case of copper clusters [10], the energy of the excited state of a neutral cluster produced by the emission of a certain electron from the anion differs from the simple negative single particle energy of this electron due to charge redistribution effects. In the case of copper clusters [10] inclusion of such effects lead to a better agreement between the calculated and the measured photoelectron spectra. This is, however, not the case here. While the distribution of the Kohn-Sham levels agree nicely with the measured spectrum, the simulated photoelectron spectrum does not fit at all; it strongly overestimates the total energy bandwidth. As the comparison between calculated and measured photoelectron spectra is one of the most important tools for the determination of cluster structures, this is a discrepancy which certainly deserves some consideration.

Among the other spectra of this group three sizes stand out, exhibiting a strongly structured and at the same time quite narrow density of states. These are the well known "magic" sizes $n = 8$, 10 and 15. As shown earlier [4], both Nb_8^- and Nb_{10}^- exhibit an enhanced bandgap. Nb_{15}^- exhibits a strongly structured spectrum very different from that of its neighboring sizes. This is due to the fact that in this size range Nb_{15}^- is the only cluster with a clear bcc structure [4,8,11]. Interestingly there is one cluster which exhibits a quite similar peak pattern in its spectrum: Nb_{10}^-. Actually the structure predicted for this size, a bicapped antiprism [6,8], has some similarity with the closed shell bcc structure of the Nb_{15}^-. Both have a

fourfold rotational symmetry, and furthermore one can rather smoothly convert the Nb_{10}^- into the Nb_{15}^- by flattening out its upper pyramid and capping it with another pyramid. This underlines the fact that in a transition metal cluster the (approximate) symmetry has a very strong influence on the overall electronic density of states.

Another cluster which is somewhat different is Nb_{12}^-. It exhibits a small pedestal extending to about 1 eV binding energy, which is almost absent in the spectra of Kietzmann *et al.* [4]. This may hint to the fact that it is due to a second isomer. Further evidence for this can be obtained from the comparison with Nb_{13}^-. This cluster exhibits an almost identical, although slightly more structured spectrum, but without the pedestal. For Nb_{13} a distorted icosahedral structure was predicted [8]. The preferred structure of Nb_{12} is the same icosahedron with one atom missing in the outer shell and some resulting distortion [8]. This would explain the similarity of both spectra, as well as the slight blurring of the pattern in the case of Nb_{12}^-. As it seems quite improbable that taking out one atom from the icosahedron shifts one level to a much higher energy while leaving the rest of the electronic structure almost unchanged, we attribute the pedestal to another isomer.

(ii) $n = 16-29$. In this group still clear changes of the spectra from size to size occur, although much less pronounced than in the first group. Actually all of the spectra show a similar pattern: up to size $n = 24$ (with the exception of $n = 20$ and $n = 21$) all clusters exhibit a deep gap between a first quite sharp double peak structure and a second broad, but still structured band. For larger sizes this gap gets more and more filled, but remains at least faintly visible all the way up to $n = 200$. Surprisingly one can observe something like a shell filling pattern in the sequence of the spectra: at size $n = 16$ there is a small peak at the threshold, indicating the bandgap of this cluster. At size $n = 17$ this peaks seems to have grown, and even more so for size $n = 18$. At $n = 19$ a new peak is visible, which seems to grow until up to size $n = 22$. This is a behaviour which is typical for free electron metals [12,13], but one would not expect it in the case of a transition metal. At size $n = 29$ the strong size dependence of the spectra decreases, and only a gradual change of the spectra can be observed for larger sizes. This might hint at some geometrical shell closing, with further atoms being added to a new shell around a core structure, but without much change to the overall electronic density of states.

It therefore seems to be the case that all clusters in this group have a common geometrical structure different to that of the smaller clusters, and with some shell closing occurring around size $n = 29$. This is indeed exactly what has been found in the calculation by Kumar and Kawazoe [8] for neutral clusters: they found hexagonal structures to be favorable for all sizes between Nb_{16} and the largest cluster simulated, Nb_{23}. These clusters consist of several six-membered rings around a linear chain. New closed shell structures are obtained by adding a ring and a central atom, that is seven atoms. This occurs for $n = 15$ (although here the bcc structure is favored), for $n = 22$ and for $n = 29$. These sizes actually have been found to be magic sizes in mass spectra of positively charged niobium clusters [14], which provides further evidence for this building principle. There is, however, one weak point in this interpretation of the observed patterns: Nb_{14} was also calculated to have hexagonal structure, but its anion does not exhibit at all the pronounced gap in the spectrum. This might be due to two reasons: either Nb_{14} is a case were the negatively charged cluster prefers a different structure than the neutral one, or there is more than one isomer present in our cluster beam, which would also explain the rather congested spectrum of Nb_{14}^-.

(iii) $n = 30-200$. Here an only gradual change of the spectra takes place. The spectra consist of a sharp peak at the threshold and two rather broad bands. With increasing size these bands shift towards the threshold; the first of them almost merges with the sharp peak at $n = 200$. This leads to a double hump structure at size $n = 200$, very similar to that observed for a vanadium cluster with 65 atoms [15]. The authors Wu *et al.* have interpreted this as the signature of a fully developed *d*-band. In our case this second bump has a much simpler explanation. In all spectra we have indicated the ionization potentials of neutral niobium cluster as determined by Knickelbein and Yang [2] by short lines. Obviously the second bands are just the spectra of the neutral clusters, which means that some of the negatively charged clusters after emission of an electron have absorbed another photon and emitted a second electron (exactly as has been observed recently for large aluminum clusters [16]). Inspection of the spectra in Figures 1 and 2 shows that such contributions from neutral clusters appear for all sizes at least down to size $n = 13$. Of course using a lower laser intensity would lead to a vanishing of these peaks due to their quadratic intensity dependence. Unfortunately no laser power dependence was measured during this first series of experiments on niobium clusters; this will be done soon.

Two remarks can be made here: first of all, if one accepts the interpretation above, one can take our spectra to check the data given by Knickelbein and Yang. There is actually a very good agreement, which shows that the peculiarly weak size dependence of the ionization potential they have observed is absolutely correct. Second: scaling of the resulting niobium cluster charging energies to the case of vanadium leads to energies in very good agreement with the separation of the two humps observed by Wu *et al.* [15]; this means that most probably also in their case the second hump is the spectrum of the neutral cluster and not some bulk-like *d*-band feature.

The electron affinities of the clusters obtained from our data together with the ionization potentials of the neutral clusters [2] are plotted in Figure 3 as a function of the inverse of the cubic root of the cluster size. Assuming a spherical shape and bulk-like density of the clusters, these energies are given by [17]:

$$\mathrm{IP}(Z) = W_\infty + (Z + \alpha)\,\frac{e^2}{r_s N^{1/3} + \delta}. \qquad (1)$$

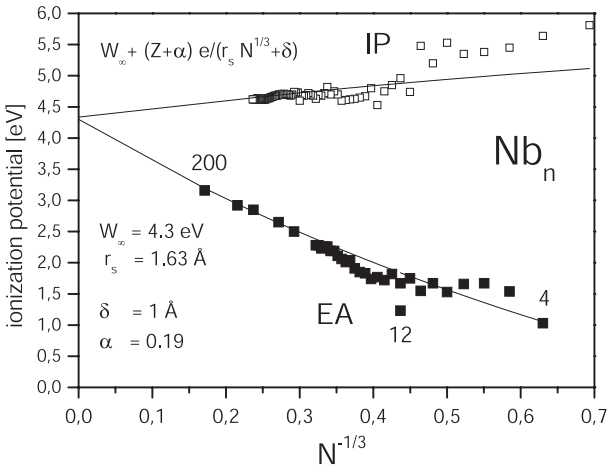

Fig. 3. Vertical electron affinity as obtained from the spectra in Figures 1 and 2 as a function of the idealized inverse cluster radius. Additionally the ionization potentials obtained by Knickelbein and Yang [2] are shown. The data sets have been fitted with the model functions for a metallic sphere (Eq. (1)).

Here r_s is the Wigner-Seitz radius of niobium (1.63 Å), Z the cluster charge state, and W_∞ the work function of the bulk (4.3 eV [18]). 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 curved surface. Classical theory [17] gives $\delta = 0$ and $\alpha = 1/2$. A fit of the data points yields $\delta =$ 1 Å and especially $\alpha = 0.19$, which is an unusually low value and indicates a strong quantum correction of the work function. This can be taken as another evidence for the peculiar properties of transition metal clusters.

The fact that the charging energy (the difference between IP and EA) of the larger clusters is nicely reproduced by the fit demonstrates that the clusters of this size already have a density close to that of the bulk as well as at least almost spherical shape. In the size range below $n = 30$ one can observe some deviations from the fit curves; this might be due to the special hexagonal geometries of the clusters in this range.

4 Summary

Photoelectron spectra of niobium cluster anions have been measured in the size range between $n = 4$ and $n = 200$. Three size ranges can be identified in the spectra: sizes $n = 4-15$ exhibit a strong variation of patterns in the spectra, indicating structural diversity. Nb_{15}^- and Nb_{10}^- show peculiar and somewhat related patterns, which might be due to the common fourfold symmetry of the bcc structure of Nb_{15} and the bicapped antiprism structure of Nb_{10}. Sizes $n = 16-29$ exhibit quite similar patterns, indicating that the hexagonal growth pattern predicted for this size range is correct. For $n > 29$ only a smooth change of the patterns is observed. In most of the spectra patterns are visible at higher binding energies which can be related to the neutral clusters. The electron affinities as the ionization potentials show a convergence towards the model functions for a metallic sphere which is completed around Nb_{29}. Niobium turns out to exhibit an unusually strong quantum correction of the work function for a curved surface, which leads to the only very weak size dependence of the ionization potentials of neutral niobium clusters.

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