

Photoelectron spectra of Nb_n^- clusters: Correlation between electronic structure and hydrogen chemisorption

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Photoelectron spectra of mass-separated Nb_n^- clusters reveal an even/odd alternation for $n = 6-17$, indicating a closed electronic shell of the neutral even-numbered clusters. The HOMO–LUMO gap of Nb_8 , Nb_{10} , and Nb_{16} is found to be larger than that of the other even-numbered clusters, which correlates with the low H_2 reactivities of these species. The spectrum of Nb_{15}^- is different from all other clusters in this size range, which might be an indication for a geometric bcc shell closing. The influence of the electronic structure of the clusters on the reactivity is discussed.

I. INTRODUCTION

The understanding of the dramatic size dependence of the chemical reactivities of small transition metal clusters^{1–7} is still a major challenge. The ionization potentials (IPs) and the vertical detachment energies (VDEs \approx electron affinities) of the bare metal clusters reveal changes in the electronic structure.^{8–12} There are several attempts to correlate the available data with the measured reactivities within the framework of an electronic charge transfer model.^{8–10} This model is supported by the correlation of the IPs^{8,9} (or the differences between IPs and VDEs¹⁰) with the reactivities of the clusters. An alternate approach considers geometric effects to be mainly responsible for the reactivity of a cluster of a certain size.^{12–15} This model is supported by the observation that in some cases the measured reactivities are almost independent of the charge states of the clusters (neutral,^{1,2,4} positive,^{2,3} negative²).

It is obvious to us that the electronic structure and the geometry of the cluster are intimately related. However, in the literature frequently the chemisorption properties of clusters are discussed, uniquely stressing either the electronic or the geometric aspects. Part of the reason for this ambiguity is the lack of data of the electronic and geometric structures of the bare clusters, which are responsible for the observed reactivities. For that reason, we studied bare Nb_n^- clusters with photoelectron spectroscopy.¹⁶ This technique yields important information about the electronic structure of the neutral cluster. If the neutral cluster has a closed electronic shell, the HOMO–LUMO gap (the gap between the *highest occupied molecular orbital* and the *lowest unoccupied molecular orbital*) can be measured directly.^{17,18}

We choose Nb_n for two reasons: (i) the reactivities of neutral Nb_n clusters with H_2 show a rather interesting and simple pattern.^{1,2,4} Nb_8 , Nb_{10} , and Nb_{16} are relatively unreactive while the other clusters readily chemisorb hydrogen. (ii) The electronic structure of the clusters of magnetic transition metals ($\text{Ni}_n, \text{Co}_n, \text{Fe}_n$) is more complicated due to

strong correlation effects.^{8,10} For example, because these clusters have high spin ground states¹⁹ they will not assume a closed electronic shell configuration corresponding to a singlet state. As we will show there are indications of a much simpler electronic structure for the Nb_n clusters. This difference between the Ni_n , Co_n , and Fe_n clusters on one hand and Nb_n clusters on the other hand is also directly visible in the size dependencies of the reactivities. While the reactivity of, e.g., Fe_n clusters varies irregularly with size,^{8,10} one of the Nb_n clusters shows only three distinct minima at $n = 8, 10, \text{ and } 16$.^{1,2,4} This resembles the observation of “magic numbers” for clusters of simple metals or rare gases. In these cases, high stabilities correspond to particularly stable structures due to an electronic or geometric shell closing, respectively.

In the following we will show that Nb_8 , Nb_{10} , and Nb_{16} are closed shell species with a relatively large HOMO–LUMO gap. In case of simple monovalent metals²⁰ the clusters with an even number of electrons are closed shell species and the HOMO–LUMO gap of the neutral cluster can be extracted directly from the photoelectron spectra of the corresponding anions.¹⁸ We applied the same method of evaluation to the photoelectron spectra of the trivalent Nb_n^- clusters, because we observe an even/odd alternation of the VDEs for Nb_6 – Nb_{17} typical for clusters of simple metals.²⁰ Our analysis has recently been confirmed for Nb_6 – Nb_8 by *ab initio* calculations.^{21,22} According to our data presented here, the low reactivities of Nb_8 , Nb_{10} , and Nb_{16} correspond to an electronic shell closing. In addition, the photoelectron spectrum of Nb_{15} exhibits a distinct pattern different from all other spectra, which might correspond to a special geometric structure (high symmetry) of this cluster.

II. EXPERIMENTAL SETUP

The experimental setup has been described in detail elsewhere.¹⁶ The negatively charged clusters are produced in a laser vaporization source. The source is cooled with liquid nitrogen (LN_2) and a “waiting room” is added to the source, which allows for a prolonged residence time of the clusters

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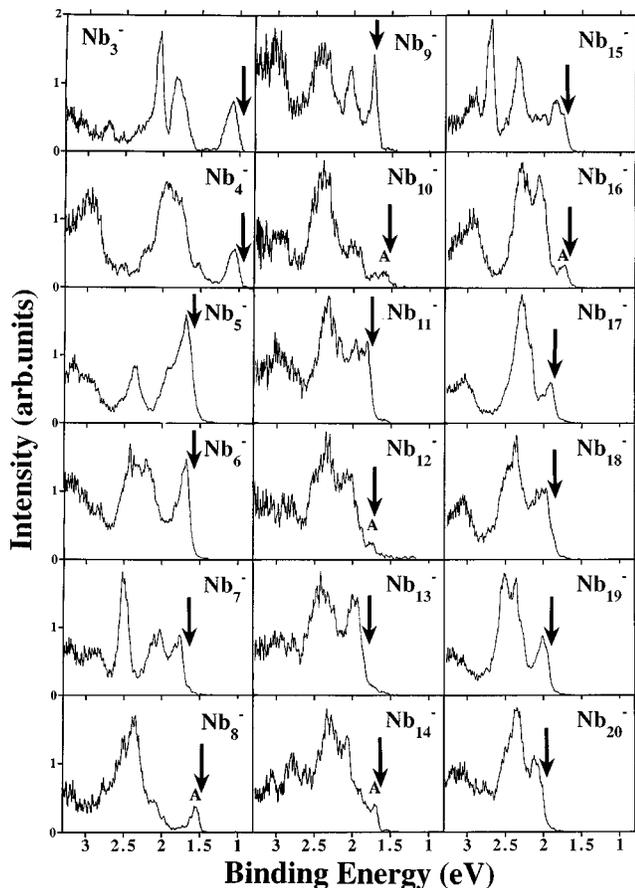


FIG. 1. Photoelectron spectra of Nb_n^- clusters with $n=3-20$ obtained with a photon energy of $h\nu=4.0$ eV. For a discussion of the marked features see the text. The arrows indicate the VDEs determined by using the procedure described in the text.

in the LN_2 cooled environment.²³ In general, the internal temperature of the anions and the isomer distribution depend on various additional parameters like the power of the vaporization laser and the He flu. The vibrational temperature is not exactly known, but we take the observation of relatively sharp features in the photoelectron spectra as indications for low temperature. The anions are accelerated in a pulsed electric field and depending on their time of flight they separate into a chain of bunches of defined cluster size. The kinetic energy of electrons detached from a selected bunch is measured in a “magnetic bottle” time-of-flight electron spectrometer. For photodetachment a XeCl excimer laser with a photon energy of $h\nu=4.0$ eV is used.

III. DATA AND DISCUSSION

Figure 1 displays photoelectron spectra of Nb_n^- clusters with $n=3-20$. Most of the spectra exhibit two to three intense features with some fine structure in the binding energy (BE) range between 1.5–2.7 eV. Only the spectra of Nb_3^- and Nb_4^- exhibit a peak at low BE (≈ 1.1 eV). In general, these features can be assigned to photoemission from occupied $4d$ and $5s/p$ valence orbitals, which gradually develop into the valence band of bulk Nb.

From the spectra shown in Fig. 1 the VDEs can be determined. A straight line is fitted to the steep part of the

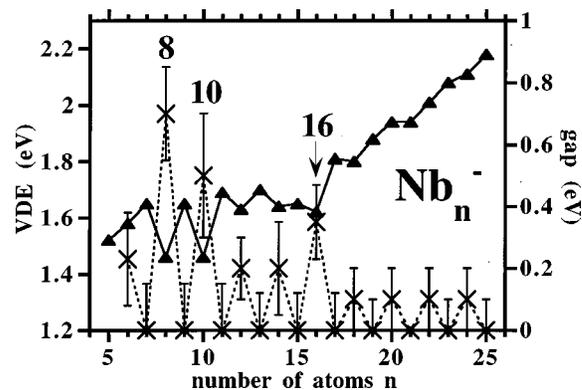


FIG. 2. Vertical detachment energies (triangles, left scale) and sizes of the HOMO–LUMO gaps (crosses, right scale) as extracted from the photoelectron spectra of the Nb_n^- clusters for $n=5-25$. All values are given in eV.

emission signal above the threshold and the intersection of this line with zero is taken as the VDE (indicated by arrows). The results of this procedure are shown in Fig. 2 (triangles, left scale) for Nb_n^- with $n=5-25$. For $n=6-17$ an even/odd alternation of the VDEs is observed with local minima at $n=8, 10$. In this size range the VDEs show only a weak overall increase, while for $n>16$ the VDEs start to increase steeply with no visible even/odd alternation. For the smallest clusters ($n<6$) no systematic pattern of the VDEs is observed with extremely low values for $n=3$ and 4 .²²

An even/odd alternation is typically found in clusters of simple metals with an odd number of electrons per atom (e.g., Na ,²⁰ Nb has $5d^4s$ valence electrons with the bulk configuration $n d^4s$). If an alternation is found, it indicates that the uppermost single-particle orbital is nondegenerate and occupied by one or two electrons corresponding to a doublet or singlet electronic ground state, respectively.

From our data we can identify three different size regimes.

(i) $n=3-6$. No simple pattern like an even/odd alternation of the VDEs is observed. However, according to a recent comparison of photoelectron spectra of Nb_n^- clusters with the results of *ab initio* calculations ($n=3-8$), the anions have low spin ground states.²² The lack of a pronounced even/odd alternation might be caused by several effects governing the electronic structure of very small clusters. For example, the valence electron orbitals might still be partially localized and, in the case of a high symmetry of the cluster, also degenerate. Moreover, correlation effects might influence the properties of the clusters. Similar observations have been made for Al_n^- clusters,²⁴ where an even/odd alternation is observed for clusters larger than Al_7^- . Accordingly, for very small clusters more complex models are necessary to explain their properties. For Nb_n clusters with $n=3-6$ generally high reactivities with hydrogen have been measured.¹⁻⁴

(ii) $n=7-16$. The observed even/odd alternation is a result of the decreasing degrees of localization²⁵ and degeneracy. The even-numbered clusters have an electronic closed shell ($n=8, 10, 12, 14, 16$). The additional electron in the negative ion occupies the LUMO of the neutral closed shell cluster and gives rise to a small peak at low BE. Therefore, for such clusters the photoelectron spectra of the anions give

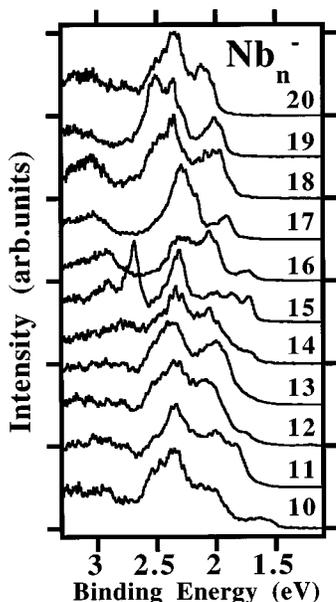


FIG. 3. A comparison of the photoelectron spectra of Nb_n^- clusters with $n = 10\text{--}20$ shown in Fig. 1.

a direct measure of the HOMO–LUMO gap. Indeed, the spectra of Nb_8 , Nb_{10} , Nb_{12} , Nb_{14} , and Nb_{16} (Fig. 1) exhibit such a peak at low BE (marked A).²⁶ The gap between this small peak and the next feature at higher BE corresponds to the HOMO–LUMO gap. However, for Nb_{12} and Nb_{14} peak A is almost hidden in the onset of the main emission feature, which is probably thermally broadened. The values of the gaps as estimated from the photoelectron spectra displayed in Fig. 1 are given in Fig. 2 (crossed, right scale). Although a quantitative determination of the gaps is difficult and hampered by the appearance of isomers,²² we conclude that the gaps are small for Nb_{12} and Nb_{14} and large for Nb_8 , Nb_{10} , and Nb_{16} . For Nb_7 and Nb_8 , the data analysis discussed above is in reasonable agreement with results of recent *ab initio* calculations²² (Nb_7 : open shell; Nb_8 : closed shell with a gap of 0.8 eV). We conclude that there is a correlation of the HOMO–LUMO gaps extracted from our photoelectron spectra with the measured H_2 reactivities. The clusters with the largest gaps ($n = 8, 10, 16$) have the lowest reactivities.

(iii) $n = 17\text{--}25$. The VDEs increase steeply and no even/odd alternation is observed. In addition, the photoelectron spectra look rather similar with basically two main features (see, e.g., Nb_{17}^- and Nb_{20}^- in Fig. 1). Around $n = 16$ there is a considerable change in the electronic and probably also the geometric structure. We cannot find indications for a HOMO–LUMO gap in these larger even-numbered clusters and estimate the gap size to be 0.1 ± 0.1 eV (see Fig. 2). In general, the gap size is expected to decrease with increasing cluster size down to zero for the bulk metal, and we expect the larger clusters to be highly reactive approaching the bulk surface reactivity.²⁷

The photoelectron spectrum of Nb_{15}^- shows a quite different pattern. Figure 3 displays an overview of the photoelectron spectra shown in Fig. 1 in the size range $n = 10\text{--}20$. The extraordinary shape of the spectrum of Nb_{15}^- is clearly apparent. In addition, at $n \geq 16$ the VDEs start to

increase considerably with cluster size (Fig. 2). These two observations might be an indication of a general change occurring at this size. A possible explanation is a geometrical shell closing occurring at $n = 15$. For an icosahedral structure the first shell closing occurs at $n = 13$, for a bulklike bcc structure at $n = 15$. Weakly bound clusters assume an icosahedral structure. However, for strongly bound clusters (e.g., NaCl ²⁸) a tendency to prefer a bulklike structure, even for the very small clusters has been found. For example, the transition from a planar structure to a compact $3d$ structure occurs at $n = 6$ for Al_n clusters,²⁴ but for Nb_n already at $n = 4$ (the smallest possible $3d$ cluster).^{21,22} Accordingly, the refractory metal clusters might prefer bulklike (bcc for Nb) structures, even for the clusters with 10–20 atoms, and the first geometric shell closing occurs at $n = 15$. This bcc shell closing might be an explanation for the special shape of the spectrum of Nb_{15}^- and, in addition, might be the reason for the general change occurring in this size range (Fig. 2).

So far, there is a surprisingly simple correlation between the photoelectron data and the pronounced minima of the hydrogen reactivities of the neutral Nb clusters. The clusters with a closed electronic shell and a large gap have low reactivities. However, this correlation is not as straightforward as it seems, if results of other related experiments are taken into account. Especially the independence of the reaction rates on the charge state of the Nb clusters is usually taken as a strong hint, that the geometric structure determines the chemical properties. In the following we discuss the experimental findings within this context.

(1) The observation of an *even/odd alternation* of the reactivities is a strong indication for the importance of the electronic structure. The low reactivities of Nb_8 , Nb_{10} , and Nb_{16} can be viewed as part of an even/odd alternation.^{1,2–4} The measured size dependence of the reactivities might depend on the temperature. As suggested by the smaller band gaps, at a considerably lower temperature the reactivities of Nb_{12} and Nb_{14} could be much smaller, continuing the even/odd alternation from Nb_8 , Nb_{10} , and Nb_{16} . Nb has five valence electrons and, therefore, the total number of valence electrons in the Nb_n clusters is either even or odd. Any property of the clusters, which alternates with increasing n is directly related to the number of electrons, i.e., to the electronic structure. It is difficult to explain such an even/odd alternation of any property using purely geometrical arguments.

(2) The correlation between the HOMO–LUMO gap extracted from our photoelectron spectra and the reactivities of the neutral Nb_n clusters is a strong argument for the electronic structure dominating the reactivity. The correlation can be explained by the model developed by Harris and Andersson.²⁹ The mechanism of H_2 chemisorption on Cu and Ni bulk metal surfaces^{29–31} depends on the “closed shell” character of the $3d$ valence electrons only (d^9 for Ni and d^{10} for Cu). If the $3d$ valence electrons form a d^{10} closed shell configuration, an entrance channel barrier builds up. Using this approach, the height of the barrier corresponds roughly to the size of the HOMO–LUMO gap, and this explains why a low reactivity at a given temperature is observed only for the three clusters with the largest gaps (Nb_8 , Nb_{10} , and

Nb₁₆). Accordingly, the reactivities of Nb₁₂ and Nb₁₄ should drop at a lower temperature. Recently, a similar approach has been taken to explain the correlation of the differences between IP and VDE with the hydrogen reactivity found for Ni, Co, and Fe clusters.¹⁰ However, clusters of these materials have high spin electronic ground states (“magnetic”) and are open shell species. In this case, the difference between IP and VDE depends on a balance of several different energies and the interpretation of this energy is different from the one of the HOMO–LUMO gap of a closed shell species.

(3) The exceptional photoelectron spectrum of Nb₁₅ might be related to a closed geometrical shell. Although this cluster seems to have a unique electronic and geometric structure, its reactivity is comparable to the other odd-numbered clusters.^{1,2,4} Smooth surfaces like the ones of single crystals are rather unreactive and, therefore, one might expect a low reactivity for a cluster with a closed geometrical shell. However, this is not the case.

(4) It has been observed that the overall shape of the reactivity pattern of the Nb clusters is roughly *independent on the charge state* of the clusters (Nb_{*n*}⁺, Nb_{*n*}[−], Nb_{*n*}⁰).^{1–4} This observation indicates that the geometric structure might be important in determining the reactivity. While the number of electrons determines whether the cluster has a closed electronic shell or not, for larger clusters the geometry probably changes only slightly with the charge state. In case of the electronic approach it might be possible to explain this independence using the model of Harris and Andersson.^{29–31} If the reactivity depends on the closed shell character of the manifold of *d* orbitals, then the charge state of the cluster should have little or no influence since the additional electron or hole will always prefer a delocalized *s/p* orbital to minimize the Coulomb repulsion. In this case, the occupation of the *d* orbitals remains unchanged. The even/odd alternation of the VDEs indicates that not only the *s/p* orbitals but also the *d* orbitals have a closed shell. Otherwise the additional electron of the cluster anion would occupy the “*d* hole” and not the next higher orbital.

IV. CONCLUSIONS

The photoelectron spectra of Nb_{*n*}[−] clusters reveal an even/odd alternation of the VDEs in the size range between *n* = 6–17. The spectra of Nb₈[−], Nb₁₀[−], and Nb₁₆[−] show evidence of a relatively large HOMO–LUMO gap of the neutral clusters, which correlates with the low reactivities found for Nb₈, Nb₁₀, and Nb₁₆. In addition, for Nb clusters the first geometrical shell closing seems to occur at *n* = 15, but the 15 atom cluster has no exceptional chemical properties. There are indications for a general change in electronic and geometric structure occurring at this size.

The hydrogen reactivities exhibit a pronounced correlation with the sizes of the HOMO–LUMO gaps of the clusters and, therefore, the electronic structure of the clusters seem to determine the chemical properties. Contrary, the limited independence of the reactivities on the charge state is a strong argument for the geometrical structure determining the reactivity. However, this experimental observation can

also be explained using the model of Harris and Andersson. If this is correct, the chemical properties of the clusters are related to the electronic structure only.

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- ²⁵An increasing degree of delocalization does not mean such a high degree of delocalization as in the case of the alkali metals.²⁰ In the Nb clusters all orbitals have a strong contribution from *d* orbitals, and the jellium model (electronic shell model) cannot be applied.
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