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Investigation of niobium clusters: Bare and CO-adsorption

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Molecular-orbital and linear combination of atomic orbitals calculations within the local-spin-density approximation formalism have been performed for niobium clusters in the range from two to ten atoms. Optimization of the geometries shows that the structures are determined by a balance between *d* and *s* electrons, giving the lowest total energies for cluster geometries with highly coordinated structures and a maximum of interatomic bonds. Evaluated binding and fragmentation energies are in fair agreement with experiments. In addition to the calculations of bare clusters, adsorption of CO on niobium clusters was investigated. These results indicate a strong cluster site and size dependence. Generally, a ''hollow'' site was preferred compared to an ''on-top'' site and a particularly low chemisorption energy was obtained for Nb_{10}. [S0163-1829(96)04628-0]

The large dispersion and the spatial confinement of electrons make cluster properties rather different from bulk or surface properties.[1] The size evolution can, in some cases, be described by scaling relations,[2] which intuitively relate the size evolution to the number of constituent atoms. However, to confirm the validity of simple models and to achieve a quantitative understanding, first-principles calculations are necessary. Computations of this type have, to a large extent, focused on alkali and metal coinage clusters, which conveniently can be treated with effective core potentials. Transition metals, however, still offer a challenge since the *d* electrons should be treated explicitly and can give rise to a complicated electronic structure with many close and/or highly mixed configurations. Nevertheless, calculations investigating the size evolution of small transition-metal clusters have appeared, for example, for Nb,[3,4] Fe,[5,6] Co,[7] Rh,[8] and Ni.[9]

In this work, we present calculations of bare niobium clusters and CO adsorption onto the clusters. Recently, Goodwin and Salahub[3] reported density-functional calculations with model potentials for Nb_2 to Nb_7. Our work includes a reinvestigation of these bare clusters with an extension to ten atoms. The CO adsorption is investigated with respect to ''hollow'' and ''on-top'' site preference and cluster size effects.

The theoretical approach is based on the density-functional theory[10] with a local-spin-density approximation (LSDA) for exchange and correlation effects.[11] This approximation has proven to be suitable for large-scale quantum systems such as transition-metal clusters. The molecular one-electron orbitals were expanded in a numerical atomic basis set. For niobium we used $4s^2 4p^6 4d^4 5s^1$ together with $4d^3 5s^0 5p^0$ for the doubly ionized niobium atom. We found it important to treat the $4p$ wave functions in a variational manner and also to include the $5p$ wave functions. To treat C and O, we used $C(2s^2 2p^2)$,$C^{2+}(2s^2 2p^0)$ and $O(2s^2 2p^4)$,$O^{2+}(2s^2 2p^2)$, respectively, together with a hydrogenic $3d$ orbital generated for boron. The inner cores were treated within the frozen-core approximation. For the self-consistent evaluation of the Kohn-Sham equations, the Poisson equation was solved using a projection technique.[12] The matrix elements were evaluated using the method of overlapping spheres.[12] The geometry optimization was performed with standard techniques and the structures were converged to 10 meV/a.u. for the largest gradient, except for Nb_7 and Nb_9, which were converged to 100 meV/a.u.

The computational scheme was tested by a comparison with experimental data for some relevant diatomic molecules Table I. For Nb_2, we obtained a binding energy of 5.68 eV and a bond distance of 3.98 a.u. The binding energy is defined as the difference between the total energy of the cluster and the total energy of the separated, spherical spin-polarized atoms. Our results are in good agreement with the LSDA calculations in Ref. 3 of 5.8 eV and 3.93 a.u. We also calculated the binding properties for the niobium oxide and the niobium carbide. The largest binding energy, 8.94 eV, was obtained for NbO. This value is larger than the configuration-interaction (CI) value of 6.92 eV by Siegbahn,[13] although the bond distance, 3.20 a.u., is in good agreement with the CI result of 3.23 a.u. The experimental value[14] falls between the LSDA and the CI calculations and is found to be 7.8 eV. For NbC, we obtained a binding energy of 6.72 eV and a bond distance close to that of NbO. The experimental binding energy is 5.8 eV.[15] For all the diatomic molecules, we obtain an overbinding with respect to the experimental results. This is a well-known deficiency of the LSDA scheme.[16] However, we have chosen not to include gradient corrections to the functional since the main objective of this work is to investigate the cluster size evolution and for this purpose the LSDA scheme is suitable; furthermore, the LSDA method has proven to describe niobium in the bulk satisfactorily.[17]

TABLE I. Comparison between theoretical and experimental values for binding energies D_e (eV) and bond distances d (a.u.) for the investigated diatomic molecules.

	Nb_2		NbC		NbO		CO	
	D_e	d	D_e	d	D_e	d	D_e	d
LSDA	5.68	3.98	6.72	3.20	8.94	3.20	12.62	2.15
Expt.	5.20[18]		5.8[15]		7.8[14]		11.09[14]	2.13[14]

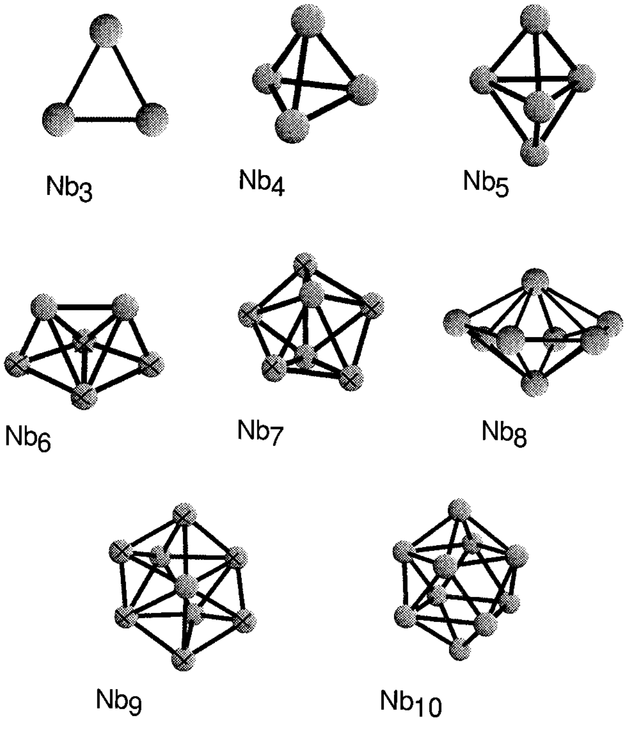

FIG. 1. Optimized cluster geometries. In some cases atoms almost in the plane are marked by crosses.

In Fig. 1, the results for the ground-state structures are shown. Geometry optimization of clusters is a difficult task and we do not state that the geometries obtained represent the true ground state, although they probably are energetically close to the ground state. For sizes up to seven atoms, the geometries in the present work have structures similar to the results reported in Ref. 3. The trimer is an acute triangle with distances of 4.25 and 4.53 a.u. For the tetramer, the ground state was a slightly distorted tetrahedron with bond lengths 4.76 and 4.74 a.u. The pentamer was a bipyramid also in C_{3v} symmetry and the two bond lengths were 5.24 a.u. for the atomic distances in the plane and 4.65 a.u. for the bond length between the plane and the top atoms, respectively. The hexamer is a dimer capped tetramer in C_{2v} symmetry. The tetramer unit of Nb_6 is not planar but slightly tilted over the short-diagonal axis. It has a long diagonal of 7.87 a.u. and a short diagonal of 5.23 a.u. The dimer distance is 4.52 a.u. and the distances between a dimer atom and the two different tetramer atoms are 4.42 and 5.56 a.u., respectively. The structures up to Nb_6 were all found to have some higher symmetry. This was not the case for the larger clusters, which were all distorted from higher symmetry. Since almost all bond distances are different for these clusters we chose not to list them here, but rather describe the main features. The septamer was found to be a ring, distorted from the plane of five atoms capped with one atom on each side of the ring. The octamer is a ring of six atoms, not in the plane but almost in C_{2v} symmetry. The ring was, as in the case of the septamer, capped with one atom on each side. A ring structure with six atoms is also present for Nb_9, but with a dimer instead of a monomer capped on one of the sides. For Nb_{10}, we found a structure close to the C_{4v} symmetry, but somewhat distorted.

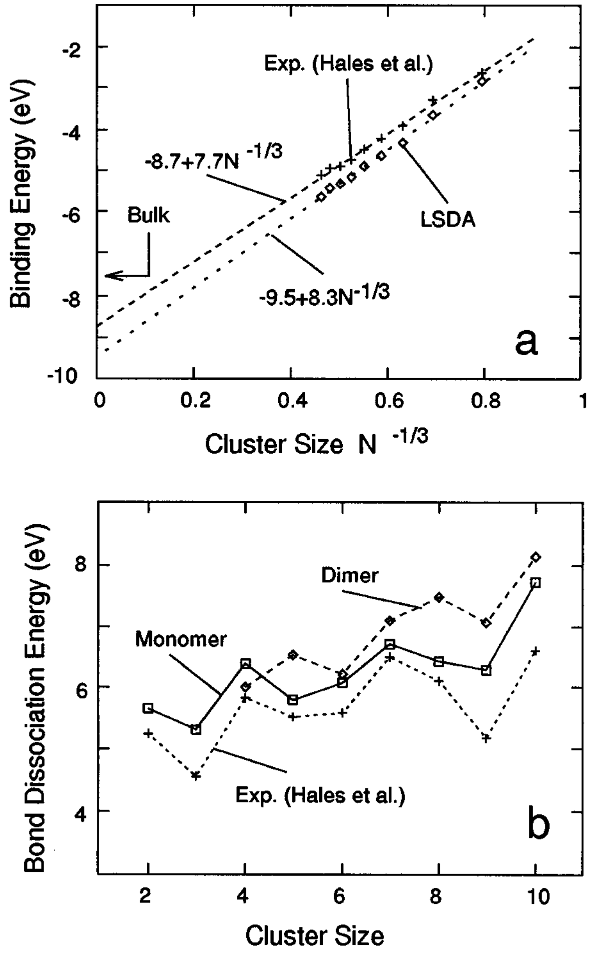

FIG. 2. (a) shows the binding energies and (b) the fragmentation energies. The experimental values by Hales *et al.* (Ref. 18) are also included.

From the computed low-energy isomers in Fig. 1, the general trend when adding atoms into larger units turns out to be a monotonic increase of the coordination number. The atoms are added to maximize the number of connected atoms. It is also important to notice that the low-energy structures are all of the type with only surface atoms, which is an effect of maximizing the coordination for *all* atoms in the cluster. The transition to structures containing shells of atoms or metal atoms that are surrounded by other metal atoms are therefore most likely to take place at larger cluster sizes than the sizes investigated here. The obtained structures, of course, reflect the open d shell, with the possibility to form bonds of covalent type. Analyzing the binding contributions from the d and the s electrons by means of a Mulliken population analysis, we find a charge transfer from the s to the d electrons. By this transfer the structures become stable also with respect to the s electrons. For example, the Mulliken analysis gives effectively 8.2 $(5s5p)$ electrons for Nb_{10}. Except for the dimer, which has a multiplicity of 3, the lowest possible spin states are obtained for all the clusters investigated.

The monotonic increase in the coordination of the atoms is accompanied by an increasing binding energy per atom for the niobium clusters. In Fig. 2(a), the binding energy per atom is shown by diamonds as a function of $N^{-1/3}$. Also included are the experimental binding energies indicated by crosses, determined by the collision-induced dissociation experiments by Hales *et al.*[18] using the ionization potentials as determined by Knickelbein and Yang.[19] The agreement between the experimental and the theoretical results are good, despite the general overbinding. The results were further analyzed with the liquid drop model $\varepsilon(N)=a_v+a_sN^{-1/3}$. a_v and $a_sN^{-1/3}$ are the volume and surface terms, respectively. Surprisingly enough, this expression predicts both the theoretical results as well as the experimental values. However, the fits to both the experimental and the theoretical results give volume energies that are too large compared to the cohesive energy of the bulk niobium.[20] Our results suggest that another type of binding will occur as the clusters start to have inner atoms, shells of atoms, that could give a smaller surface energy coefficient. In Fig. 2(b), the deviation from a monotonic increase in the binding energy: the monomer fragmentation energies, or bond dissociation energies, are displayed. The fragmentation energies are calculated as the difference in binding energy between adjacent clusters and are compared to the experimental data in Ref. 18. The experimental trend is well reproduced by the calculations, which indicate that the structures we obtained as the ground state isomers are energetically close to the experimental ground state configurations. In Fig. 2(b), the dissociation into units containing the dimer is also shown (dashed line). This channel is always more energetically costly compared to the monomer fragmentation, except for the tetramer. This could be viewed as an effect of the monotonic increase of the cohesive energy, i.e., all added atoms are strongly bound.

A challenging problem is the underlying reasons for the strong size fluctuations in the reactivity pattern of niobium clusters, observed in various experiments.[21,24] Nb_8 and Nb_{10} were, for example, measured as low reactive in the reaction with H_2.[21(a),21(c)] This led to speculations whether or not the reactivity was influenced by the ionization potential, since both Nb_8 and Nb_{10} have high ionization potentials. Theoretically, the influence of the Fermi level on chemisorption energies have been investigated for the H_2-Ni system showing no particular correlation.[22] Instead, the importance of symmetry matching between the adsorbate and the metal frontier orbital has been stressed.[22,23] Recently, the experimental CO reactivity with niobium has been reported.[24] Also in this reaction Nb_{10} appeared to be unreactive, while Nb_8 was as reactive as the adjacent cluster sizes. To investigate the reason for the size variations in this experiment, we have also studied CO adsorption on the optimized niobium clusters.

Two different adsorption sites—a hollow and an on-top site — were investigated. In a first step, all atoms were kept fixed. The on-top site was modeled by d(C-O) = 2.19 a.u. and d(C-Nb) = 4.0 a.u. This represents the optimized values for CO chemisorbed on Nb_3. The hollow site was modeled according to the optimized values for Nb_4, d(C-O) = 2.25 a.u., and the distance from the plane spanned by the three Nb atoms and the C atom was 3.50 a.u. In Fig. 3, we show the results for the chemisorption energy as a function of cluster size and chemisorption site. With the exception of Nb_{10}, the hollow site is preferred with respect to the on-top site. The trend for the on-top chemisorption is an increase in chemisorption energy with increasing cluster size. A trend, however, which is broken for Nb_7 and Nb_{10}. For the hollow position, a general decrease in chemisorption energy was found with increasing cluster size. These trends could be an effect of the change in coordination as the clusters become larger, yielding fewer dangling d orbitals. The result that the hollow is preferred to the on-top site is expected from the atomic configuration of niobium and the common picture for CO adsorption: 5σ donation and $2\pi^*$ backdonation.[25] In the hollow site, the backdonation is efficient because of the unfilled d orbitals and the Coulomb repulsion in the donation is smaller than for the on-top site. To reduce the repulsion in the on-top position, the systems would have to be excited and the $4d^55s^0$ configuration is 1.4 eV above the $4d^45s^1$ configuration. To quantitatively reveal the donation and backdonation, we analyze the atomic Mulliken populations for the carbon C($2s$) and C($2p$) orbitals. For the free molecule, the occupation is 1.85 and 2.01, respectively. At chemisorption on Nb_4, this changes to 1.59 (1.67) and 2.45 (2.20) for the hollow (on-top) position. These values for the hollow and the on-top site were found to show just minor variations with clusters size.

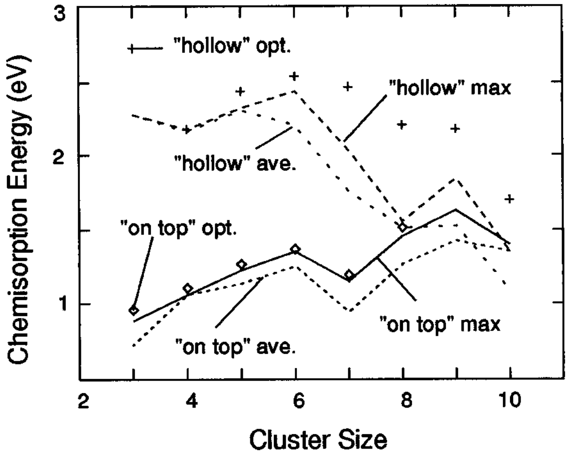

FIG. 3. Adsorption energies for different clusters and adsorption sites. Results denoted ‘‘max’’ are the highest chemisorption energy for each cluster with fixed bond distances. ‘‘ave.’’ are the fixed bond distances computations averaged over all different sites. ‘‘opt.’’ represent the optimized chemisorption energies.

In a second step, we let the CO molecule relax from the sites where the largest chemisorption energies were obtained in the static computation. In Fig. 3, the results are indicated by crosses and diamonds. For the on-top position, the optimization resulted in a slight shift in the chemisorption energies. The CO internuclear distance did not change on average from the value used above, while the NbC distance was enlarged to 4.14 a.u. The molecule did not, to any large extent, bend away from the initial orientation. This was, on the other hand, the case for the hollow position. As shown in Fig. 3, a large change in the chemisorption energy was seen for cluster sizes larger than the tetramer.

In qualitative agreement with experiments,[24] we obtained a low chemisorption energy for CO on Nb_{10}. Since Nb_8 and Nb_{10} in some respects have similar electronic properties, with a low-lying HOMO level and a large HOMO-LUMO (Ref. 26) separation ($\sim$ 1 eV), we look for possible reasons for the differences in chemisorption energy other than the differences in cluster stability [Fig. 2(b)]. We do this by turning the optimized geometries of Nb_8 and Nb_{10} into a C_{2v} symmetry, which for both clusters were a fairly small geometrical adjustment. In this symmetry group, π^* corresponds to b_1 and b_2, while σ corresponds to a_1. Analysis of the computed energy spectrum gives that the symmetry orbitals near the Fermi level of Nb_8 was of b_1 and b_2 character while the highest occupied orbital for Nb_{10} was of a_2 character. A suggestion is, therefore, that the smaller chemisorption energy for Nb_{10} partly is due to a less efficient and energetically more costly backdonation.

In conclusion, we have analyzed the electronic and geometrical properties of niobium clusters in the range from two to ten atoms. The calculations are in good agreement with experimental data. The bonding is characterized by a balance between s and d electrons. The open d shell gives strong bonds and tends to maximize the number of nearest neighbors. A charge transfer from the s to the d electrons stabilizes the structures also with respect to the s electrons. In addition, the reactivity of CO towards the niobium clusters was investigated. All different on-top and hollow sites were investigated. For all clusters, the hollow site is predicted as the preferred chemisorption site. The results indicate cluster size effects with a local minimum for Nb_{10}.

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[26] HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital