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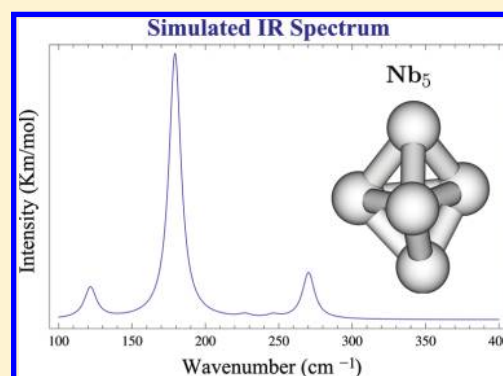
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Structures, Frequencies, and Energy Properties of Small Neutral, Cationic, and Anionic Niobium Clusters

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ABSTRACT: A density functional study of small neutral, cationic, and anionic niobium clusters ranging from two to six atoms using the linear combination of Gaussian-type orbitals density functional theory (LCGTO-DFT) approach was performed. The calculations employed a gradient-corrected exchange-correlation functional and a newly developed niobium scalar-relativistic model core potential optimized for gradient-corrected density functional calculations. For neutral and charged systems, several isomers and different multiplicities were studied with the aim to determine the lowest energy structures. A vibrational analysis was performed to characterize these isomers. Structural parameters, harmonic frequencies, ionization potentials, and electron affinities are reported. The obtained results are compared with available data from the literature. Based on this comparison new assignments for the ground state structures of the pentamer and hexamer niobium clusters are proposed.



1. INTRODUCTION

Transition metal (TM) clusters have received considerable attention from different experimental and theoretical research groups due to their particular physical, chemical, electronic, and magnetic properties (see, for example, refs 1–21 and references therein). The knowledge of their properties furnishes information about how the transition from atom or molecules to the solid state may occur. Therefore, the determination of structural properties and the growth pattern of these clusters offer a first step toward the understanding of the development of a solid. Often the electronic and geometric structures of small TM clusters vary considerably with cluster size. To gain insight into how these properties vary with system size, it is important to use reliable computational methods for the study of neutral as well as for positive and negative TM charged systems. Niobium clusters are among the most thoroughly studied TM clusters. In fact, several investigations have been performed on small to medium sized niobium clusters focusing on both chemical reactivity and physical properties, including dissociation energies, ionization potential, electron affinities, and electric static polarizabilities.^{22–27} However, different studies on the structural features and the electronic properties of niobium clusters performed through different theoretical methods^{28–34} have provided different results. Therefore, many features of these clusters are still not well understood, and several questions about the correct ground state structure and multiplicity of these systems are still open. Moreover, despite the availability of a consistent number of articles on small neutral niobium clusters, much less attention has been paid to the study of structure and properties of their corresponding cationic and anionic systems. In this work, with the aim to gain more insight into the structural evolution and the electronic properties of niobium clusters, we have intensively studied

neutral, cationic, and anionic niobium clusters until to the hexamer employing DFT as it is implemented in the deMon2k code.³⁵ For this purpose, a newly developed scalar Relativistic Model Core Potential (RMCP) GGA optimized basis set for the niobium atom was employed. The structure optimization was performed considering different topologies and spin multiplicity to scan as much as possible each of the studied potential energy surfaces (PES) and to find the lowest energetic structures. In the following sections the optimized ground state structures of Ni_n , Ni_n^+ , and Ni_n^- ($n \leq 6$) clusters obtained from our RMCP-GGA Linear Combination Gaussian Type Orbital–Kohn–Sham DFT (LCGTO-KS-DFT) calculations are presented. The stability of the structures was tested by harmonic frequency analysis calculations. Structural parameters, harmonic frequencies, energy, ionization potential, and electron affinity are reported. The calculated values are compared with available experimental and theoretical data. To the best of our knowledge, this represents one of the most extensive studies performed on small neutral niobium clusters and their ions.

2. COMPUTATIONAL DETAILS

All calculations were performed using the DFT deMon2k program.³⁵ The exchange-correlation potential was numerically integrated on an adaptive grid.³⁶ The grid accuracy was set to 10^{-5} in all calculations. The Coulomb energy was calculated by the variational fitting procedure proposed by Dunlap, Connolly, and Sabin.^{37,38} The structure optimizations were performed with the generalized gradient approximation (GGA) employing the

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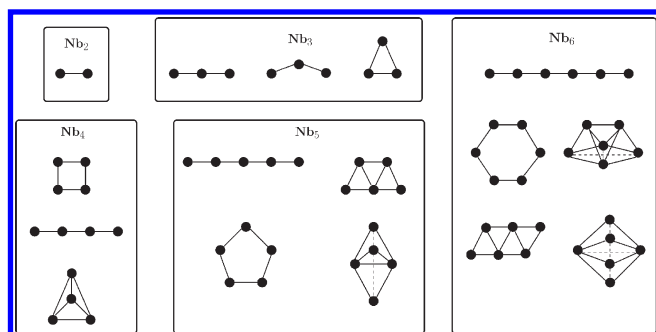


Figure 1. Different topologies considered as initial structures for the geometry optimization of Nb_n , Nb_n^+ , and Nb_n^- ($n = 2-6$) clusters.

exchange-correlation functional proposed by Perdew and Wang (PW86).^{39,40} The basis set employed for the niobium atom is a newly developed scalar RMCP optimized for gradient-corrected functionals. Here we name this newly developed basis set as RMCP-GGA. The exponents and contraction coefficients of this RMCP-GGA are listed in the Appendix. The contraction coefficients have been optimized following the same procedure of our previous works for the optimization of GGA basis sets of 3d TM elements.^{41,42} For the fitting of the density, the auxiliary function set A2* was automatically generated.^{41,43} We named this auxiliary function set as GEN-A2*. For the structure optimization, a quasi-Newton method in internal redundant coordinates with analytic energy gradients was used.⁴⁴ The convergence was based on the Cartesian gradient and displacement vectors with a threshold of 10^{-4} and 10^{-3} au, respectively.

To distinguish between stable structures and transition state structures, a frequency analysis was performed. The second derivatives were calculated by numerical differentiation (two-point finite difference) of the analytic energy gradients using a displacement of 0.001 au from the optimized geometry for all 3N coordinates. The harmonic frequencies were obtained by diagonalizing the mass-weighted Cartesian force constant matrix. The obtained harmonic frequencies of the neutral and cationic pentamer and hexamer niobium clusters have been used to simulate the vibrational spectra without scaling. The calculated stick spectra are folded with a Gaussian function with line width of 5 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1. Atomic Calculation and Cluster Ground State Structures. The ground state of the niobium atom is a ^6D state with electronic configuration $[\text{Kr}]4\text{d}^45\text{s}^1$.⁴⁵ The first excited state is an ^4F state with electronic configuration $[\text{Kr}]4\text{d}^35\text{s}^2$, lying 0.18 eV above the atomic ground state.⁴⁵ The excitation energies and ionization potentials of the TM atoms are notoriously difficult to compute accurately. Our calculations predict, in agreement with the experimental data, a ^6D state followed at 0.26 eV by an ^4F state. This result made us confident that the newly developed RMCP-GGA optimized for the niobium atom is reliable for the prediction of structural and spectroscopic properties of larger clusters.

The experimental ionization potential (IP) for the Nb atom is 6.75 eV.⁴⁵ We calculated an IP value of 7.24 eV. The experimental atomic electron affinity (EA) is 0.894 eV.⁴⁶ Our calculations predict an EA value of 0.99 eV. Considering these results, for the niobium clusters we expect errors in the calculated IP and EA of around 0.5 eV for the IP and 0.1 eV for the EA, respectively.

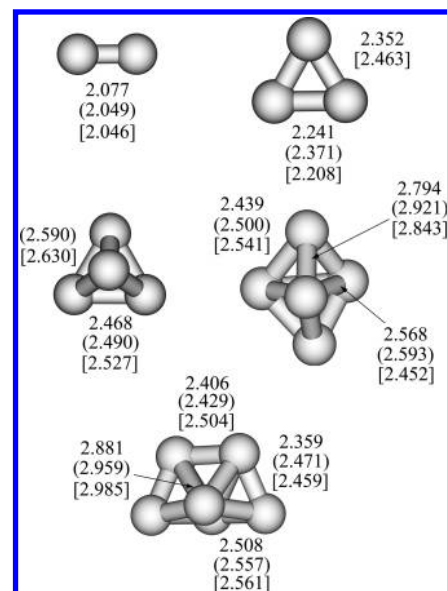


Figure 2. Ground state structures and bond lengths (in Å) of Nb_n , Nb_n^+ , and Nb_n^- ($n = 2-6$) clusters. The calculations have been performed with the RMCP-GGA basis set in combination with the PW96 functional.

The source of these errors is thought to be primarily due to the different self-interaction energy in neutral, anionic, and cationic systems which is present in current DFT methods^{47,48} since approximate exchange functionals fail to exactly cancel the self-interaction that is present in the Coulomb energy.

Full geometry optimization of the neutral, positive, and negative charged niobium clusters was performed considering as initial structures the different topologies illustrated in Figure 1. For each topology several multiplicities were studied to find the lowest minima on each PES. In Figure 2, the found ground state structures and their corresponding bond lengths in angstroms for the neutral (values without brackets), cationic (values in round brackets), and anionic (values in square brackets) niobium cluster structures are presented.

The niobium dimer is one of the most experimentally studied niobium clusters.^{12,22-24,49,50} The ground state of the Nb_2 is a triplet $^3\Sigma_g$ state which is derived from the electron configuration $1\pi_u^41\sigma_g^22\sigma_g^21\delta_g^2$. The experimental bond distance for the Nb_2 molecule is 2.07781(18) Å.²² The accuracy of the used DFT method for the determination of bond lengths and angles is estimated to be within 1–2 pm and 1–2 degrees, with respect to experiment, respectively. To find the Nb_2 ground state structure, several PESs as singlet, triplet, quintet, septet, and nonet were investigated. Our employed RMCP-GGA/PW86 method predicts the Nb_2 ground state structure on the triplet PES (see Figure 2). The calculated ground state multiplicity is in good agreement with the one determined experimentally via rotationally resolved electronic spectroscopy.²² We calculated an equilibrium bond length of 2.077 Å which is in good agreement with the reported experimental value (Figure 2). This result made us confident that this method is adequate to predict the ground state structure of larger neutral niobium clusters. In our calculations the niobium dimer ground state is followed at 0.06 eV by a low-lying state on the singlet PES which has a longer bond distance of about 0.8 Å with respect to the triplet ground state. The isomers on the quintet, septet, and nonet PESs lie much higher in energy with respect to the Nb_2 ground state.

Table I. Vibrational Frequencies [cm^{-1}] of Nb_n , Nb_n^+ , and Nb_n^- ($n = 2-6$) Ground State Structures^a

method	Nb_2	Nb_3	Nb_4	Nb_5	Nb_6
RMCP-GGA/PW86	459	171, 246, 360	161, 164, 233 236, 238, 340	79, 109, 118 141, 179, 227 246, 270, 331	81, 91, 126 150, 177, 186 201, 207, 213 221, 277, 281
method	Nb_2^+	Nb_3^+	Nb_4^+	Nb_5^+	Nb_6^+
RMCP-GGA/PW86	483	240, 241, 364	134, 160, 174 180, 188, 340	71, 121, 134 142, 218, 220 224, 258, 325	26, 69, 102 107, 143, 151 176, 207, 216 232, 268, 300
method	Nb_2^-	Nb_3^-	Nb_4^-	Nb_5^-	Nb_6^-
RMCP-GGA/PW86	458	120, 214, 357	134, 135, 148 156, 212, 302	71, 73, 138 159, 213, 215 238 241, 300	61, 83, 116 147, 164, 171 187, 203, 209 215, 273, 280

^a The calculations were performed with the RMCP-GGA/PW86 method. The optimized cluster structures are given in Figure 2.

To the best of our knowledge, the experimental bond lengths for Nb_2^+ and Nb_2^- are still unknown. For both cation and anion dimers, the doublet, quartet, and sextet PESs were investigated. The Nb_2^+ ground state is found on the quartet PES (Figure 2). This result is in agreement with the one reported previously by other authors.³¹ The found Nb_2^+ ground state is followed by a low-lying state in the doublet PES.

For Nb_2^- our computations predict the ground state on the doublet PES followed at 0.03 eV by a low-lying state on the quartet PES. For both Nb_2^+ and Nb_2^- ground states the calculated bond lengths are about 3 pm shorter with respect to the one calculated for the neutral molecule (Figure 2).

To find the niobium trimer ground state structure and the ground state structure of its corresponding cation and anion, the three topologies illustrated in Figure 1 were studied. For the neutral niobium trimer the multiplicities 2, 4, 6, and 8 were considered. In our study, the found ground state structure for Nb_3 is a triangular C_{2v} structure on the doublet PES with a short bond length of 2.241 Å and two longer bond lengths of 2.352 Å (see Figure 2). This result is in good agreement with the results obtained by other authors.^{28–30,34} The first low-lying state is a triangular C_{2v} structure on the quartet PES which lies at 0.39 eV above the found ground state. All linear isomers with different multiplicities as well as the triangular structures with higher multiplicities lie much higher in energy with respect the ground state structure.

For the ionic niobium trimers, the multiplicities 1, 3, and 5 were, respectively, studied. For the Nb_3^+ , as ground state structure, we find a triangular D_{3h} structure on the triplet PES with a bond length of 2.371 Å (Figure 2). This ground state structure is followed at 0.28 eV by a triangular C_{2v} structure on the quartet PES.

The Nb_3^- ground state structure is a triangular C_{2v} structure on the triplet PES (Figure 2). This structure is followed by two low-lying states in triangular C_{2v} structures on the quintet and singlet PES which lie at 0.17 and 0.19 eV above the found ground state, respectively.

To determine the ground state structure of the neutral niobium tetramer, we carried out full geometry optimizations

of the tetrahedral, rhomboid, and linear topologies illustrated in Figure 1 considering the singlet, triplet, quintet, septet, and nonet PESs, respectively. During the optimization procedure, all the rhomboid structures fall into tetrahedral structures. A regular tetrahedral structure on the singlet PES was found as the ground state structure (Figure 2). The optimized bond length is 2.468 Å. This result is in agreement with the results obtained in refs 28, 29, 33, and 34, but it differs from the ground state structure reported in ref 30 where a slightly distorted tetrahedron was obtained. From our calculations, it was found that this ground state structure is well separated in energy with respect to all found low-lying states. In fact, the first low-lying state we found is a distorted tetrahedral structure on the triplet PES which lies at 0.66 eV above the found Nb_4 ground state structure.

For the study of the ionic niobium tetramers, the different initial isomers were studied in the doublet, quartet, and sextet PESs. For both positive and negative charged clusters, the ground state structure is found as a distorted tetrahedral structure on the PES with lowest multiplicity. The first low-lying state is in both cases a distorted tetrahedral structure on the quartet PES which lies at 0.97 eV and at 0.53 eV, for the cationic and the anionic cluster, respectively.

The four different topologies illustrated in Figure 1 were considered for the study of the niobium pentamer. For the neutral cluster, all initial structures were studied in multiplicity 2, 4, 6, and 8, respectively. During the optimization procedure, all planar and trapezoidal topologies fall into three-dimensional structures. For the Nb_5 cluster, our calculations predict a distorted trigonal bipyramid structure on the doublet PES (Figure 2). This structure is followed by two isoenergetic distorted trigonal bipyramid structures on the quartet and sextet PESs, respectively, which lie at 0.75 eV above it. Our result is in fair agreement with the ground state structures predicted in refs 28, 29, 33, and 34.

The ground state structure of the Nb_5^+ cluster is a distorted trigonal bipyramid structure on the triplet PES (Figure 2) followed at 0.11 eV by a similar structure on the singlet PES. For the Nb_5^- cluster, the ground state structure found in this

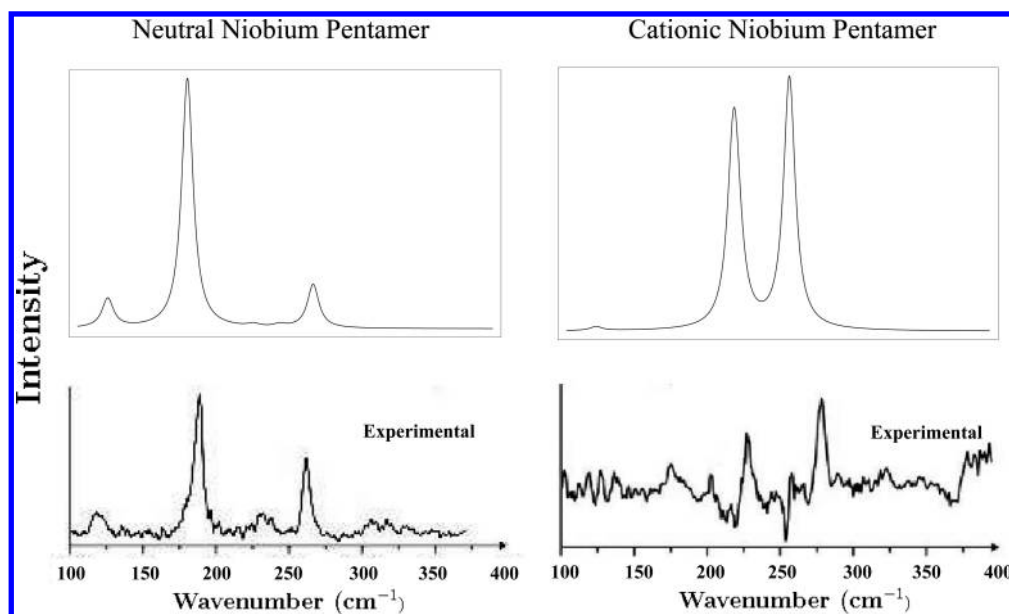


Figure 3. Simulated IR spectra of the ground state structures of Nb_5 (left) and Nb_5^+ (right) clusters. The experimental spectra reported in ref 27 for comparison are also shown.

work is a distorted trigonal bipyramid structure on the lowest PES (Figure 2). In this case, the first low-lying state is a distorted trigonal bipyramid structure on the triplet PES which lies at only 0.10 eV above the found ground state structure.

To determine the ground state structure of the Nb_6 cluster, full geometry optimization was performed considering as initial structures five different topologies (see Figure 1). For the neutral cluster, the multiplicity 1, 3, 5, and 7 were considered, whereas for the corresponding positive and negative charged clusters the multiplicity 2, 4, 6, and 8 were, respectively, studied. During the optimization procedure, almost all topologies fall into structures characterized by a distorted prisms shape. In the case of the neutral niobium cluster, such a structure on the singlet PES was found as the ground state structure (Figure 2). This result is in agreement with the ground state structure reported in ref 29. However, the first low-lying state is on the triplet PES at only 0.005 eV. From these calculations alone it is not possible to determine which of the two isomers is the ground state structure for this cluster. Fortunately, Fielicke and co-workers recorded the far-infrared (IR) spectrum of Nb_5 .²⁷ The simulation of this spectrum will help us to elucidate this point as it will be discussed in the next section. In the case of the cationic niobium cluster, the first low-lying state is a tetragonal-square bipyramidal structure on the doublet PES which lies at 0.05 eV above the ground state. This structure was found as a ground state structure in previous studies using different methodologies.³⁴ The next low-lying state we found for this cluster is a distorted prism at 0.51 eV above the found ground state. The first low-lying state of the Nb_6^- cluster is a distorted prism on the quartet PES at 0.76 eV above the ground state structure.

We notice that, in general, for the ground state structures of the neutral clusters a low multiplicity is preferred. Moreover, a deeper analysis of the clusters as the number of Nb atoms increases shows that for the larger niobium clusters we studied (i.e., pentamer and hexamer) no change in topology occurs if one electron is added to or if it is taken away from the neutral cluster.

Finally, we notice that in general the ground state structures of small niobium clusters obtained in this work agree well with the results obtained in a recent DFT work where larger basis sets for the niobium atom were used.³⁴

3.2. Ground State Harmonic Frequencies. To characterize the calculated ground state structures of the studied Nb clusters as well as to provide clues for further desirable experimental investigations on these systems, the harmonic vibrational frequencies have been calculated by two-point numerical differentiation of the energy gradients. The results are collected in Table I for the neutral, cationic, and anionic ground state structures, respectively. As can be seen from Table I, all the ground state structures presented have no imaginary frequency, and therefore they are real minima on the PES.

We notice that, fortunately, for the Nb_2 as well as for the neutral and cationic niobium pentamer and hexamer clusters IR experimental data with which we can compare our calculated harmonic frequencies are available.^{22,27}

For the dimer, our methodology predicts a vibrational frequency of 459 cm^{-1} which is in good agreement with the experimental value of 424.8917(12) cm^{-1} reported by James and co-workers.²² The accuracy of the used DFT methodology in the determination of harmonic frequencies is of about 50 cm^{-1} with respect to experiment. The ground state structure determination of the neutral and cationic Nb_5 and Nb_6 clusters has been the subject of controversy in the literature which has been partly elucidated only very recently.³⁴ With the aim to gain more insight into these clusters and to try to make a better assignment of their ground state structures, we have simulated the IR spectra of these clusters and compared those with the experimental spectra presented by Fielicke and co-workers in ref 27.

In Figure 3 the simulated spectra of the ground state structure of neutral (left) and cationic (right) Nb_5 clusters are graphically displayed. These calculated spectra cover the range below 300 cm^{-1} (Figure 3). In the case of the neutral niobium pentamer cluster, we calculated three peaks at 118, 179, and 270 cm^{-1} , the peak at 179 cm^{-1} being the most intense. For the

cationic cluster, we obtained two intense peaks at 218 and 258 cm^{-1} , respectively, with the last resulting in the most intense peak. We noticed that for the Nb_5 cluster there is a quite remarkable agreement between the calculated and experimental IR spectra and that the simulated IR spectrum of the corresponding cationic cluster is also satisfactory since the positions of the calculated peaks agree well with the two most intense bands observed experimentally (see Figure 3).

In Figure 4 are graphically displayed the experimental spectra (a) and the simulated IR spectra for the ground state (b) and first low-lying state (c) we obtained for the neutral (left) and cationic (right) niobium hexamer, respectively. For the distorted prism of the neutral structure in low multiplicity, we obtained intense peaks at 150, 177, 185, 207, and 281 cm^{-1} . The calculated most intense peak is at 207 cm^{-1} followed by the one at 281 cm^{-1} . The other three peaks present much less intensity with respect to these two. The calculated IR spectrum of the distorted prism structure on the triple PES is characterized by two intense bands at around 192 and 259 cm^{-1} , respectively. The comparison of the two simulated IR spectra for the neutral niobium hexamer with the experimental spectrum clearly indicates that both these structures are responsible for the observed IR spectrum of this cluster.

For the cationic Nb_6 cluster, our result indicates that the simulated IR spectrum for the tetragonal-square bipyramidal structure (Figure 4, structure c) is in better agreement with the observed experimental IR spectrum. For this structure, three intense peaks at 207, 221, and 277 cm^{-1} were obtained. As was

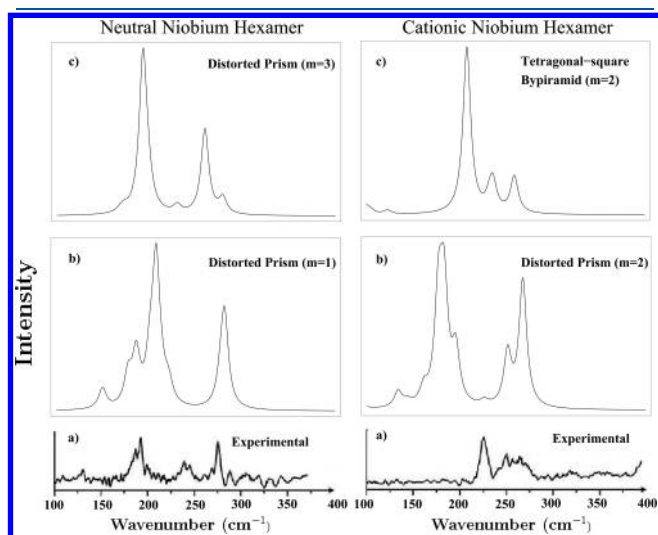


Figure 4. Simulated IR spectra of the ground state (b) and first low-lying (c) structures of Nb_6 (left) and Nb_6^+ (right) clusters. The experimental spectra (a) reported in ref 27 for comparison are also shown.

already pointed out in the literature, the relative stability energy of some small niobium clusters is very sensitive to the used methodology.³⁴ Therefore, for this cluster we have also performed geometry optimization calculations with other GGA functionals. Indeed, our calculations show that an interchange of the found ground state structure with the found first low-lying structure might occur. Therefore, the tetragonal-square bipyramidal structure is with high probability the structure responsible for the observed IR spectrum of the Nb_6^+ cluster despite the fact that the two peaks with low intensity are not clearly identified in the experiment.

To the best of our knowledge, this work represents one of the most systematic vibrational analysis studies reported for neutral, positive, and negative charged Nb clusters up to the hexamer. Therefore, this work provides additional information about these systems.

3.3. Ionization Potentials and Electron Affinities. In Table II, the results of the calculated adiabatic ionization potential (IP) are listed. For comparison, the experimental IP values for niobium clusters up to six atoms are also reported.^{23,24,45,50–53} As we can see from Table II, for some small niobium clusters such as Nb_2 , Nb_3 , and Nb_4 , different experimental IPs are available. We notice that for these clusters a not negligible spread in between the different measured IP values exists and that the reported experimental values present in the same cases very large error bars (Table II). Therefore, our first-principles calculations are very useful in trying to understand which of the experimental values could be considered as the most reliable. Our calculated IPs decrease going from the atom to the hexamer (Table II). As we were expecting from the atomic calculations, our computed IP values overestimate the experimental values by about 0.5 eV for all studied niobium clusters. As we already discussed, the reason for this overestimation could be due to the different self-interaction energy in the neutral and cationic clusters. Since the ratio between the average of the two reported atomic experimental IPs and our calculated value is 0.933, we use this factor to scale our calculated IPs. The scaled values are reported in parentheses in Table II. We can observe that the scaled values obtained with the RMCP-GGA/PW86 method are in much better agreement with the experimental IP values. In our opinion, these values can be taken as reliable, to obtain improved experimental results for the IP of small niobium clusters. In particular, for the niobium trimer, which is one of the niobium clusters which presents a quite large spread in between the reported experimental IPs, from our calculations we suggest a value of 5.52 eV.

In Table III the results obtained for the adiabatic electron affinity (EA) are reported. The available experimental values, for comparison, are also given.^{25,54} We notice that for the Nb_2 cluster the experimental EA is still not available. As it can be noticed from Table III, the available experimental values indicated that

Table II. Adiabatic Ionization Potential (IP) in eV for Nb_n ($n = 1–6$) Clusters in Their Calculated Ground States^a

method	Nb_1	Nb_2	Nb_3	Nb_4	Nb_5	Nb_6
RMCP-GGA/PW86	7.24	6.71 (6.26)	5.92 (5.52)	5.86 (5.47)	5.68 (5.30)	5.55 (5.18)
exp.	6.75 ^b	6.23 ± 0.33 ^d	5.32 ± 0.65 ^d	5.64 ± 0.05 ^f	5.45 ± 0.05 ^f	5.38 ± 0.05 ^f
	6.77 ^c	5.92 ± 0.32 ^e	5.6 ± 0.8 ^g	5.58 ± 0.1 ^h		
		6.2 ± 0.1 ^f	5.81 ± 0.05 ^f	5.80 ± 0.31 ^d		

^a The calculations have been performed with the RMCP-GGA/PW86 method. Scaled IP values are reported in parentheses. The experimental data, for comparison, are also reported. ^b Ref 51. ^c Ref 45. ^d Ref 23. ^e Ref 24. ^f Ref 50. ^g Ref 52. ^h Ref 53.

Table III. Adiabatic Electron Affinity (EA) in eV for Nb_n (n = 1–6) Clusters in Their Calculated Ground States^a

method	Nb ₁	Nb ₂	Nb ₃	Nb ₄	Nb ₅	Nb ₆
PW86/RMCP-GGA	0.99	1.03 (0.930)	1.17 (1.06)	1.22 (1.10)	1.74 (1.57)	1.80 (1.62)
exp.	0.894 ^b		1.09 ^c	1.10 ^c	1.52 ^c	1.58 ^c

^a The calculations have been performed with the RMCP-GGA/PW86 method. Scaled AE values are reported in parentheses. The experimental data, for comparison, are also reported. ^b Ref 25. ^c Ref 54.

the EA increases with cluster size up to the niobium hexamer. The increase of EA is moderate from the niobium atom to the niobium tetramer, whereas it is much more pronounced going from the tetramer to the hexamer (Table III). As expected from our atomic calculation, the calculated values overestimate the experimental values by about 0.1 eV or less. Since the ratio between the atomic experimental EA and our calculated values is 0.903, we use this factor to scale our calculated EAs. The scaled EA values are reported in parentheses in Table III. As can be seen from Table III, the agreement between the experimental and the scaled EA values is quite satisfying. Therefore, we feel confident to suggest the computational method proposed in this study as an alternative and reasonable method for future studies on much larger niobium clusters than those presented in this work. The calculated EAs reproduce well the experimental trend. In fact, our calculated EA values increase slowly from the niobium atom up to the Nb₄ cluster. The calculated EA increases then about 0.5 eV going from the Nb₄ to the Nb₆ clusters (see Table III).

4. CONCLUSIONS

In this work, LCGTO-DFT-GGA first-principles all-electron calculations for the structural and spectroscopic properties of neutral, cationic, and anionic small Nb clusters up to the hexamer were presented. For the niobium atom a newly developed RMCP basis set optimized for GGA calculations was proposed and employed for the structure optimization and for the property calculations of the studied niobium clusters. Several topological structures in different PESs were investigated for the neutral clusters as well as for the ionic systems. All found minima were characterized by vibrational analysis. The found ground state structures are in good agreement with the ones obtained using much larger basis sets. These results can be used to guide future experiments. Structural parameters, harmonic frequencies, adiabatic ionization potentials, and adiabatic electron affinities were presented. The obtained results were compared with the experimental data available in the literature. The trends of the obtained energetic properties are in good agreement with the ones reported experimentally. By the comparison of the simulated and experimental IR spectra, new assignments for the ground state structures of the Nb₅ and Nb₆ clusters are proposed. Therefore, the employed newly developed RMCP-GGA basis sets in combination with GGA functionals might be an adequate method to be considered for the study of structures and properties of larger niobium clusters. This investigation is currently underway in our laboratory.

■ APPENDIX

Exponents and contraction coefficients of the GGA-optimized RMCP for niobium.

subsets	exponents	contraction coefficients
s subset	388.50288000	−0.02528
	32.53781100	0.10002
	4.86646180	−0.26910
	0.62454462	0.62379
s subset	0.05881572	1.00000
s subset	0.02299026	1.00000
p subset	264.11451000	0.03804
	70.74282000	0.11550
	7.12287900	−0.44168
	0.90685454	1.00000
p subset	0.31997984	1.00000
d subset	50.19475000	−0.04852
	12.18337100	−0.17090
	0.77944347	0.58376
	0.21348255	0.46633
d subset	0.06968391	1.00000
d subset	0.02725280	1.00000

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