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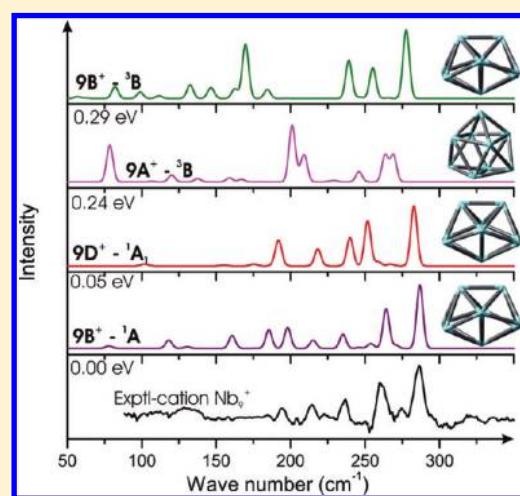
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Electronic Structures, Vibrational and Thermochemical Properties of Neutral and Charged Niobium Clusters  $\text{Nb}_n$ ,  $n = 7-12$ Pham Vu Nhat,<sup>†,‡</sup> Vu Thi Ngan,<sup>†</sup> Truong Ba Tai,<sup>†</sup> and Minh Tho Nguyen<sup>\*,†,§</sup><sup>†</sup>Department of Chemistry and Mathematical Modeling and Computational Science Center (LMCC), Katholieke Universiteit Leuven, B-3001 Leuven, Belgium<sup>‡</sup>Department of Chemistry, Can Tho University, Can Tho, Vietnam<sup>§</sup>Institute for Computational Science and Technology of HoChiMinh City, Thu Duc, HoChiMinh City, Vietnam

S Supporting Information

**ABSTRACT:** Geometric and electronic structures, vibrational properties, and relative stabilities of niobium clusters  $\text{Nb}_n$ ,  $n = 7-12$ , are studied using both DFT (BPW91 and M06 functionals) and CCSD(T) calculations with the cc-pVnZ-PP basis set. In each cluster, various lower-lying states are very close in energy in such a way that the ground state cannot be unambiguously established by DFT computations. Nb clusters tend to prefer the lowest possible spin state as the ground state, except for  $\text{Nb}_{12}$  ( $^3\text{A}_g$ ). The optimal structure of the cluster at a certain size does not simply grow from that of the smaller one by adding an atom randomly. Instead, the Nb clusters prefer a close-packed growth behavior.  $\text{Nb}_{10}$  has a spherically aromatic character, high chemical hardness and large HOMO–LUMO gap. Electron affinities, ionization energies, binding energy per atom, and the stepwise dissociation energies are evaluated. Energetic properties exhibit odd–even oscillations. Comparison with experimental values shows that both BPW91 and M06 functionals are reliable in predicting the EA and IE values, but the BPW91 is deficient in predicting the binding and dissociation energies. We re-examine in particular the experimental far IR spectra previously recorded using the IR-MPD and free electron laser spectrometric techniques and propose novel assignments for  $\text{Nb}_7$  and  $\text{Nb}_9$  systems. The IR spectra of the anions are also predicted.



## 1. INTRODUCTION

Clusters of niobium are in recent times the subject of continuing experimental and theoretical investigations. Previous experiments<sup>1–15</sup> on  $\text{Nb}_n$  mainly focused on their mass, optical, photoelectron, and infrared spectrometric properties and thermochemical parameters, including ionization energies, electron affinities, and atomization energies, as well as their chemical reactivity in the gas phase. Measurements of ionization energies and electron affinities pointed out an even–odd oscillation for clusters in the size range of 6–16 atoms. Along the curve of ionization energy values as a function of the size, local maxima have been seen experimentally at  $n = 8, 10$ , and 16. Photoemission studies also confirmed that these cluster sizes have larger frontier orbital energy gaps than the others. Such results are in line with the low reactivities of  $\text{Nb}_8$  and  $\text{Nb}_{10}$  with small molecules such as  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{CO}$ ,<sup>11,12</sup> and, hence, suggest that these systems have a closed electronic shell structure in their ground state. Reactions of niobium cation clusters  $\text{Nb}_n^+$  ( $n$  up to 28) with  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and a variety of simple organic compounds were extensively investigated by several groups.<sup>13,14</sup> Ferroelectricity in neutral cluster  $\text{Nb}_n$  with  $n$  ranging from 2 to 150, was

also recorded.<sup>15</sup> The optical absorption spectra of small and isolated Nb clusters from 7 to 20 atoms were measured from 334 to 614 nm via photodepletion of  $\text{Nb}_n \cdot \text{Ar}$  van der Waals complexes.<sup>4</sup> Recently, the far-infrared spectra of both neutral  $\text{Nb}_n$  and cationic  $\text{Nb}_n^+$  clusters ( $n = 5-9$ ) were experimentally recorded in the region of 85–600  $\text{cm}^{-1}$  using IR-MPD technique in conjunction with free electron laser (FELIX) spectroscopy and the observed bands were assigned by Fielicke and co-workers with the help of DFT computations.<sup>7</sup>

Most of previous theoretical investigations focused on clusters smaller than  $\text{Nb}_{10}$  and employed density functional theory (DFT) methods, and only a few computational studies used MO methods.<sup>16,17</sup> Recently, we have re-examined the structural, electronic, and vibrational properties of the smallest  $\text{Nb}_n$  clusters, with  $n = 2-6$ , in their neutral, cationic, and anionic states. Using different MO and DFT methods, we revealed the novel identity

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of the ground states of the  $\text{Nb}_5$  and  $\text{Nb}_6$  systems and, thereby, proposed new assignments for the vibrational spectra.<sup>18</sup>

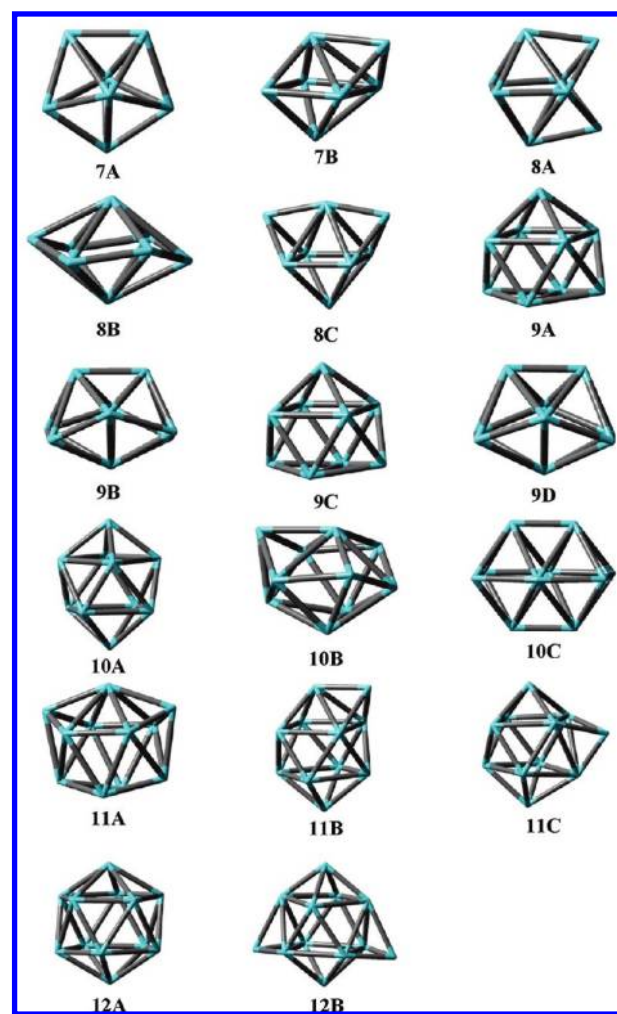
For the larger systems, earlier DFT study using the LSD and BLYP computations<sup>19</sup> of the 8–10 Nb clusters found two geometrical isomers that compete for the ground state of  $\text{Nb}_9$ , but only one low-energy isomer for  $\text{Nb}_{10}$ . An early study on neutral clusters  $\text{Nb}_n$ , with  $n$  up to 7,<sup>20</sup> found a close-packed growth behavior for these systems. A similar behavior was also observed in a subsequent DFT study on  $n = 2$ –23 neutral clusters.<sup>21</sup> Among the clusters in the small size range, being up to 10 atoms, the identity of ground state of not only the neutral  $\text{Nb}_9$ , but also the cation  $\text{Nb}_9^+$  remains a matter of discussion because there is an emergence of quasi-degenerate lower-lying states. Structures of the anionic clusters up to  $n = 8$  have been investigated by comparing the experimental energetic results with the local spin density functional (LSD) calculations.<sup>8</sup>

In relation to our recent theoretical studies on  $\text{Nb}_n$  clusters,<sup>18</sup> we set out to determine the properties of the neutral and both positively and negatively charged  $\text{Nb}_n$  compounds in the following size ranging from the heptamer to the dodecamer ( $n = 7$ –12). Together with the reported results, we then discuss the growth behavior and electronic structure by comparing the calculated IR spectra, electron affinities (EA), ionization energies (IE), and dissociation energies ( $D_e$ ) with available experimental data. Because the identity of the ground state of some oligomers is still not clear, the main purpose of the current work is to determine the relevant structures and subsequently assign the corresponding spectral properties, in particular, the IR spectra.

## 2. COMPUTATIONAL METHODS

Initial geometry optimizations and subsequent determination of the harmonic vibrational frequencies are carried out using density functional theory (DFT) with the pure BPW91 functional and the correlation-consistent cc-pVDZ-PP basis set,<sup>22</sup> where PP stands for a pseudopotential, or an effective core potential (ECP). The electrons in the inner shells are strongly bound and do not play an important role in the chemical bonding between atoms. Hence, these electrons, along with the nucleus, are considered as the inert core and thus described by an effective core potential. For Nb, the 4s, 4p, 4d, 5s, and 5p orbitals are thus taken as valence orbitals. As in our previous study,<sup>18</sup> we select the BPW91 functional, in conjunction with a correlation-consistent basis set, because they were proven to be applicable for niobium clusters. For each cluster, we consider the two lowest spin states. Calculated harmonic vibrational frequencies are employed to characterize the stationary points and to simulate the vibrational spectra. The initial structures for the optimization were constructed using two different routes. In the first route, the initial geometries of a certain size  $\text{Nb}_n$  is generated from some lowest-lying isomers of the smaller size  $\text{Nb}_{n-1}$  by adding an extra Nb atom randomly. This procedure can also be called as a successive growth algorithm. In the second route, we employed the reported results of other transition metal clusters at similar sizes as a guide.

Some thermochemical properties including ionization energy, electron affinity, atomization and dissociation energy are computed by employing the more recently developed M06 functional, which appears to be suitable for transition metals.<sup>23</sup> To improve relative energies, we perform single-point electronic energy calculations for quasi-degenerate states competing for the ground state using the coupled-cluster theory CCSD(T) and the



**Figure 1.** Selected geometries of  $\text{Nb}_n$  and their ions (BPW91/cc-pVDZ-PP).

cc-pVDZ-PP basis set on the basis of the BPW91/cc-pVDZ-PP optimized geometries. All electronic structure calculations are carried out using the Gaussian 03<sup>24</sup> and Molpro 2009 suites of programs.<sup>25</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Equilibrium Structures and Vibrational Spectra.** In Figure 1 we present the selected structures of the neutral  $\text{Nb}_n$  considered and their singly charged species. As a convention, each structure is designated by a number  $n$ , with  $n = 7$ –12, followed by a letter A, B, C, and so on. The superscripts  $+$  and  $-$  refer obviously to the cation and anion, respectively. For each size, the relative energies obtained at the BPW91/cc-pVDZ-PP + ZPE level with respect to the lowest-lying structures are summarized in Table 1.

*A. Heptamers.* Two structures 7A and 7B are predicted to be the most stable forms of  $\text{Nb}_7$ . While the former can be considered as a distorted pentagonal  $C_s$  bipyramid, which is substantially distorted from a  $D_{5h}$  symmetry, the latter is a capped octahedron (also  $C_s$ ). For the neutral  $\text{Nb}_7$ , the ground state is confirmed to be the  $^2A''$  state of 7A, as reported in previous studies.<sup>20,21</sup> The corresponding high spin  $^4A''$  state of this form is energetically less favorable by 0.48 eV (BPW91/cc-pVDZ-PP). In the second

**Table 1.** Ground and Lower-Lying States of  $\text{Nb}_n^{0,\pm 1}$  ( $n = 7-12$ ) and Relative Energies (RE) at the BPW91/cc-pVDZ-PP Level

cluster	state	RE (eV)	cluster	state	RE (eV)
Nb <sub>7</sub> 7A (C <sub>s</sub> )	<sup>2</sup> A''	0.00	Nb <sub>9</sub> <sup>-</sup> 9B <sup>-</sup> (C <sub>2</sub> )	<sup>1</sup> A	0.03
	<sup>4</sup> A''	0.48		<sup>3</sup> A	0.11
7B (C <sub>s</sub> )	<sup>2</sup> A'	0.92	9C <sup>-</sup> (C <sub>2v</sub> )	<sup>1</sup> A <sub>1</sub>	0.54
	<sup>4</sup> A''	1.15		<sup>3</sup> A <sub>2</sub>	0.42
Nb <sub>7</sub> <sup>+</sup> 7A <sup>+</sup> (C <sub>s</sub> )	<sup>3</sup> A''	0.00	9D <sup>-</sup> (C <sub>2v</sub> )	<sup>1</sup> A <sub>1</sub>	0.28
	<sup>1</sup> A'	0.07		<sup>3</sup> A <sub>2</sub>	0.16
7B <sup>+</sup> (C <sub>s</sub> )	<sup>3</sup> A''	1.00	Nb <sub>10</sub> 10A (D <sub>4</sub> )	<sup>1</sup> A <sub>1</sub>	0.00
	<sup>1</sup> A'	1.15		<sup>1</sup> A <sub>1</sub>	0.45
Nb <sub>7</sub> <sup>-</sup> 7A <sup>-</sup> (C <sub>s</sub> )	<sup>1</sup> A'	0.00	10A (D <sub>4d</sub> )	<sup>3</sup> B <sub>1</sub>	0.36
	<sup>3</sup> A'	0.31		<sup>3</sup> A'	0.99
7B (C <sub>s</sub> )	<sup>1</sup> A'	0.91	10C (D <sub>2h</sub> )	<sup>1</sup> A <sub>g</sub>	1.66
	<sup>3</sup> A'	1.10		<sup>2</sup> A <sub>1</sub>	0.00
Nb <sub>8</sub> 8A (C <sub>2v</sub> )	<sup>1</sup> A <sub>1</sub>	0.00	Nb <sub>10</sub> <sup>+</sup> 10A <sup>+</sup> (D <sub>4</sub> )	<sup>2</sup> A <sub>2</sub>	0.07
	<sup>3</sup> B <sub>2</sub>	0.46		<sup>4</sup> B <sub>1</sub>	0.41
8B (D <sub>3d</sub> )	<sup>1</sup> A <sub>1g</sub>	0.33	10B <sup>+</sup> (C <sub>s</sub> )	<sup>2</sup> A'	0.44
	<sup>1</sup> A <sub>1</sub>	2.00		<sup>2</sup> B <sub>1u</sub>	1.10
8C (C <sub>2v</sub> )	<sup>1</sup> A <sub>1</sub>	0.00	10C <sup>+</sup> (D <sub>2h</sub> )	<sup>2</sup> A <sub>1</sub>	0.00
	<sup>4</sup> A <sub>1</sub>	0.59		<sup>2</sup> A <sub>2</sub>	0.01
Nb <sub>8</sub> <sup>+</sup> 8A <sup>+</sup> (C <sub>2v</sub> )	<sup>2</sup> A <sub>2</sub>	0.00	Nb <sub>10</sub> <sup>-</sup> 10A <sup>-</sup> (D <sub>4</sub> )	<sup>2</sup> A <sub>1</sub>	0.00
	<sup>2</sup> B <sub>2</sub>	1.70		<sup>2</sup> A <sub>2</sub>	0.01
8B <sup>+</sup> (C <sub>s</sub> )	<sup>2</sup> A''	0.37	10A <sup>-</sup> (C <sub>2v</sub> )	<sup>4</sup> B <sub>2</sub>	0.71
	<sup>2</sup> B <sub>2</sub>	1.70		<sup>2</sup> A'	0.86
8C <sup>+</sup> (C <sub>2v</sub> )	<sup>2</sup> B <sub>1</sub>	0.00	10C <sup>-</sup> (D <sub>2h</sub> )	<sup>2</sup> B <sub>1g</sub>	1.47
	<sup>4</sup> B <sub>2</sub>	0.83		<sup>2</sup> B <sub>2</sub>	0.00
Nb <sub>8</sub> <sup>-</sup> 8A <sup>-</sup> (C <sub>2v</sub> )	<sup>2</sup> A'	0.39	Nb <sub>11</sub> 11A (C <sub>2v</sub> )	<sup>4</sup> A <sub>2</sub>	0.62
	<sup>2</sup> B <sub>2</sub>	1.67		<sup>2</sup> A''	1.14
8B <sup>-</sup> (C <sub>s</sub> )	<sup>2</sup> B <sub>2</sub>	1.67	11B (C <sub>s</sub> )	<sup>2</sup> A''	1.28
	<sup>2</sup> B <sub>2</sub>	1.67		<sup>1</sup> A <sub>1</sub>	0.00
8C <sup>-</sup> (C <sub>2v</sub> )	<sup>2</sup> A	0.00	Nb <sub>11</sub> <sup>+</sup> 11A <sup>+</sup> (C <sub>2v</sub> )	<sup>3</sup> A <sub>2</sub>	0.43
	<sup>4</sup> B	0.40		<sup>1</sup> A'	1.13
Nb <sub>9</sub> 9A (C <sub>2</sub> )	<sup>2</sup> A	0.04	11B <sup>+</sup> (C <sub>s</sub> )	<sup>1</sup> A'	1.45
	<sup>4</sup> B	0.31		<sup>1</sup> A'	1.45
9B (C <sub>2</sub> )	<sup>2</sup> A <sub>1</sub>	0.24	11C <sup>+</sup> (C <sub>s</sub> )	<sup>1</sup> A <sub>1</sub>	0.00
	<sup>4</sup> B <sub>1</sub>	0.47		<sup>3</sup> B <sub>2</sub>	0.005
9C (C <sub>2v</sub> )	<sup>2</sup> A <sub>1</sub>	0.06	Nb <sub>11</sub> <sup>-</sup> 11A <sup>-</sup> (C <sub>s</sub> )	<sup>1</sup> A'	0.99
	<sup>4</sup> B <sub>2</sub>	0.37		<sup>1</sup> A'	1.00
9D (C <sub>2v</sub> )	<sup>3</sup> B	0.24	11B <sup>-</sup> (C <sub>s</sub> )	<sup>1</sup> A'	1.00
	<sup>1</sup> A	0.31		<sup>1</sup> A'	1.00
Nb <sub>9</sub> <sup>+</sup> 9A <sup>+</sup> (C <sub>2</sub> )	<sup>3</sup> B	0.24	11C <sup>-</sup> (C <sub>s</sub> )	<sup>1</sup> A'	1.00
	<sup>1</sup> A	0.31		<sup>1</sup> A'	1.00
9B <sup>+</sup> (C <sub>s</sub> )	<sup>1</sup> A	0.00	Nb <sub>12</sub> 12A (C <sub>i</sub> )	<sup>1</sup> A <sub>g</sub>	0.00
	<sup>3</sup> B	0.29		<sup>3</sup> A <sub>g</sub>	0.04
9C <sup>+</sup> (C <sub>2v</sub> )	<sup>1</sup> A <sub>1</sub>	0.36	12B (C <sub>2v</sub> )	<sup>1</sup> A <sub>1</sub>	3.36
	<sup>3</sup> B <sub>1</sub>	0.47		<sup>2</sup> A <sub>u</sub>	0.00
9D <sup>+</sup> (C <sub>2v</sub> )	<sup>1</sup> A <sub>1</sub>	0.05	Nb <sub>12</sub> <sup>+</sup> 12A <sup>+</sup> (C <sub>i</sub> )	<sup>4</sup> A <sub>g</sub>	0.98
	<sup>3</sup> A <sub>2</sub>	0.39		<sup>2</sup> A <sub>1</sub>	4.13
Nb <sub>9</sub> <sup>-</sup> 9A <sup>-</sup> (C <sub>2</sub> )	<sup>1</sup> A	0.00	12B <sup>+</sup> (C <sub>2v</sub> )	<sup>2</sup> A <sub>1</sub>	4.13
	<sup>3</sup> A	0.21		<sup>2</sup> A <sub>u</sub>	0.00
			Nb <sub>12</sub> <sup>-</sup> 12A <sup>-</sup> (C <sub>i</sub> )	<sup>4</sup> A <sub>u</sub>	0.03
				<sup>2</sup> B <sub>1</sub>	2.94

shape, 7B, the <sup>2</sup>A' state is also more stable than the corresponding high spin <sup>4</sup>A'' state. The separation gaps of both doublet and quartet states of 7B, relative to 7A (<sup>2</sup>A''), amount to 0.92 and 1.15 eV, respectively.

At their equilibrium point, the lowest-energy isomer of either the cation Nb<sub>7</sub><sup>+</sup> or the anion Nb<sub>7</sub><sup>-</sup> is a distorted pentagonal bipyramid having a C<sub>s</sub> point group as well. In ref 7, a C<sub>s</sub> singlet ground state for Nb<sub>7</sub><sup>+</sup> was reported, and a C<sub>2</sub> triplet state is 0.47 eV higher in energy. In contrast, our DFT results point out

two states, namely, <sup>1</sup>A' 7A-1<sup>+</sup> and <sup>3</sup>A'' 7A-3<sup>+</sup>, both having the 7A geometrical shape, to be nearly degenerate. The <sup>3</sup>A'' state was not found in ref 7. In fact, the singlet–triplet gap is calculated to be only 0.07 (BPW91) or 0.01 eV (M06). However, single point CCSD(T) results reverse the state ordering in predicting that the <sup>1</sup>A' is ~0.17 eV lower in energy than the <sup>3</sup>A'' state. The relative energies of other electronic states computed at the BPW91/cc-pVDZ-PP level are listed in Table 1.

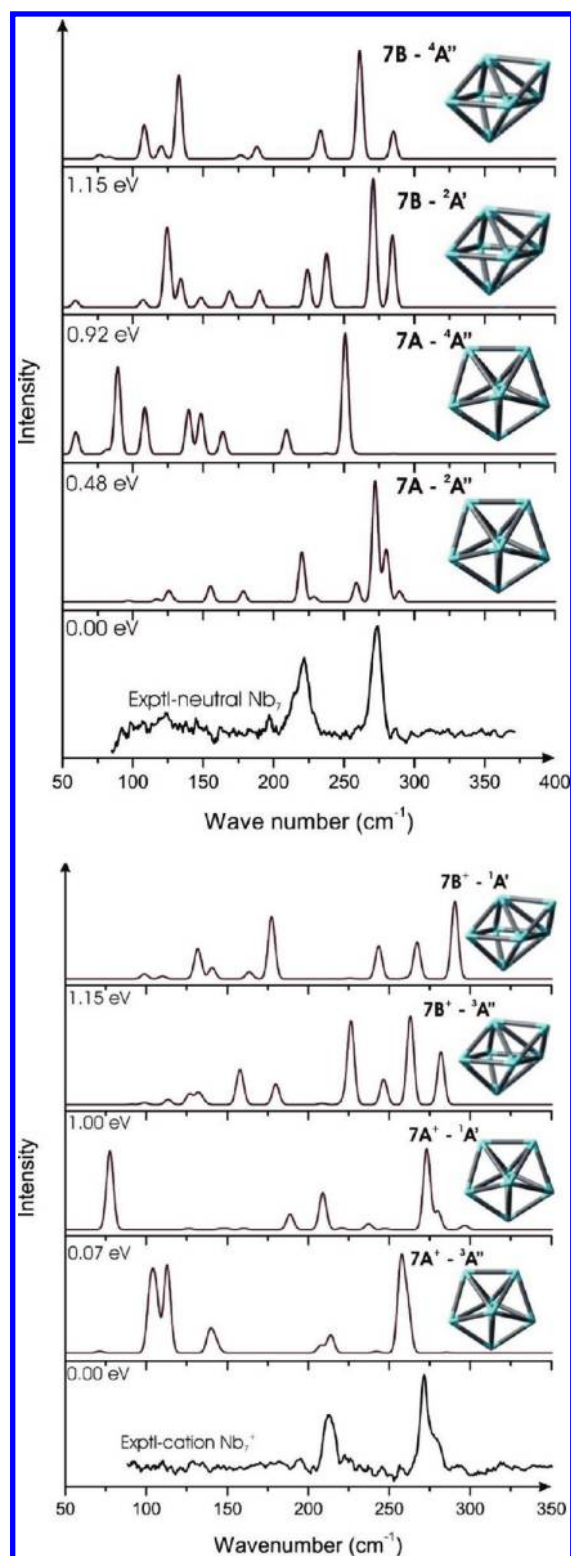
The geometrical shapes and IR spectra of some lower-lying structures of Nb<sub>7</sub> and Nb<sub>7</sub><sup>+</sup> determined using BPW91/cc-pVDZ-PP calculations are illustrated in Figure 1 along with the experimental spectra taken from ref 7 for the purpose of comparison. For the neutral heptamer, in agreement with a previous assignment,<sup>7</sup> the calculated vibrational spectrum of 7A (C<sub>s</sub>, <sup>2</sup>A'') clearly gives the best match to experiment. The calculated vibrational spectrum for the ground state <sup>2</sup>A' 7A of Nb<sub>7</sub> covers the range below 300 cm<sup>-1</sup> with two characteristic peaks centered at around 225 and 275 cm<sup>-1</sup>, which are also seen experimentally. This allows us to conclude that the distorted pentagonal bipyramid 7A (C<sub>s</sub>, <sup>2</sup>A'') is actually the Nb<sub>7</sub> ground state and manifested in its observed far IR spectrum.

For the cation Nb<sub>7</sub><sup>+</sup>, comparison of the theoretical IR spectra of the four low-lying isomers with experiment leads to a view that the singlet 7A-1<sup>+</sup> (C<sub>s</sub>, <sup>1</sup>A') is the main carrier of the observed spectrum. Thus, along with the energetic results stated above, this agreement on the IR properties allow us to suggest that the Nb<sub>7</sub><sup>+</sup> cation possesses a closed-shell ground state, but with a small singlet–triplet gap. Furthermore, a low-frequency mode (~80 cm<sup>-1</sup>) is theoretically found for Nb<sub>7</sub><sup>+</sup>, but unfortunately, the experiment did not cover the range below 90 cm<sup>-1</sup>. The calculated spectrum for the lowest-lying state of the anion is plotted in Figure 5. The anion Nb<sub>7</sub><sup>-</sup> is predicted to vibrate in a range below 300 cm<sup>-1</sup> with five significant bands. The IR spectra of the lower-lying states of the anion are plotted in Figure S1 of the Supporting Information (ESI). In addition, for the sake of comparison, we also used the M06 functional. Geometries were reoptimized using the M06 functional with the same basis set. The IR spectra of Nb<sub>7</sub> and Nb<sub>7</sub><sup>+</sup> that were calculated using both BPW91 and M06 functionals along with the experiments are given in Figures S13 and S14 of ESI. In general, the IR results BPW91 obtained from BPW91 are more reliable than the M06. Therefore, the former functional was utilized to generate vibrational frequencies.

**B. Octamers.** We find several possible structures for the octamers, including 8A, 8B, and 8C, displayed in Figure 1. These structures can be viewed as consisting of a six-atom core with two caps. The lowest-energy Nb<sub>8</sub> form is a bicapped distorted octahedron 8A (Figure 3) with a C<sub>2v</sub> symmetry and a closed-shell <sup>1</sup>A<sub>1</sub> state. The 8B and 8C structures also correspond to capping of a hexagon, with the caps being in either a *trans* (D<sub>3d</sub>) or *cis* (C<sub>2v</sub>) configuration, respectively, but both are higher in energy. 8B (<sup>1</sup>A<sub>1g</sub>) lies 0.33 eV above, while 8C (<sup>1</sup>A<sub>1</sub>) is 2.0 eV above 8A (BPW91 values).

Following electron removal or attachment, the shape 8A is also giving rise to the most stable form 8A<sup>+</sup> for Nb<sub>8</sub><sup>+</sup> and 8A<sup>-</sup> for Nb<sub>8</sub><sup>-</sup>. Such a shape is also reported in earlier studies as the most stable configuration for Nb<sub>8</sub> and its singly charged species.<sup>8,19</sup> Both HOMO and LUMO of 8B (D<sub>3d</sub>) are degenerate, so adding or removing an electron reduces its symmetry because of a Jahn–Teller effect. Therefore, the cation 8B<sup>+</sup> as well as anion 8B<sup>-</sup> prefer a C<sub>s</sub> point group. Starting from the third isomer 8C, which is much less stable than 8A and 8B, the two states 8C<sup>+</sup> (cation, <sup>2</sup>B<sub>1</sub>) and 8C<sup>-</sup> (anion, <sup>2</sup>B<sub>2</sub>) are calculated to lie 1.70 and 1.67 eV higher in energy than the ground states 8A<sup>+</sup> (Nb<sub>8</sub><sup>+</sup>) and 8A<sup>-</sup> (Nb<sub>8</sub><sup>-</sup>), respectively.





**Figure 2.** Experimental and theoretical IR spectra of  $\text{Nb}_7$  (upper) and  $\text{Nb}_7^+$  (lower).

The far IR spectra of both  $\text{Nb}_8$  and  $\text{Nb}_8^+$  were recorded in a prior experiment and reported in ref 7. For the purpose of comparison, we again regenerate them in Figure 2, along with our calculated results. For the neutral, the best match to the experimental IR spectrum obviously comes from isomer  $8\text{A}$  ( $^1\text{A}_1$ ), which exhibits three intense

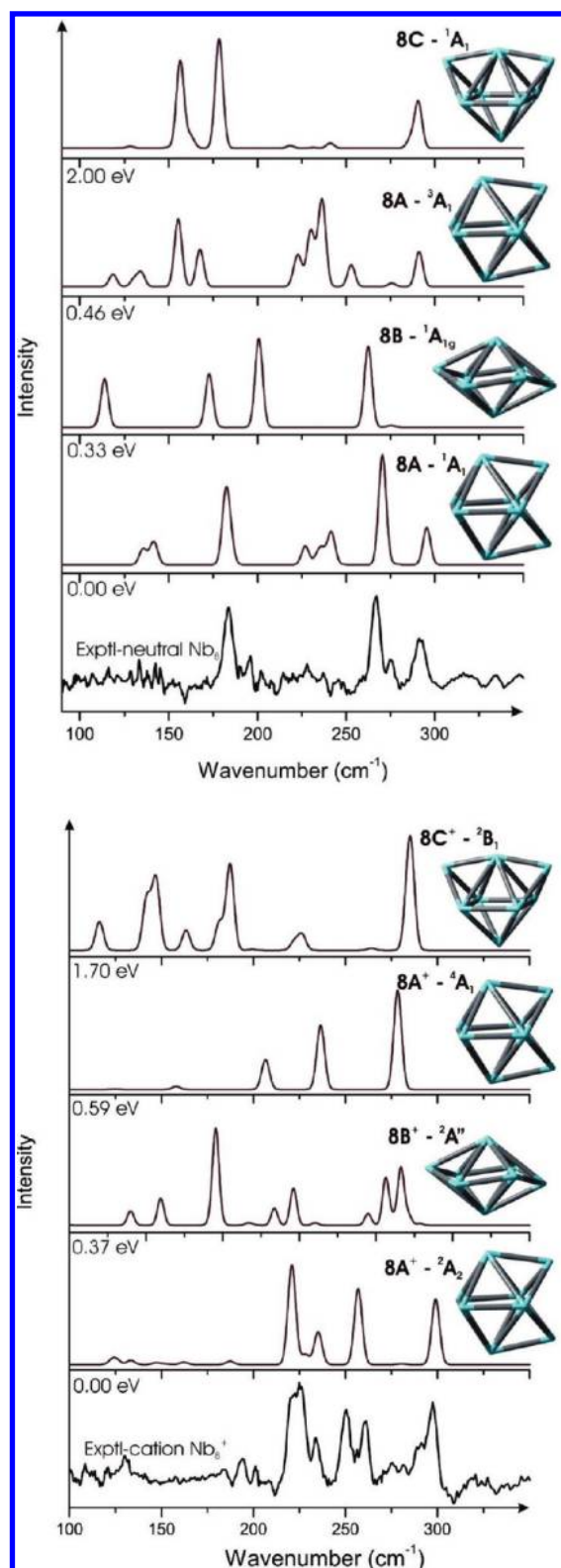
**Table 2.** Relative Energies of Lower-Lying States at Various Levels (Using the cc-pVDZ-PP Basis Set)

			relative energies (eV)		
cluster		state	BPW91	M06	CCSD(T)
cation	7A <sup>+</sup>	3A <sup>''</sup>	0.00	0.00	0.17
		1A <sup>'</sup>	0.07	0.01	0.00
neutral	9A	2A	0.00	0.11	0.18
	9B	2A	0.04	0.00	0.00
	9D	2A <sub>1</sub>	0.06	0.08	0.31
cation	9B <sup>+</sup>	1A	0.00	0.00	0.04
	9D <sup>+</sup>	1A <sub>1</sub>	0.05	0.09	0.00
anion	9A <sup>−</sup>	1A	0.00	0.18	1.76
	9B <sup>−</sup>	1A	0.06	0.00	0.00
cation	10A <sup>+</sup>	2A <sub>1</sub>	0.00	0.00	0.00
		2A <sub>2</sub>	0.07	0.27	0.17
anion	10A <sup>−</sup>	2A <sub>1</sub>	0.00	0.00	0.16
		2A <sub>2</sub>	0.01	0.11	0.00
anion	11A <sup>−</sup>	1A <sub>1</sub>	0.00	0.00	0.00
		3B <sub>2</sub>	0.005	0.06	2.60
neutral	12A	1A <sub>g</sub>	0.00	0.00	0.40
		3A <sub>g</sub>	0.04	0.09	0.00
anion	12A <sup>−</sup>	2A <sub>u</sub>	0.00	0.00	0.00
		4A <sub>u</sub>	0.03	0.05	0.18

bands centered at around 186, 276, and  $300\text{ cm}^{-1}$ . The low-frequency modes with very low intensities are also seen theoretically and experimentally for  $\text{Nb}_8$ . Even though the  $\text{Nb}_8$  and  $\text{Nb}_8^+$  have a very similar geometry in their ground electronic state, their IR spectra are much different from each other. The IR spectrum of  $\text{Nb}_8^+$  in the bicapped distorted octahedron  $8\text{A}^+$  ( $\text{C}_{2v}$ ,  $^2\text{A}_2$ ) contains four typical peaks, which are also all detected experimentally. The higher spin  $^4\text{A}_1$  states are much higher in energy and their IR spectra do not comply with experimental findings. These facts suggest that the low-spin states of  $8\text{A}$  and  $8\text{A}^+$  are actually manifested in the observed IR spectra as reported by Filiecke et al.<sup>7</sup> Figure 5 also displays the IR spectrum of the anion  $\text{Nb}_8^-$  in its  $8\text{A}^-$  structure. It is clearly distinguishable from the spectra of the neutral and cation. For the sake of completeness, the IR spectra of the anions in different low-lying forms are plotted in Figure S2 of ESI.

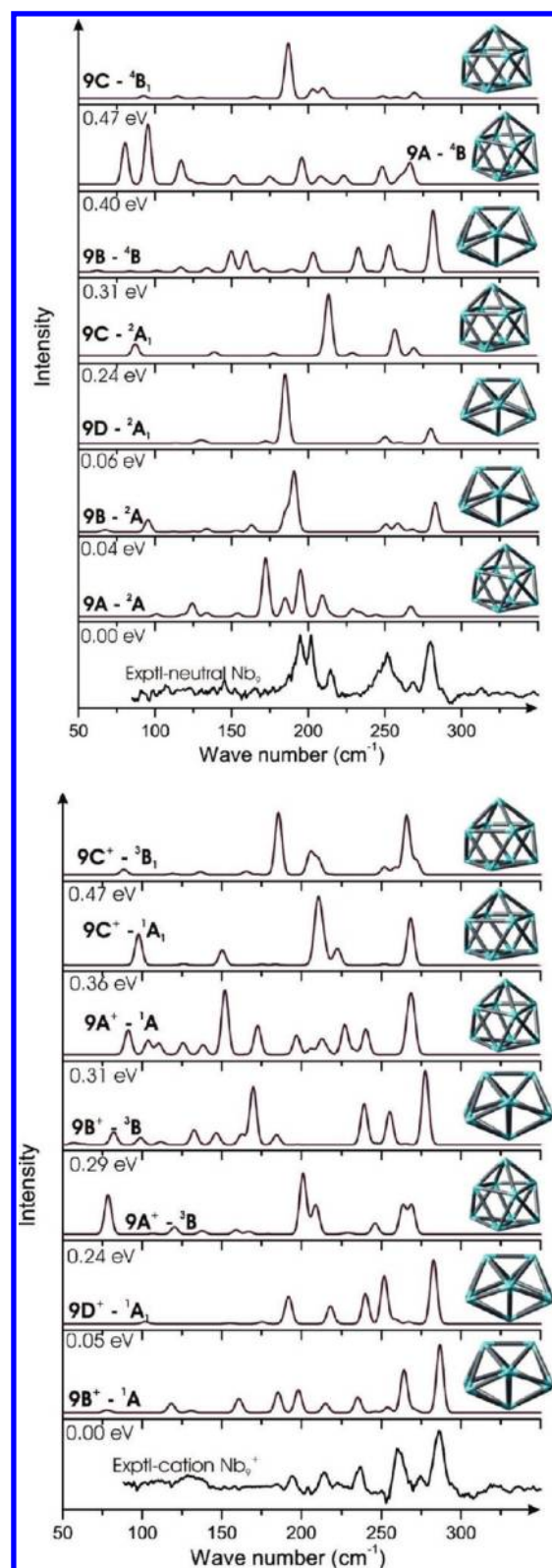
**C. Nonamers.** Gronbeck and co-workers<sup>19</sup> reported that the distorted bicapped pentagonal bipyramid  $9\text{B}$  is the lowest-energy  $\text{Nb}_9$ . In subsequent studies, Filiecke et al.<sup>7</sup> and Kumar et al.<sup>21</sup> agreed with each other that the lowest-energy isomer of  $\text{Nb}_9$  is rather a distorted tricapped trigonal prism  $9\text{A}$  (Figure 1). Our DFT calculations reveal three quasi-isoenergetic structures  $9\text{A}$  ( $^2\text{A}$ ),  $9\text{B}$  ( $^2\text{A}$ ), and  $9\text{D}$  ( $^2\text{A}_1$ ), thus, competing as the ground state of  $\text{Nb}_9$ . The shape  $9\text{A}$  arises from a distortion of a tricapped trigonal prism and  $9\text{B}$  from a distorted bicapped pentagonal bipyramid with the caps located at two adjacent trigonal faces.  $9\text{D}$  is analogous to  $9\text{B}$  but in higher symmetry ( $\text{C}_{2v}$ ). BPW91 calculations predict  $9\text{A}$  as the ground state of  $\text{Nb}_9$  with two states  $9\text{B}$  ( $^2\text{A}$ ) and  $9\text{D}$  ( $^2\text{A}_1$ ) being only marginally, 0.04 and 0.06 eV, above  $9\text{A}$ . Calculations using the M06 functional yield a preference for  $9\text{B}$  ( $^2\text{A}$ ) and both states  $9\text{A}$  ( $^2\text{A}$ ) and  $9\text{D}$  ( $^2\text{A}_1$ ) are now 0.11 and 0.08 eV above  $9\text{B}$ . Another local minimum is the  $9\text{C}$  form, whose geometry is similar to  $9\text{A}$ , but being more symmetric ( $\text{C}_{2v}$ ).

Similarly, structures  $9\text{A}^-$  and  $9\text{B}^-$  turn out to be the lowest and the second-lowest isomers of the anion  $\text{Nb}_9^-$ . The closed-shell



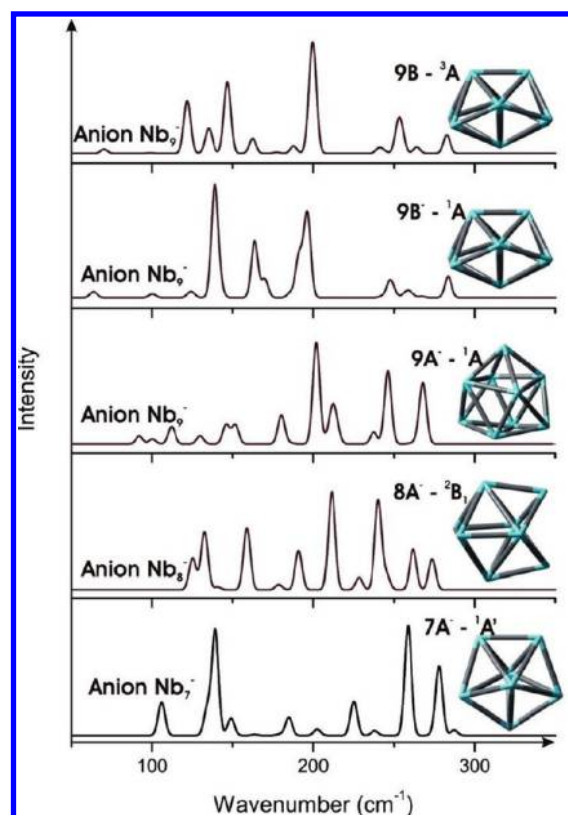
**Figure 3.** Experimental and theoretical IR spectra of  $\text{Nb}_8$  (upper) and  $\text{Nb}_8^+$  (lower).

${}^1\text{A}$  ( $\text{C}_{2v}$ ) states of both forms are also quasi-degenerate (BPW91) and separated by  $\sim 0.06$  eV, in which  $9\text{A}^-$  is the lower state of the two. Conversely, the functional M06 predicts  $9\text{A}^-$  to be  $\sim 0.18$  eV above  $9\text{B}^-$ .



**Figure 4.** Experimental and theoretical IR spectra of  $\text{Nb}_9$  (upper) and  $\text{Nb}_9^+$  (lower).

For the cation  $\text{Nb}_9^+$ , both functionals confirm  $9\text{B}^+$  ( $\text{C}_{2v}$ ,  ${}^1\text{A}$ ) as the lowest-energy isomer.  $9\text{D}^+$  ( $\text{C}_{2v}$ ,  ${}^1\text{A}_1$ ) is now found to lie marginally close, as it is only 0.05 (BPW91) or 0.09 eV (M06) higher in energy than  $9\text{B}^+$ . Thus, it is interesting that several



**Figure 5.** Predicted IR spectra for low-lying states of  $\text{Nb}_7^-$ ,  $\text{Nb}_8^-$ ,  $\text{Nb}_9^-$ .

quasi-degenerate states compete for the ground states of the  $\text{Nb}_9$  systems.

In an attempt to calibrate the DFT results obtained above using both BPW91 or M06 functionals, we perform the CCSD(T)/cc-pVDZ-PP single-point electronic energy calculations for the lower-lying states. Results recorded in Table 2 show a different energy landscape. For the neutral  $\text{Nb}_9$ ,  $9\text{B}$  ( $C_2$ ,  $^2\text{A}$ ) becomes the lowest-energy structure. The doublet states  $9\text{A}$  ( $^2\text{A}$ ) and  $9\text{D}$  ( $^2\text{A}_1$ ) are now 0.18 and 0.31 eV higher in energy than  $9\text{B}$ , respectively. Concerning the  $\text{Nb}_9^+$  cation, CCSD(T) calculations point out that both states  $9\text{B}^+$  and  $9\text{D}^+$  differ by only 0.04 eV from each other but in favor of  $9\text{B}^+$ . Such a small difference could again be changed when a full geometry optimization at the CCSD(T) level could be carried out. Hence, both states  $9\text{B}^+$  and  $9\text{D}^+$  can be regarded as quasi-degenerate states competing for the ground state of  $\text{Nb}_9^+$ . For anion  $\text{Nb}_9^-$ , two isomers  $9\text{A}^-$  and  $9\text{B}^-$  in their singlet state are no longer isoenergetic at CCSD(T)/cc-pVDZ-PP level of theory. Accordingly,  $9\text{B}^-$  ( $^1\text{A}$ ) is found to be 1.76 eV lower than  $9\text{A}^-$  ( $^1\text{A}$ ). Overall, the distorted bicapped pentagonal bipyramid form  $9\text{B}$  emerges as the favored form for nine-niobium systems, irrespective of the charged state.

We now consider the FIR spectra of some low-lying states of  $\text{Nb}_9$  and  $\text{Nb}_9^+$  clusters, which are plotted in Figure 4. For the neutral, comparison of the computed and experimental spectra allows a conclusion to be made that  $9\text{A}$  is not present in the experimental spectrum. In this case,  $9\text{B}$  ( $C_2$ ,  $^2\text{A}$ ) is the main carrier of the observed spectrum, even though  $9\text{D}$  ( $C_{2v}$ ,  $^2\text{A}_1$ ) may contribute to a certain extent. Previously, Fielicke et al.<sup>7</sup> also suggested the  $9\text{B}$  ( $C_2$ ) structure to be responsible for the observed spectrum albeit this structure is not the most stable form and the intensities do not match well.

For  $\text{Nb}_9^+$ , it is clear that the isomer  $9\text{B}^+$  ( $C_2$ ) provides us with the best accord with experiment. However, the calculated spectrum of the quasi-isoenergetic isomer  $9\text{D}^+$  ( $^1\text{A}_1$ ) also agrees well with experimental findings. In addition, these states are energetically quasi-degenerate at both DFT and CCSD(T) levels of theory. In this context, we can deduce that the recorded IR spectrum of  $\text{Nb}_9^+$  most likely arises from vibrations of both isomers, rather than from a sole carrier. A previous study<sup>7</sup> assigned  $9\text{B}^+$  as the main carrier for the observed spectrum. The calculated IR spectrum of  $\text{Nb}_9^-$  is also plotted in Figure 5. As for  $\text{Nb}_7^-$  and  $\text{Nb}_8^-$ , an experimental FIR spectrum of  $\text{Nb}_9^-$  is not available yet. The predicted IR spectra of the different anionic forms are shown in Figure S3 of the ESI.

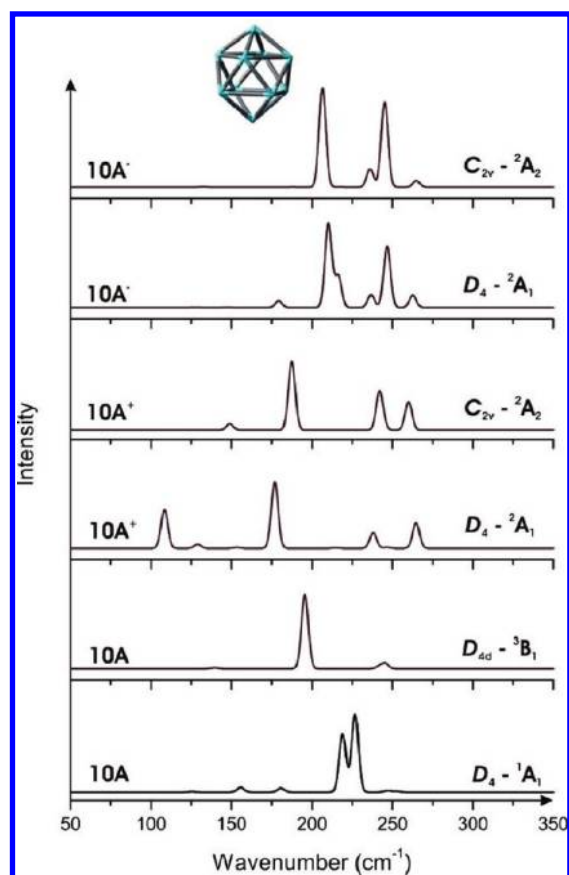
**D. Decamers.** The global minimum of  $\text{Nb}_{10}$  as well as of their ions  $\text{Nb}_{10}^+$  and  $\text{Nb}_{10}^-$  corresponds to a distorted bicapped antiprism (structures  $10\text{A}$ ,  $10\text{A}^+$ , and  $10\text{A}^-$ ) all with  $D_4$  symmetry. Previously, such a conformation but with  $C_4$  symmetry was confirmed to be the global minimum for both neutral  $\text{Nb}_{10}$  and cation  $\text{Nb}_{10}^+$ .<sup>26</sup> In the present work, the  $\text{Nb}_{10}$  ground state is a singlet state  $10\text{A}$  ( $D_4$ ,  $^1\text{A}_1$ ), which is found to be strongly favored over all the isomers we have located. In fact,  $10\text{B}$  ( $^3\text{A}'$ ) and  $10\text{C}$  ( $^1\text{A}_g$ ) are, respectively, located at 0.99 and 1.66 eV above. The low spin  $^1\text{A}_1$  state with  $D_{4d}$  symmetry is energetically less favorable by 0.45 eV, and is in addition a transition structure having an imaginary frequency of  $409i\text{ cm}^{-1}$ . The first excited state, whose energy gap is 0.36 eV, is the high spin  $^3\text{B}_1$  state of  $10\text{A}$  but now with  $D_{4d}$  symmetry.

Our DFT results indicate that both  $\text{Nb}_{10}^+$   $10\text{A}^+$  and  $\text{Nb}_{10}^-$   $10\text{A}^-$  ions also prefer the distorted bicapped square antiprism form with  $D_4$  symmetry and a low spin  $^2\text{A}_1$  state. Again, at the BPW91 level, other quasi-degenerate states emerge competing to be the ground state of the ions. For  $\text{Nb}_{10}^+$ , the  $^2\text{A}_2$  ( $C_{2v}$ ) state of  $10\text{A}^+$  is computed at only 0.07 eV above the  $^2\text{A}_1$  state. However, the M06 functional significantly increases this gap to 0.27 eV. CCSD(T) single-point calculations support the latter DFT results in predicting that the  $^2\text{A}_1$  state is still favored by  $\sim 0.17$  eV over the  $^2\text{A}_2$  counterpart.

Similarly, for  $\text{Nb}_{10}^-$ , two states  $^2\text{A}_1$  ( $10\text{A}^-$ ,  $D_4$ ) and  $^2\text{A}_2$  ( $10\text{A}^-$ ,  $C_{2v}$ ) have a similar energy content, with a separation gap from 0.01 (BPW91) to 0.11 eV (M06). At the CCSD(T) level, this difference is considerably enlarged, but the  $^2\text{A}_2$  state is now 0.16 eV lower in energy than the  $^2\text{A}_1$  state. Additional local minima on the potential-energy surface obtained for  $\text{Nb}_{10}^+$  and  $\text{Nb}_{10}^-$  include the form  $10\text{B}^+$  and  $10\text{C}^+$  and  $10\text{B}^-$  and  $10\text{C}^-$ . Nevertheless, such geometries are much higher in energy than the relevant  $10\text{A}^\pm$  counterpart (see Table 1).

As far as we are aware, no experimental IR data are actually available for the 10-Nb species. The calculated IR spectra for some selected structures of these systems are shown in Figures S4–6 of the ESI. As for a prediction, the IR spectra of the ground states of the neutral and singly charged states are given in Figure 6. It is clear that removing or adding one electron leads to a significant change in vibrational spectra. The predicted spectrum of the neutral  $10\text{A}$  contains two distinct peaks centered at  $\sim 220$  and  $230\text{ cm}^{-1}$ . For the two low-lying states  $^3\text{B}_1$  and  $^1\text{A}_1$  ( $D_{4d}$ ), the spectra become simpler with the most intense bands centered at around 200 and  $215\text{ cm}^{-1}$ , respectively. On the contrary, the IR spectrum of  $\text{Nb}_{10}^+$  in its ground state becomes much more complicated including the presence of four intense peaks in the range of 100– $300\text{ cm}^{-1}$ . The quasi-degenerate state  $^2\text{A}_2$  exhibits three distinct bands in the range of 175– $276\text{ cm}^{-1}$ . For the  $\text{Nb}_{10}^-$  ground state  $10\text{A}^-$ , two distinct bands appear at around 215 and  $245\text{ cm}^{-1}$ , and the other very low intensity peaks seen in the vicinity.

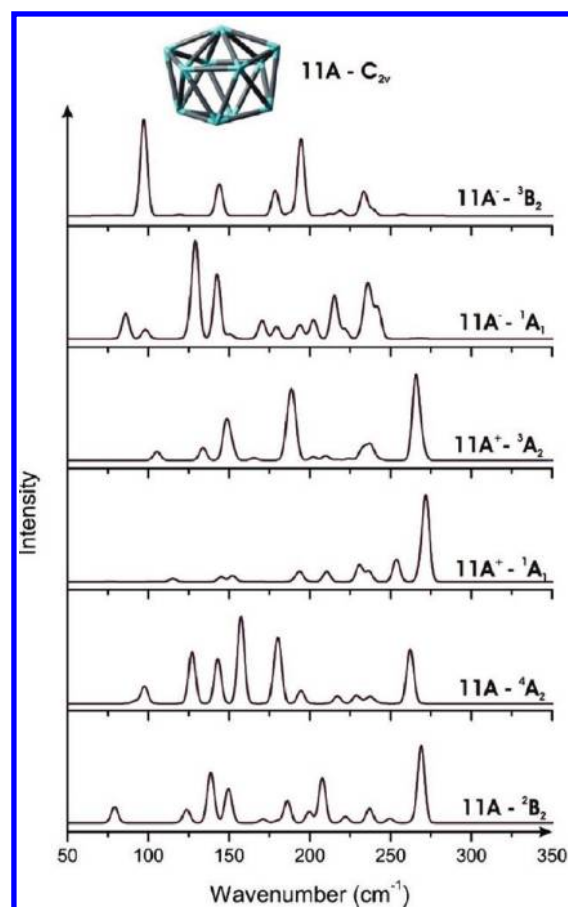




**Figure 6.** Predicted IR spectra for low-lying states of 10-Nb atom systems.

*E. Undecamers.* Previous DFT calculations by Kumar et al.<sup>21</sup> revealed that the lowest-energy geometry of Nb<sub>11</sub> neutral could be described as two pentagonal bipyramids fused at a triangular face. Our findings concur with this and demonstrate in addition that such a shape (11A in Figure 1) turns out to be the energetically optimized configuration for both ions Nb<sub>11</sub><sup>+</sup> and Nb<sub>11</sub><sup>−</sup>. The <sup>2</sup>B<sub>2</sub> state 11A is the ground state of Nb<sub>11</sub>, while a <sup>1</sup>A<sub>1</sub> state is the ground state for both Nb<sub>11</sub><sup>+</sup> 11A<sup>+</sup> and Nb<sub>11</sub><sup>−</sup> 11A<sup>−</sup>. Our DFT results also predict that the anion has two degenerate low-energy states, namely, the <sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>2</sub> states of 11A<sup>−</sup>. At both BPW91 and M06 levels, the triplet state lies only 0.005 and 0.06 eV, respectively, higher than the singlet state. However, CCSD(T) calculations drastically increase this gap to 0.6 eV in favor of the low spin state. For Nb<sub>11</sub> and Nb<sub>11</sub><sup>+</sup>, the higher spin states <sup>4</sup>A<sub>2</sub> and <sup>3</sup>A<sub>2</sub> are, respectively, located at 0.62 and 0.43 eV higher in energy than the corresponding ground states (BPW91).

The two next lowest-energy isomers are 11B and 11C. Both can be considered as arising from adding one niobium atom to the lowest-energy isomer of Nb<sub>10</sub> 10A. However, these geometries are much less stable than the form 11A. In fact, for neutral Nb<sub>11</sub>, the doublet <sup>2</sup>A'' states 11B and 11C are 1.14 and 1.28 eV above the <sup>2</sup>B<sub>2</sub>, respectively (BPW91). Concerning Nb<sub>11</sub><sup>+</sup>, the singlet <sup>1</sup>A' states of these shapes, 11B<sup>+</sup> and 11C<sup>+</sup>, are 1.13 and 1.45 eV above the corresponding ground state. The relevant energy separations obtained for the anion 11B<sup>−</sup> and 11C<sup>−</sup> amount to 0.99 and 1.00 eV (BPW91). These results suggest that the energetically preferred growth route of the clusters tends to yield a compact structure. In other words, the optimal structure of an Nb cluster is not simply



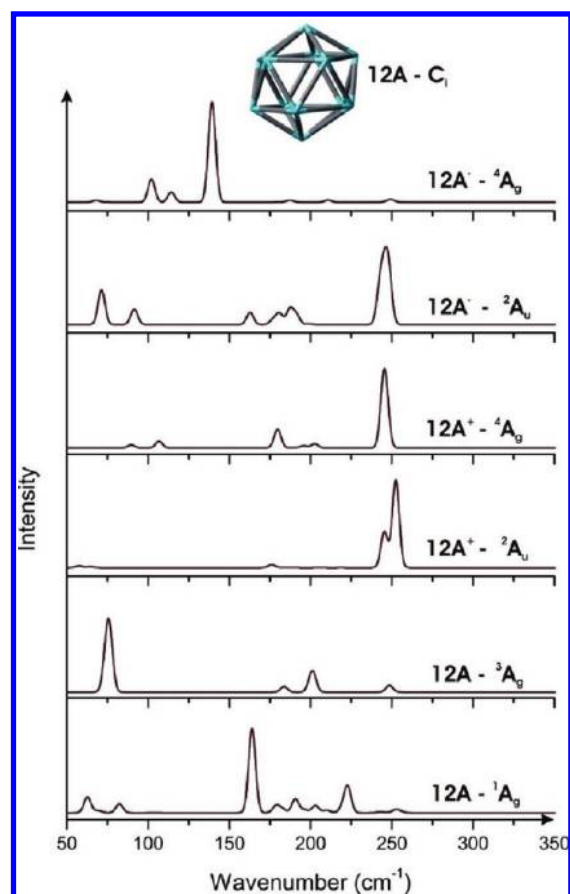
**Figure 7.** Predicted IR spectra for low-lying states of 11-Nb atom systems.

built up from that of the smaller size cluster by adding one atom randomly.

Figures S7–S9 show the vibrational spectra computed at the BPW91/cc-pVDZ-PP level for some low-lying states of the 11-atom clusters. Again, no experimental IR spectrum is available for these systems. Figure 7 displays the vibrational spectra of the lowest-lying forms in different charge states. The calculated vibrational spectrum of the neutral ground state 11A (<sup>2</sup>B<sub>2</sub>) covers the range below 280 cm<sup>−1</sup> with five specific peaks, where the most intense one is centered at around 270 cm<sup>−1</sup>. As mentioned above, the spectra of these systems are also strongly dependent on the addition or removal of an electron from the neutral. We actually observe significantly large changes in band intensities of the cation spectrum. As seen from Figure 7, the highest intensity peak is at 270 cm<sup>−1</sup>, whereas the intensities of other bands below 250 cm<sup>−1</sup> are substantially reduced. For Nb<sub>11</sub><sup>−</sup> 11A<sup>−</sup>, at least four distinct absorption bands can be found in the range below 250 cm<sup>−1</sup> and there exists no band above 250 cm<sup>−1</sup>. We, in addition, realize that upon the electron attachment two intense bands of the neutral at 150 and 138 cm<sup>−1</sup> are slightly red-shifted by ~10 cm<sup>−1</sup>. The peak at around 128 cm<sup>−1</sup> becomes mostly visible.

*F. Dodecamers.* The lowest-energy structure of Nb<sub>12</sub> has previously been reported<sup>21</sup> to be a capped pentagonal bipyramid or a distorted icosahedron (cf. structure 12A). Our calculated results concur with this finding and in addition confirm that such geometry with the C<sub>i</sub> symmetry and low spin electronic state is the most stable form of the monoions Nb<sub>12</sub><sup>+</sup> and Nb<sub>12</sub><sup>−</sup>. Furthermore, for Nb<sub>12</sub>,





**Figure 8.** Predicted IR spectra for low-lying states of 12-Nb atom systems.

two states  $^1A_g$  and  $^3A_g$  of  $12A$  are evaluated with a tiny energy difference by  $\sim 0.04$  (BPW91) to  $0.09$  eV (M06). However, R/UCCSD(T)/cc-pVDZ-PP calculations point out that the triplet  $^3A_g$  state is  $0.40$  eV lower in energy than the  $^1A_g$  counterpart. Recently, Moro et al.<sup>27</sup> based on magnetic deflection experiments revealed a total spin of zero for all the even-sized Nb clusters. Again, for  $Nb_{12}^-$ , two lowest-lying states  $^2A_u$  and  $^4A_u$  of structure  $12A^-$  are very close in energy in which the low spin  $^2A_u$  is only  $0.03$  eV (BPW91) or  $0.05$  (M06) to  $0.18$  eV (CCSD(T)) more stable than the high spin  $^4A_u$  state. On the contrary, the cation  $Nb_{12}^+$   $12B^+$  clearly prefers a low spin  $^2A_u$  state, as the doublet-quartet ( $^2A_u$ – $^4A_g$ ) separation gap is markedly enlarged to  $0.98$  eV (BPW1).

Another local minimum  $12B$ , based on a dimer capping of  $10A$ , is much less stable than  $12A$ . In fact, the states  $^1A_1$  and  $^2A_1$  we obtain here for  $Nb_{12}$  and  $Nb_{12}^+$ , respectively, are much higher energies, namely,  $3.66$  and  $4.13$  eV, than the respective ground states. For  $Nb_{12}^-$ , the  $^2B_1$  state of this form  $12B^-$  lies  $2.94$  eV above the ground  $^2A_u$  state. Such relatively large energy difference is expected to yield a prominent abundance of the isomer is form  $12A$  in experiment.

The computed IR spectra of the two lowest-lying states  $^1A_g$  and  $^3A_g$  of  $Nb_{12}$  are shown in Figure 8. For both states, the vibrational fundamentals appear below  $275$   $cm^{-1}$ . The spectrum of the  $^1A_g$  state is rather different, with indications for two bands located at around  $160$  and  $220$   $cm^{-1}$ , and some very low intensity peaks emerged in the vicinity. Again, even though the neutral and its ions have a very similar structural feature, each one owns a typical IR spectrum. The  $^2A_u$  cation ground state  $12A^+$  contains two closely spaced peaks at

$245$  and  $255$   $cm^{-1}$  (Figure 8). In general, the vibrational spectrum of the first excited  $^4A_g$  state is surprisingly similar to that of the  $^2A_u$  ground state, with a small red shift from the peak around  $255$ – $245$   $cm^{-1}$ . As a result, the  $^4A_g$  state has the most recognizable peak centered at  $\sim 245$   $cm^{-1}$ . There also exists a typical band on the spectroscopic signatures of the  $^2A_u$  anion ground state at  $\sim 245$   $cm^{-1}$ . Besides, one can detect (at least) five lower intensity bands in the range below  $200$   $cm^{-1}$ . The quasi-degenerate state  $^4A_u$  also exhibits the band at around  $250$   $cm^{-1}$ , but with a very small intensity (Figure 8).

**3.2. Energetic Properties.** The basic energetic parameters of niobium clusters have been determined experimentally by the measurement of their detachment energies and ionization energies. Kietzmann and co-workers<sup>8</sup> evaluated the vertical detachment energies (VDEs) of  $Nb_n^-$  clusters in the range of  $n = 3$ – $20$  from the corresponding photoelectron spectra. Table 2 lists, along with available experimental VDEs, the adiabatic electron affinities (ADEs) and vertical detachment energies (VDEs) of the anions considered at various levels of theory. The VDEs are calculated at the anion geometry, whereas the ADEs refer to the values obtained using the optimized structures of the neutral and the anion.

In general, our computed VDEs given in Table 2 are in good agreement with the measured VDE values reported in ref 8. Of the two functionals employed, the M06 gives slightly higher VDEs than the BPW91, except for  $Nb_{10}^-$ . The VDEs of  $Nb_{10}^-$  obtained at M06 and BPW91 levels amount to  $1.44$  and  $1.48$  eV, respectively, and both compared well to the experimental value of  $1.45$  eV.<sup>8</sup> However, the calculated VDE of  $Nb_{12}^-$  of  $1.06$  (BPW91) or  $1.17$  eV (M06) appears underestimated as compared to the experimental value of  $1.65$  eV reported in ref 8. Nevertheless, in a more recent study on UPE spectra of  $Nb_4^-$  to  $Nb_{200}^-$ , Wrigge et al.<sup>9</sup> found that the photoelectron spectrum of  $Nb_{12}^-$  does exhibit a low intensity peak at a lower binding energy of  $\sim 1.0$  eV, which has not been detected in the previous experiment.<sup>8</sup> We therefore would suggest that the neutral 12-atom cluster indeed possesses the lowest electron affinity ( $\sim 1.0$  eV).

Noticeably, we find an even–odd alternation of VDEs, as well as of ADEs, with local minima at  $n = 8, 10$ , and  $12$ . Such a pattern is not observed for clusters smaller than  $Nb_6^-$ . This is in line with experimental findings. As expected, the VDEs of even-numbered clusters  $Nb_8^-$ ,  $Nb_{10}^-$ , and  $Nb_{12}^-$  are smaller than those of  $Nb_7^-$ ,  $Nb_9^-$ , and  $Nb_{11}^-$ , simply due to the electronic closed shell of their neutrals. A theoretical difference of  $0.25$  eV (BPW91) can be derived for the pair  $Nb_{11}^-$ – $Nb_{12}^-$ . In addition, the even–odd alternation of the VDEs indicates that the frontier orbitals in the system could be strongly delocalized and nondegenerate. An analogous observation is typically found in metal clusters with an odd number of electrons per atom such as Na and Al.<sup>28,29</sup>

The ionization energies (IEs) of  $Nb_n$  clusters in the size range of  $n = 2$ – $76$  were determined experimentally by Knickelbein and Yang using photoionization efficiency (PIE) spectrometry.<sup>2</sup> We now compute both vertical and adiabatic IEs for clusters with  $n = 7$ – $12$  (Table 3). For the purpose of comparison, the values for the smaller clusters reported in ref 15 are also given. It appears that the reported experimental IEs correspond to the vertical values. In general, the results we obtain in Table 4 are in good agreement with experiment, with an exception of  $Nb_{12}$ . For this size, it is largely overestimated by  $\sim 0.5$  (M06) to  $\sim 0.7$  eV (BPW91), while the average deviation obtained for other sizes is only  $\sim 0.1$  eV at both levels of theory.

In the sizes of  $n = 7$ – $10$ , an odd–even pattern of VIEs is also observed, with local minima at  $n = 9, 11$ . For even-numbered clusters  $Nb_8$  and  $Nb_{10}$  that have closed electron shell and low spin

**Table 3. Adiabatic Electron Affinities (ADE, eV) and Vertical Detachment Energies (VDE, eV) of Nb<sub>n</sub><sup>−</sup> (n = 7–12) Clusters (Using the cc-pVDZ-PP Basis Set)**

reaction	ADE		VDE		expt <sup>a</sup> (eV)
	BPW91	M06	BPW91	M06	
Nb <sub>2</sub> <sup>−</sup> ( <sup>4</sup> Σ <sub>u</sub> <sup>+</sup> ) → Nb <sub>2</sub>	0.82	0.85	0.83	1.05	
Nb <sub>3</sub> <sup>−</sup> ( <sup>3</sup> A <sub>2</sub> ) → Nb <sub>3</sub>	0.98	1.06	1.03	1.13	1.09
Nb <sub>4</sub> <sup>−</sup> ( <sup>2</sup> B <sub>2</sub> ) → Nb <sub>4</sub>	0.83	0.98	0.86	1.05	1.10
Nb <sub>5</sub> <sup>−</sup> ( <sup>1</sup> A <sub>1</sub> <sup>′</sup> ) → Nb <sub>5</sub>	1.38	1.50	1.48	1.57	1.52
Nb <sub>6</sub> <sup>−</sup> ( <sup>2</sup> A) → Nb <sub>6</sub>	1.36	1.40	1.50	1.50	1.58
Nb <sub>7</sub> <sup>−</sup> ( <sup>1</sup> A <sup>′</sup> ) → Nb <sub>7</sub>	1.42	1.73	1.57	1.80	1.65
Nb <sub>8</sub> <sup>−</sup> ( <sup>2</sup> B <sub>1</sub> ) → Nb <sub>8</sub>	1.31	1.47	1.33	1.49	1.45
Nb <sub>9</sub> <sup>−</sup> ( <sup>1</sup> A) → Nb <sub>9</sub>	1.38	1.64	1.53	1.65	1.65
Nb <sub>10</sub> <sup>−</sup> ( <sup>2</sup> A <sub>1</sub> ) → Nb <sub>10</sub>	1.31	1.29	1.48	1.44	1.45
Nb <sub>11</sub> <sup>−</sup> ( <sup>1</sup> A <sub>1</sub> ) → Nb <sub>11</sub>	1.25	1.36	1.30	1.41	1.65
Nb <sub>12</sub> <sup>−</sup> ( <sup>2</sup> A <sub>u</sub> ) → Nb <sub>12</sub>	0.88	0.92	1.06	1.17	1.65

<sup>a</sup> The data are taken from ref 8.**Table 4. Theoretical and Experimental Ionization Energies (AIE and VIE, eV) of Nb<sub>n</sub> (n = 7–12) Clusters (Using cc-pVDZ-PP Basis Set)**

reaction	AIE		VIE		expt <sup>a</sup> (eV)
	BPW91	M06	BPW91	M06	
Nb <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>−</sup> ) → Nb <sub>2</sub> <sup>+</sup>	6.26	6.43	6.29	6.45	6.20 <sup>+0.1</sup> <sub>−0.0</sub>
Nb <sub>3</sub> ( <sup>2</sup> A <sub>2</sub> ) → Nb <sub>3</sub> <sup>+</sup>	5.72	5.85	5.86	6.08	5.81 ± 0.05
Nb <sub>4</sub> ( <sup>1</sup> A <sub>1</sub> ) → Nb <sub>4</sub> <sup>+</sup>	5.56	5.95	5.66	6.01	5.64 ± 0.05
Nb <sub>5</sub> ( <sup>2</sup> B <sub>2</sub> ) → Nb <sub>5</sub> <sup>+</sup>	5.25	5.35	5.27	5.39	5.45 ± 0.05
Nb <sub>6</sub> ( <sup>1</sup> A <sub>1</sub> ) → Nb <sub>6</sub> <sup>+</sup>	5.01	5.29	5.22	5.32	5.38 ± 0.05
Nb <sub>7</sub> ( <sup>2</sup> A <sup>′′</sup> ) → Nb <sub>7</sub> <sup>+</sup>	5.13	5.34	5.35	5.39	5.35 ± 0.05
Nb <sub>8</sub> ( <sup>1</sup> A <sub>1</sub> ) → Nb <sub>8</sub> <sup>+</sup>	5.28	5.38	5.45	5.62	5.53 ± 0.05
Nb <sub>9</sub> ( <sup>2</sup> A) → Nb <sub>9</sub> <sup>+</sup>	4.77	4.81	4.75	4.84	4.92 ± 0.05
Nb <sub>10</sub> ( <sup>1</sup> A <sub>1</sub> ) → Nb <sub>10</sub> <sup>+</sup>	5.29	5.41	5.40	5.58	5.48 ± 0.05
Nb <sub>11</sub> ( <sup>2</sup> B <sub>2</sub> ) → Nb <sub>11</sub> <sup>+</sup>	4.58	4.52	4.63	4.58	4.74 ± 0.05
Nb <sub>12</sub> ( <sup>1</sup> A <sub>g</sub> ) → Nb <sub>12</sub> <sup>+</sup>	4.10	4.17	4.29	4.37	4.96 ± 0.05

<sup>a</sup> The data are taken from ref 2.

electronic state, the calculated VIEs (BPW91) are about 0.1 and 0.3 eV higher than those of Nb<sub>7</sub> and Nb<sub>9</sub>, respectively, which are in line with the experimental observation. In contrast, for the pair of Nb<sub>11</sub> and Nb<sub>12</sub>, the even/odd alternation of VIEs is not clearly identified. According to available experiment, Nb<sub>11</sub> has a lower VIP (by ~0.2 eV) than Nb<sub>12</sub>. However, our calculations reverse the experimental trend by ~0.3 eV. This implies that the frontier orbitals in Nb<sub>12</sub> might be somewhat more localized and degenerate due to their higher symmetry, as compared to other systems considered in this work. Overall, this suggests that the experimental IE value for Nb<sub>12</sub> was not well evaluated.

It is also worth noting that Nb<sub>8</sub> and Nb<sub>10</sub> have a particularly large ionization potential and low electron affinity among these clusters considered. This indicates a kinetic stability toward donating or accepting of electrons. In addition, the high global hardness  $\eta$  ( $\eta \sim \text{IE} - \text{EA}$ ) denotes that the clusters are unwilling to undergo an addition reaction with either an electrophile or a nucleophile.

Of the clusters considered, the nine-niobium cluster appears remarkable, as there are several lower-lying forms competing for

the ground state, in particular the near-degeneracy of **9A** and **9B**. The BPW91 calculated VDEs of **9A**<sup>−</sup> and **9B**<sup>−</sup> are 1.53 and 1.43 eV, respectively. Using the M06 functional, such values are reduced to 1.63 and 1.65 eV, which can be compared to the experimental value of 1.65 eV. On the contrary, isomer **9A** has a much higher theoretical VIE than that of isomer **9B** at both levels. The computed VIEs for **9A** and **9B** structures amount to 5.10 and 4.75 eV (BPW91), respectively. By employing the M06 functional, such values are 5.25 and 4.84 eV. Two IE values of Nb<sub>9</sub> cluster have also been recorded experimentally, namely, 5.20 and 4.92 eV.<sup>2</sup> This suggests the existence of both pairs of isomers.

The presence of structural isomers in small niobium clusters was previously reported for Nb<sub>9</sub>, Nb<sub>11</sub>, and Nb<sub>12</sub> in an earlier study on N<sub>2</sub> and D<sub>2</sub> reaction kinetics by Hamrick et al.<sup>30</sup> However, there was no information about the geometries of these isomers. As mentioned above, we also found two quasi-degenerate structures, that is, **9A** and **9B** for Nb<sub>9</sub>. IP measurements by Knickelbein and Yang and our calculations also confirm the existence of such isomers. On the contrary, in agreement with previous prediction by Kumar et al.,<sup>31</sup> **11A** is much more stable than other isomers. Furthermore, other experiments performed by Bérces and co-workers<sup>32</sup> did not detect an evidence for structural isomers for this size. Therefore, it is rather hard to confirm or deny the presence of structural isomers of Nb<sub>11</sub>. Based on N<sub>2</sub> and D<sub>2</sub> reaction kinetics, Hamrick et al.<sup>27</sup> also revealed evidence of geometrical isomerism for Nb<sub>12</sub>. Previously, Kumar et al.<sup>28</sup> predicted that there is one metastable isomer of Nb<sub>12</sub>, namely, structure **12A**, while others are located at at least 0.92 eV above. Our calculations support this finding, but in addition, we find that the two states <sup>1</sup>A<sub>g</sub> and <sup>3</sup>A<sub>g</sub>, both having the **12A** shape, are nearly degenerate. Hence, in this case, the presence of different electronic states of one isomer, instead of distinct structural isomers, can be established, and their reactivity also differ from each other. Recently, structural isomerism for cation Nb<sub>10</sub><sup>+</sup> was observed by Berg et al.,<sup>33</sup> in which one isomer is very reactive with respect to C<sub>2</sub>H<sub>4</sub>, whereas the other is much less reactive. As for Nb<sub>12</sub>, we find that the two iso-energetic states <sup>2</sup>A<sub>1</sub> and <sup>2</sup>A<sub>2</sub> of **10A** may simultaneously be present under such experimental conditions.

**3.3. Relative Stabilities.** To analyze the stability, we consider the average binding energy per atom, the second-order difference of energy  $\Delta^2 E$ , and the stepwise dissociation energy  $D_e$ . For pure niobium clusters, these parameters are defined by the following equations:

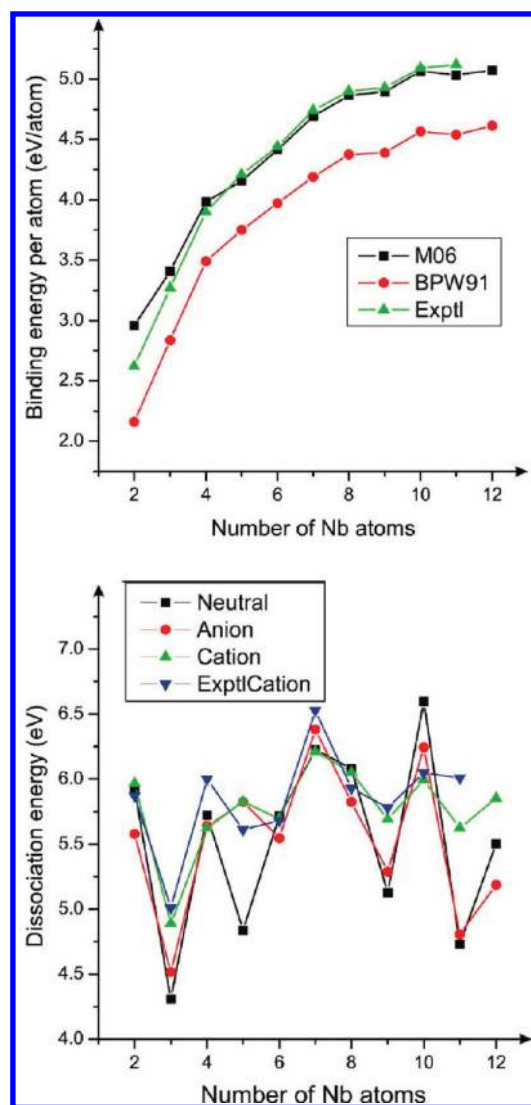
$$\text{BE}(\text{Nb}_n^x) = [(n-1) \times E(\text{Nb}) + E(\text{Nb}^x) - E(\text{Nb}_n^x)]/n$$

$$\Delta^2 E(\text{Nb}_n^x) = E(\text{Nb}_{n+1}^x) + E(\text{Nb}_{n-1}^x) - 2E(\text{Nb}_n^x)$$

$$D_e(\text{Nb}_n^x) = E(\text{Nb}_{n-1}^x) + E(\text{Nb}) - E(\text{Nb}_n^x)$$

where  $x = 0, +1, -1$ ;  $E(\text{Nb}_n^x)$  is the lowest energy of Nb<sub>n</sub><sup>x</sup> cluster.

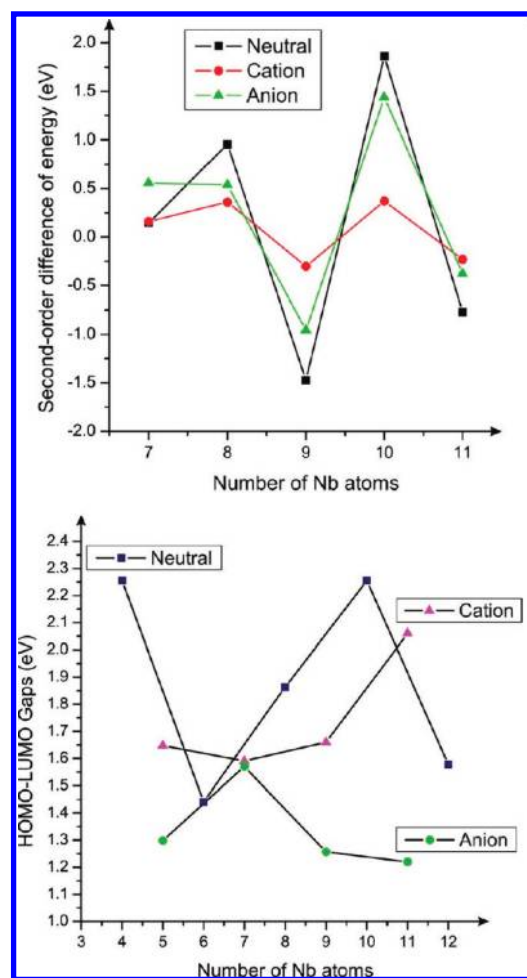
The theoretical and experimental binding energies per atom for neutral clusters are plotted together in Figure 9. The BE values calculated at various levels for cationic and anionic clusters are given in Table S1 of the ESI. First, we note that these systems can form clusters with larger size, since they are observed to gain energy during the growth. Figure 9 points out that the BEs increase monotonically with respect to the cluster size, with local maxima at  $n = 8, 10$ , and  $12$ . The overall tendency is in line with the experimental observation. However, our computed BEs are likely underestimated with respect to the experimental values.



**Figure 9.** Binding energies per atom for the neutral Nb clusters (upper) and dissociation energies for neutral and charged Nb clusters (lower) vs cluster size. The experimental values are taken from ref 3.

The calculated BE of Nb<sub>10</sub> is about 4.60 eV/atom (BPW91) or 5.06 eV/atom (M06) as compared to the experimental value of  $5.09 \pm 0.27$  eV/atom. In general, the M06 functional appears to provide better results for this quantity than the BPW91. The average errors are  $<0.1$  eV for M06 and  $\sim 0.5$  eV for BPW91.

As shown in Figure 9 the dissociation energy  $D_e$  values as a function of cluster size obey the odd–even staggering in the region of  $n = 8–12$ . Among these clusters, Nb<sub>9</sub> and Nb<sub>11</sub> are characterized by the lowest  $D_e$  values, implying their low thermodynamic stability. On the contrary, Nb<sub>10</sub> is expected to be the most stable one, as it has the largest  $D_e$  value. Other noticeable peaks are found at  $n = 7, 8$ , and 12, indicating that these systems are also relatively stable. The  $D_e$  values of Nb<sub>7</sub><sup>+</sup>, Nb<sub>8</sub><sup>+</sup>, and Nb<sub>10</sub><sup>+</sup> are higher than other cations and all these values are larger than 5.0 eV. Among anions, Nb<sub>7</sub><sup>−</sup> has the largest  $D_e$  value. In fact, the previous study by Kietzmann et al.<sup>8</sup> confirmed the particular stability for the seven-atom anionic cluster. Nb<sub>10</sub><sup>−</sup> also has the especially large  $D_e$  value, implying that it is relatively stable. This could be due to the dominance of a geometric effect in which the stability of these clusters is more determined by the number of atoms rather than by the number of electrons.

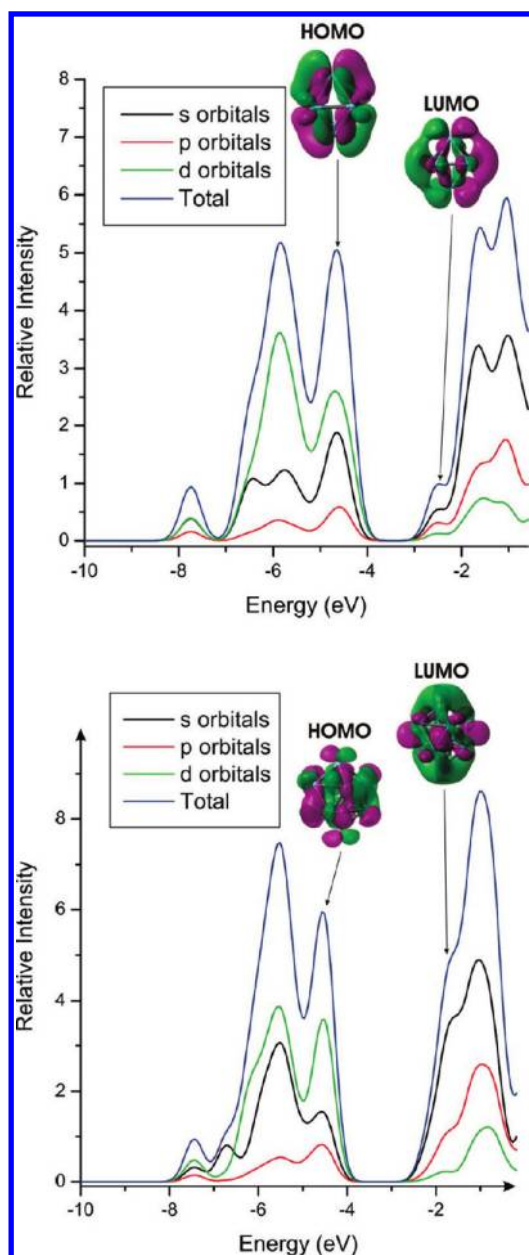


**Figure 10.** Second-order difference of energy (upper) and HOMO–LUMO gaps (lower) vs cluster size for neutral and charged Nb clusters.

Available experimental dissociation energies of the cationic species are also included in Figure 9 for comparison. Both DFT methods employed in this analysis follow familiar trends in dissociation energy predictions and tend to underestimate the experimental results. The M06 functional reaches again a closer agreement with experiment than the BPW91. The average absolute deviations relative to experiment of M06 and BPW91 methods are  $\sim 0.2$  and  $\sim 0.6$  eV, respectively. For the neutral and anionic systems, the BPW91 functional is also gives less good agreement with experiment than the M06 functional when predicting the bond dissociation energies of Nb clusters (see Table S2 of ESI).

The second-order difference of energy ( $\Delta^2E$ ) is also an important indicator that measures the relative stability of a cluster with respect to its immediate neighbors. In particular, peaks in the graph of  $\Delta^2E$  as a function of cluster sizes were found to be well correlated with peaks in the experimental mass spectra.<sup>34</sup> Figure 10 illustrates the variations of the  $\Delta^2E$  values. A cluster with the positive value of  $\Delta^2E$  is considered to be more stable as compared to the nearby smaller and larger size clusters. The  $\Delta^2E$  values of both neutral and anionic systems clearly exhibit odd–even fluctuations, in that  $\Delta^2E_{\text{even}} > \Delta^2E_{\text{odd}}$ . A cluster with an even number of atoms is likely much more stable than the neighboring odd-numbered ones. Nb<sub>10</sub> and Nb<sub>8</sub> are thus found to have particularly large values of  $\Delta^2E$ , indicating their higher stabilities. Comparable similar trend holds true for the anionic

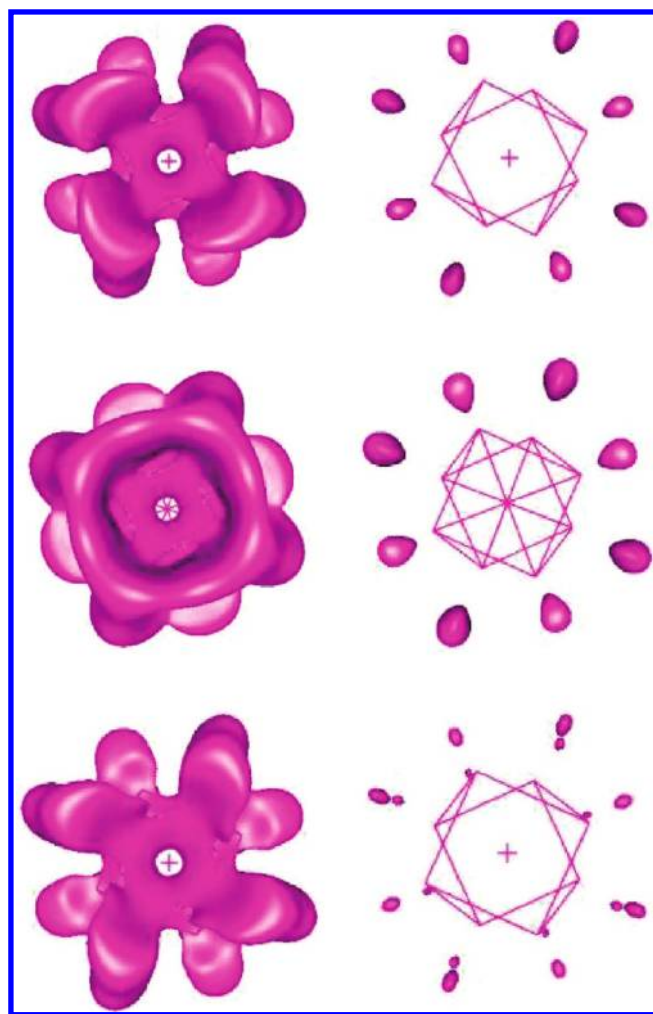




**Figure 11.** Total and partial density of states of  $\text{Nb}_8$  (upper) and  $\text{Nb}_{10}$  (lower).

system. The  $\Delta^2E$  value of  $\text{Nb}_{10}^-$  is especially positive among the anionic clusters. For the cationic system, such an alternation is not as sharply observed as in the neutral and anionic systems.

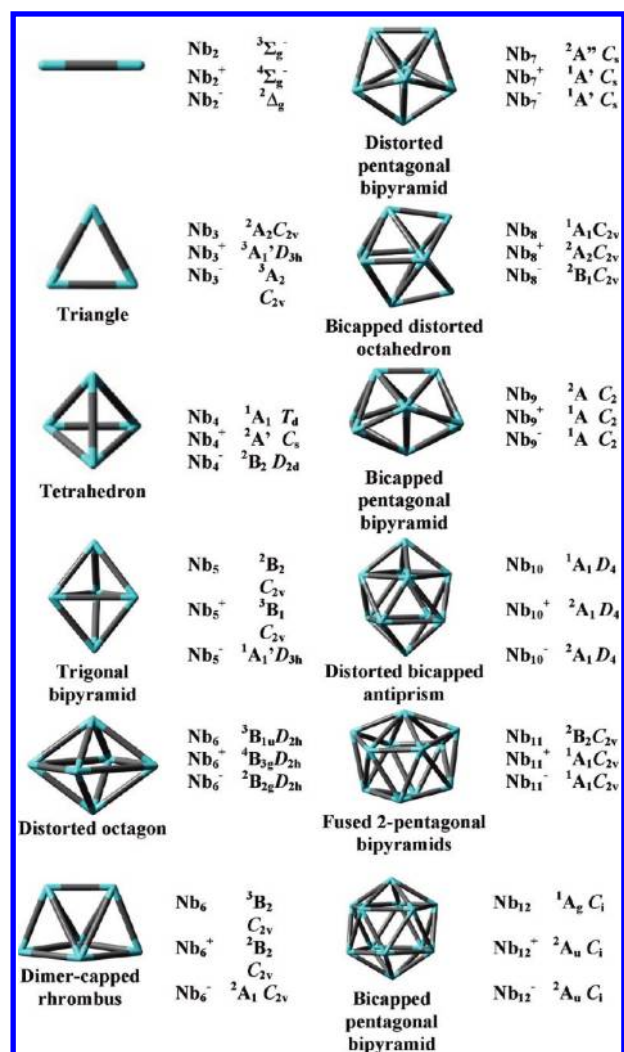
Another important parameter to estimate the electronic stability of small clusters is the energy separation between the frontier orbitals (HOMO–LUMO gap, denoted by  $E_{\text{HL}}$ ). The gaps for the lowest-energy structures of neutral and ionic niobium clusters are depicted in Figure 10. Because the HOMO–LUMO gaps of the closed-shell species and SOMO–LUMO gaps of the open-shell radicals cannot directly be compared, we only plot such gaps for closed-shell clusters. Among neutrals,  $\text{Nb}_{10}$  has the largest band gaps, indicating the low reactivity or high kinetics stability. These results together with the high IEs point toward a higher stability and inertness of  $\text{Nb}_{10}$ , as compared to its immediate neighbors. In fact, low reactivities



**Figure 12.** ELF isosurfaces for valence electrons of  $\text{Nb}_{10}$  neutral (top),  $\text{Nb}_{10}$  anion (middle), and  $\text{Nb}_{10}$  cation (bottom). Values of ELF are equal to 0.40 (left) and 0.60 (right).

toward  $\text{H}_2$  and  $\text{N}_2$  were detected experimentally for this cluster.<sup>11</sup> The reactivity of the cationic clusters was also experimentally investigated. For instance, Wu and Yang<sup>35</sup> revealed that the reactivity of  $\text{Nb}_n^+$  with NO and  $\text{NO}_2$  decreases with increasing cluster size for small clusters ( $\text{Nb}_2$ – $\text{Nb}_{10}$ ) and then increases slowly with increasing cluster size for larger clusters ( $\text{Nb}_{11}$ – $\text{Nb}_{16}$ ). Several groups also investigated the reaction of  $\text{Nb}_n^+$  cations ( $n$  up to 30) with simple hydrocarbons.<sup>13,33,36</sup> It is found that no size is much less reactive than the other; the difference between the more reactive and the less reactive forms is insignificant. Our theoretical results tend to concur with these observations in predicting that no cation is exceptionally inert or particularly stable.

In our previous study,<sup>18</sup> we confirmed that  $\text{Nb}_2$  and  $\text{Nb}_4$  are magic as they hold the number of valence electrons corresponding to the closed shell in the sequence (1S/1P/2S/1D/1F, ...). In these clusters, each niobium atom contributes five electrons to forming molecular orbitals in the valence band. Similarly, as seen from the densities of states (DOS) graphics, which are displayed in Figure 11 using the PyMolyze-2.0 program,<sup>37</sup> the valence bands of  $\text{Nb}_8$  and  $\text{Nb}_{10}$  are principally formed by overlaps of atomic orbitals 4d and 5s. In addition, these electrons are strongly delocalized. Hence, 40 valence electrons in  $\text{Nb}_8$  and 50 valence



**Figure 13.** Structures for the ground states of the neutral and charged Nb clusters containing 2–12 atoms.

electrons in Nb<sub>10</sub> correspond to the closed-shell assigned as 1S, 1P, 2S, 1D, 1F, 2P and 1S, 1P, 2S, 1D, 1F, 2P, 2D, respectively.<sup>38</sup> In other words, owing to the closed electronic shells, the Nb<sub>8</sub> and Nb<sub>10</sub> systems are also magic. Apparently, the magic clusters are those in which the shells in Nb<sub>n</sub> have 5*n* electrons (*n* = 2, 4, 8, 10).

The particular stability and inertness of Nb<sub>10</sub> can further be understood on the basis of a 3D aromaticity. The Nb<sub>10</sub> cluster has a spherical shape containing 50 valence electrons, and it, thus, is expected to have a spherical aromatic character as its number of valence electrons satisfies the 2(*N* + 1)<sup>2</sup> rule.<sup>39</sup> In addition, the highly negative nucleus independent chemical shift (NICS) value is another suggestion for an aromatic character of Nb<sub>10</sub>. The NICS value of a ghost atom placed at center of the cage is computed to be −34.2 ppm for Nb<sub>10</sub> as compared to −10.5 ppm for Nb<sub>10</sub><sup>+</sup> (M06/cc-pVDZ-PP). Overall, the spherical aromatic character of Nb<sub>10</sub> is an appropriate parameter to account for its strong magic behavior.

Besides a highly symmetric structure, strong thermodynamic and kinetic stability, aromatic metal clusters usually possess a perfect electron delocalization. For more thorough insights into the electron distribution and chemical bonding of Nb<sub>10</sub>, we perform an analysis of the electron localization function (ELF) for its global minima

using the BPW91/LanL2DZ density. The ELF isosurfaces of Nb<sub>10</sub>, Nb<sub>10</sub><sup>−</sup>, and Nb<sub>10</sub><sup>+</sup> are displayed in Figure 12. As expected, the valence electrons are delocalized over the whole system. In addition, the ELF map generated for these clusters with an ELF value of 0.60 shows that the electrons are mostly localized in eight basins that are distributed around the sphere.

#### 4. CONCLUDING REMARKS

We study the geometric and electronic structures, vibrational properties and relative stabilities of a series of niobium clusters in the range from 7–12 atoms using both DFT and coupled-cluster CCSD(T) calculations, in conjunction with the pseudopotential basis set cc-pVDZ-PP. The two functionals employed are the BPW91 and M06.

In general, our results suggest that the clusters considered here prefer the lowest possible spin state as the ground state, except for Nb<sub>12</sub> in which CCSD(T) calculations suggest the lowest state to be the high spin <sup>3</sup>A<sub>g</sub> state. As in smaller niobium clusters (2–6 atoms), various lower-lying states of these clusters are very close in energy, in such a way that their ground electronic state cannot clearly be established by DFT computations. From a growth mechanism point of view, we find that the optimal structure of the cluster at a certain size is not simply generated from that of the smaller one by adding an atom randomly. Instead, these clusters prefer a close-packed growth behavior (see Figure 13). Owing to the valence electrons that satisfy the 2(*N* + 1)<sup>2</sup> rule, Nb<sub>10</sub> is observed to have a spherically aromatic character, high chemical hardness and large HOMO–LUMO gap.

We also investigate the electron affinities, ionization energies, binding energy per atom, the stepwise dissociation energies, and, in particular, the IR spectra. In general, the energetic properties exhibit odd–even oscillations. Comparison with experimental data, both functionals BPW91 and M06 are reliable in predicting the EA and IE values. However, the BPW91 is deficient at predicting the binding energy per atom and dissociation energies in niobium clusters. The average absolute errors relative to experiment of BPW91 method are ~0.6 eV for *D<sub>e</sub>* and 0.5 for *BE*, as compared to ~0.2 and <0.1 eV using the M06 functional. For the vibrational spectra, we propose new assignments for Nb<sub>7</sub> and Nb<sub>9</sub>, in both neutral and cationic states.

#### ■ ASSOCIATED CONTENT

**S Supporting Information.** Additional data and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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