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QUANTUM CHEMICAL STUDY OF $NbSi_5^{-/0}$ CLUSTERS: STRUCTURES AND ELECTRON DETACHMENT ENERGIES

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Abstract

The structures and properties of the $NbSi_5^{-/0}$ cluster have been studied using density functional theory (DFT) and the CASPT2 method. The ground states of the negatively charged and neutral clusters were established as the $^1A_1$ and $^2B_1$ states of a tetragonal bipyramidal isomer with C_{4v} symmetry. The adiabatic and vertical detachment energies (ADE and VDEs) of the transition from the anionic ground state to the neutral ground state were found to be 2.72 and 2.74 eV, respectively. A vibrational progression with three peaks at a frequency of 212 cm^{-1} was observed for this transition in the Franck-Condon factor simulation. Furthermore, the VDEs of the transitions to the excited $^2B_1$, 1^2A_1, 1^2E, 2^2E, and 2^2A_1 states were computed as 3.10, 3.32, 3.77, and 4.67 eV, respectively. The recorded photoelectron spectrum of the $NbSi_5^-$ cluster was elucidated by the transitions to the $^2B_1$, 1^2A_1, 1^2E, and 2^2E states.

Keywords: *Electron detachment energy, electronic state, Franck-Condon factor, geometrical structure, relative energy.*

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NGHIÊN CỨU HÓA HỌC LƯỢNG TỬ VỀ CÁC CỤM NGUYÊN TỬ $NbSi_5^{-/0}$: CẤU TRÚC VÀ NĂNG LƯỢNG TÁCH ELECTRON

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Tóm tắt

Cấu trúc và tính chất của các cụm nguyên tử $NbSi_5^{-/0}$ đã được nghiên cứu bằng phương pháp lý thuyết hàm mật độ và phương pháp CASPT2. Trạng thái cơ bản của cụm nguyên tử anion và trung hòa được xác định lần lượt là $^1A_1$ và $^2B_1$ của đồng phân hình lưỡng tháp tam giác với đối xứng C_{4v}. Năng lượng tách electron ADE và VDE của quá trình chuyển từ trạng thái cơ bản của cụm nguyên tử anion sang trạng thái cơ bản của cụm nguyên tử trung hòa lần lượt là 2,72 và 2,74 eV. Bước tiến dao động với ba đỉnh ở tần số 212 cm^{-1} đã được ghi nhận cho quá trình chuyển electron này trong kết quả mô phỏng hệ số Franck-Condon. Hơn nữa, năng lượng tách electron VDE của các quá trình chuyển electron đến các trạng thái kích thích $^2B_1$, 1^2A_1, 1^2E, 2^2E và 2^2A_1 có giá trị lần lượt là 3,10; 3,32; 3,77 và 4,67 eV. Phổ quang electron của cụm nguyên tử $NbSi_5^-$ được giải thích bằng các quá trình chuyển đến các trạng thái $^2B_1$, 1^2A_1, 1^2E và 2^2E.

Từ khóa: *Cấu trúc hình học, hệ số Franck-Condon, năng lượng tách electron, năng lượng tương đối, trạng thái electron.*

1. Introduction

Incorporation of niobium into silicon clusters has attracted considerable scientific interest due to their potential applications in cluster-assembled materials. Previous studies have demonstrated that niobium-doped silicon clusters can adopt stable cage structures, making them promising building blocks for nanomaterials (Koyasu et al., 2007, 2008; Lu et al., 2016; Xia et al., 2016). The geometrical and electronic properties of small niobium-doped silicon clusters have been investigated using both theoretical and experimental methods (Gunaratne et al., 2013; Hamrick & Weltner, 1991; Koyasu et al., 2007, 2008; Lu et al., 2016; Oakley et al., 2021; Sevy et al., 2017; V. T. Tran, 2023; Wu & Su, 2006). Researchers have employed various techniques such as density functional theory (B3LYP functional), coupled cluster with single, double, and perturbative triple excitations [CCSD(T)], and photoelectron spectroscopy to explore the electronic structures and properties of $NbSi_5^{-/0}$ clusters.(Lu et al., 2016) The recorded photoelectron spectrum of the $NbSi_5^-$ cluster, measured at a photon energy of 266 nm, exhibited distinctive features, including a low-intensity peak at 2.74 eV, a shoulder peak at 3.13 eV, a broad and intense peak at 3.35 eV, as well as several partially resolved peaks ranging from 3.7 to 4.3 eV. Computational calculations conducted at CCSD(T)/cc-PVDZ/Si/aug-cc-PVDZ-PP/Nb and B3LYP/6-311+G(d)/Si/LanL2DZ/Nb levels revealed that the anionic and neutral ground states corresponded to the $^1A_1$ and $^2B_2$ states, respectively, in a C_{4v} tetragonal bipyramidal isomer. The adiabatic and vertical detachment energies (ADEs and VDEs) associated with the transition from the anionic $^1A_1$ ground state to the neutral $^2B_2$ ground state were computed as 2.71 and 2.74 eV, respectively. These calculated values align well with the experimentally determined values of 2.50 and 2.74 eV for the first peak. Additionally, the simulated density of state spectrum was investigated as part of the analysis.

While the ground states of the $NbSi_5^{-/0}$ clusters have been determined using the DFT and CCSD(T) methods, little is known about their excited states. However, understanding these excited states is crucial for comprehending the relevant characteristics observed in the photoelectron spectrum of the anionic cluster. To address this gap, the multiconfigurational CASSCF/CASPT2 method, renowned for its ability to explore electronic states in transition-metal-containing clusters, is employed (Nguyen et al., 2017, 2019; Pham & Nguyen, 2016, 2017; Thao et al., 2018; Q. T. Tran & Tran, 2016; V. T. Tran et al., 2019; V. T. Tran, Nguyen, et al., 2017; V. T. Tran, Tran, et al., 2017; V. T. Tran & Hendrickx, 2014; V. T. Tran & Tran, 2016, 2018). This method effectively accounts for electron correlation effects, resulting in relatively accurate energy calculations for the electronic states. In this study, we apply the CASSCF/CASPT2 method to investigate the electronic states of $NbSi_5^{-/0}$ clusters. The obtained computational results are then utilized to provide an explanation for all the features observed in the photoelectron spectrum of the anionic cluster.

2. Computational Details

To optimize geometries and calculate the vibrational frequencies of electronic states in $NbSi_5^{-/0}$ clusters, a DFT approach was employed. Specifically, the BP86 functional, in conjunction with the def-TZVPP basis sets for Nb and Si, was utilized. It is worth mentioning that the def-TZVPP basis set for Nb included an effective core of 28 electrons. The DFT calculations were conducted using NWCHEM 7.0.2 (Valiev et al., 2010). For obtaining single-point energies of the electronic states, CASSCF/CASPT2 calculations were performed using OpenMolcas 20.10 (Fdez. Galván et al., 2019). ANO-RCC basis sets with a construction scheme of 8s7p5d3f2g1h for Nb and 6s5p3d2f1g for Si were employed (Roos et al., 2004, 2005). For the CASSCF calculations, 15 orbitals were chosen to create the active space. The anionic cluster utilized this active space with 16 electrons, while the neutral cluster had 15 electrons within the active space. The construction of the active space considered a total of 21 valence orbitals, including the 4d and 5s orbitals of Nb, as well as the 3p orbitals of Si. To ensure computational feasibility, six antibonding orbitals were excluded from the active space. It is important to note that the chosen active space of 15 orbitals is sufficient for accurately estimating the relative energies of electronic states in clusters containing transition metals (Nguyen et al., 2017; V. T. Tran et al., 2019; V. T. Tran, Tran, et al., 2017; V. T. Tran & Hendrickx, 2014; V. T. Tran & Tran, 2016, 2018). To study the vibrational progression of the electron detachment processes, simulations of Franck-Condon factors were performed using the MOLFC code (Borrelli & Peluso, 2003, 2008), based on the BP86 geometries and vibrational frequencies.

3. Results and Discussion

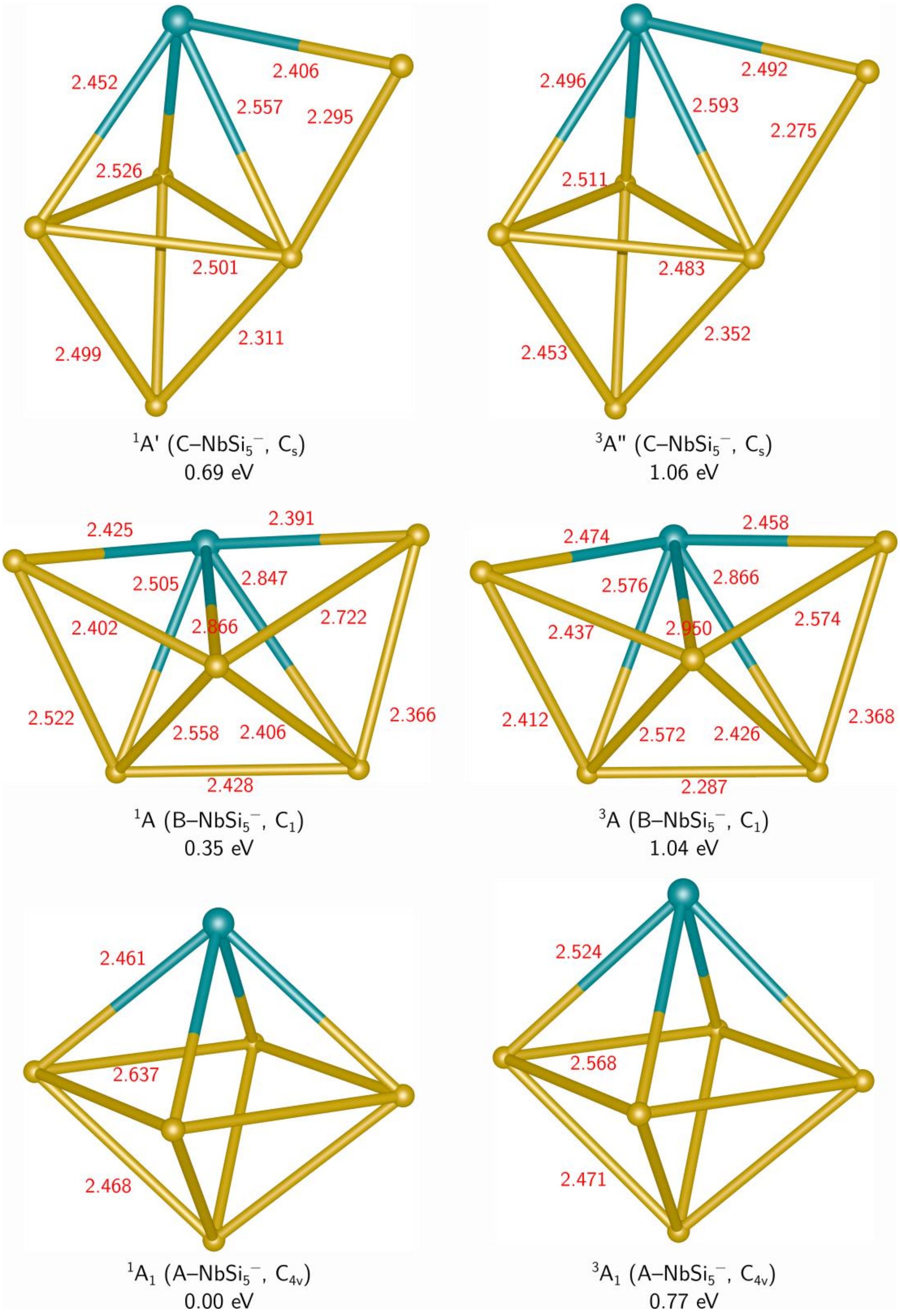
3.1. $NbSi_5^-$

The structures of $NbSi_5^-$ clusters obtained from calculations using the BP86 functional are depicted in Figure 1. Three isomers with low energy, labeled as A-$NbSi_5^-$, B-$NbSi_5^-$, and C-$NbSi_5^-$, are identified. The A-$NbSi_5^-$ isomer exhibits a tetragonal bipyramidal geometry, with the niobium atom positioned axially. This isomer can belong to either the C_{2v} or C_{4v} point group, but for consistency with the CASSCF/CASPT2 method employed in OpenMolcas, calculations for A-$NbSi_5^-$ isomer were performed using the C_{2v} point group. Notably, the A-$NbSi_5^-$ isomer consists of two symmetric planes, each containing Nb and three Si atoms. On the other hand, both the B-$NbSi_5^-$ and C-$NbSi_5^-$ isomers are formed by adding a silicon atom to the surface of a triangular bipyramidal $NbSi_4$ structure.

Table 1. Relative energies (REs) and vibrational frequencies of the electronic states of anionic $NbSi_5^-$ clusters as obtained with BP86 functional

state	sym.	vibrational frequency (cm^{-1})	RE (eV)
A-$NbSi_5^-$			
$^1A_1$	C_{4v}	173, 173, 212, 222, 224, 280, 280, 323, 354, 368, 368, 416	0.00
$^3A_1$	C_{4v}	165, 166, 172, 194, 250, 280, 280, 304, 338, 338, 339, 414	0.77
B-$NbSi_5^-$			
^1A	C_1	84, 111, 183, 221, 234, 280, 317, 333, 350, 391, 415, 428	0.35
^3A	C_1	62, 114, 114, 201, 229, 253, 282, 304, 333, 399, 409, 449	1.04
C-$NbSi_5^-$			
$^1A'$	C_s	100, 178, 180, 247, 277, 285, 298, 326, 354, 382, 406, 519	0.69
$^3A''$	C_s	42, 168, 170, 227, 259, 287, 290, 305, 322, 372, 396, 512	1.06

Table 1 displays the relative energies and vibrational frequencies of the electronic states of the $NbSi_5^-$ cluster as computed using density functional theory. The presence of real vibrational frequencies in all calculated electronic states indicates that these structures are located at minima on the potential energy surface. The analysis reveals that the ground state of the anionic cluster corresponds to the $^1A_1$ state of the A-$NbSi_5^-$ isomer, with a Nb-Si bond length of 2.461 Å and Si-Si bond lengths of 2.637 and 2.468 Å. The excited state $^3A_1$ of A-$NbSi_5^-$ exhibits a relative energy of 0.77 eV, with a Nb-Si bond length of 2.524 Å and Si-Si bond lengths of 2.568 and 2.471 Å. Additionally, the ^1A and ^3A states of B-$NbSi_5^-$, as well as the $^1A'$ and $^3A''$ states of C-$NbSi_5^-$, are found to have energies above the ground state by 0.35, 1.04, 0.69, and 1.06 eV, respectively. The results obtained using the BP86 functional corroborate previous calculations conducted with the B3LYP method, confirming the determination of the ground state as the $^1A_1$ state of a tetragonal bipyramidal $NbSi_5^-$ structure in C_{4v} symmetry (Lu et al., 2016).



^{1}A' (C–NbSi$_5^-$, C$_s$)
0.69 eV

^{3}A" (C–NbSi$_5^-$, C$_s$)
1.06 eV

^{1}A (B–NbSi$_5^-$, C$_1$)
0.35 eV

^{3}A (B–NbSi$_5^-$, C$_1$)
1.04 eV

^{1}A$_1$ (A–NbSi$_5^-$, C$_{4v}$)
0.00 eV

^{3}A$_1$ (A–NbSi$_5^-$, C$_{4v}$)
0.77 eV

Figure 1. Structures, symmetries, and relative energies of the electronic states of the anionic A-NbSi$_5^-$, B-NbSi$_5^-$, and C-NbSi$_5^-$ isomers as obtained in the geometry optimizations with the BP86 functional

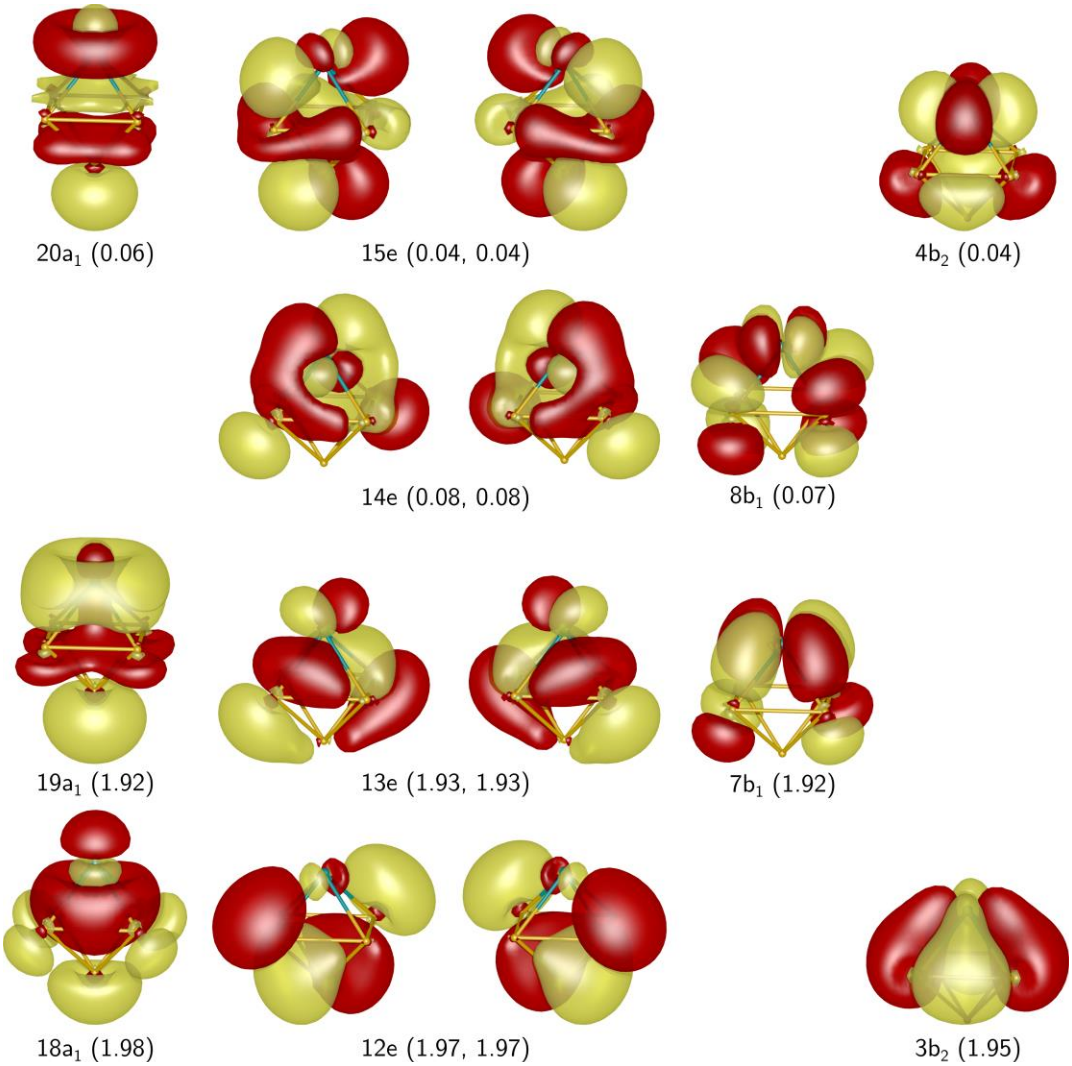
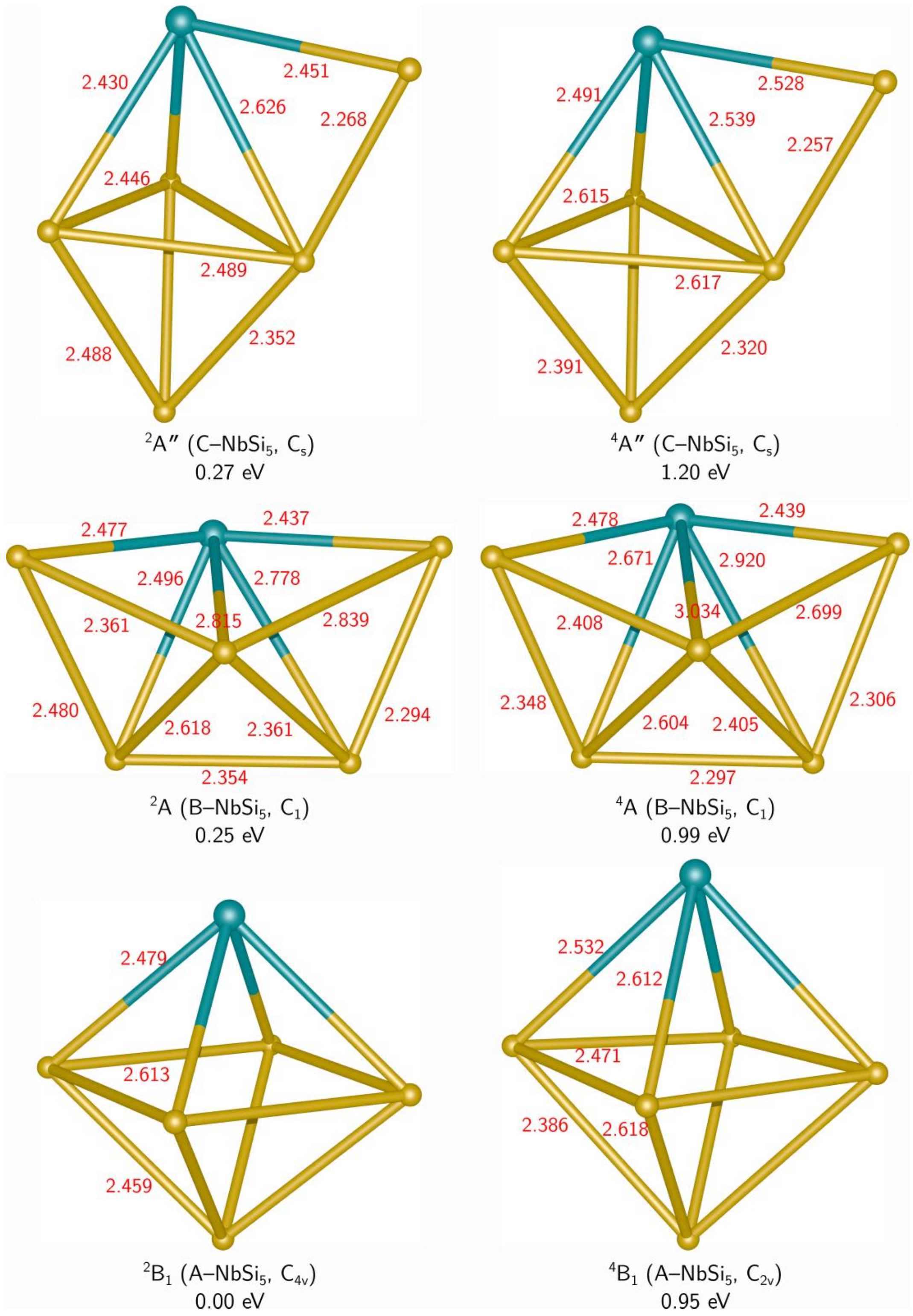


Figure 2. The occupation numbers of molecular orbitals in the active space of the $^1A_1$ state of the anionic A-NbSi$_5^-$ isomer as obtained in the CASSCF calculation

In Figure 2, the CASSCF molecular orbitals and electron occupation numbers of the $^1A_1$ ground state of the anionic NbSi$_5^-$ are depicted. The figure reveals that the $18a_1$, $19a_1$, 12e, 13e, $7b_1$, and $3b_2$ orbitals are doubly occupied, while the remaining orbitals remain unoccupied. Notably, the figure highlights significant orbital combinations involving the 4d and 5s orbitals of Nb and the 3p orbitals of Si. The doubly occupied orbitals exhibit bonding character, whereas the unoccupied orbitals possess antibonding properties. Specifically, the $18a_1$ and $19a_1$ orbitals primarily consist of the $4d_{z^2}$ and 5s orbitals of Nb. The $7b_1$ orbital is primarily influenced by the $4d_{x^2-y^2}$ orbital. The 13e orbitals are primarily shaped by the $4d_{xz}$ and $4d_{yz}$ orbitals, respectively. Lastly, the $3b_2$ orbital is predominantly composed of the $4d_{xy}$ orbital.

3.2. NbSi$_5$

In Figure 3, the geometries of the electronic states for the neutral NbSi$_5$ cluster are depicted.



$^2A''$ (C–NbSi$_5$, C$_s$)
0.27 eV

$^4A''$ (C–NbSi$_5$, C$_s$)
1.20 eV

^2A (B–NbSi$_5$, C$_1$)
0.25 eV

^4A (B–NbSi$_5$, C$_1$)
0.99 eV

$^2B_1$ (A–NbSi$_5$, C$_{4v}$)
0.00 eV

$^4B_1$ (A–NbSi$_5$, C$_{2v}$)
0.95 eV

Figure 3. Structures, symmetries, and relative energies of the electronic states of the neutral A-NbSi$_5$, B-NbSi$_5$, and C-NbSi$_5$ isomers as obtained in the geometry optimization with the BP86 functional

Like the anionic cluster, the neutral cluster identify three notable isomers: A-NbSi$_5$, B-NbSi$_5$, and C-NbSi$_5$. Table 2 provides information on the vibrational frequencies and relative energies of the electronic states for the neutral cluster. It is worth noting that all proposed structures of the electronic states are deemed stable due to the presence of real vibrational frequencies. The neutral ground state is proposed to be the $^2B_1$ state of A-NbSi$_5$ in C_{4v} symmetry. In this state, the Nb-Si bond length is determined to be 2.479 Å, and the Si-Si bond lengths are specified as 2.613 and 2.459 Å. The neutral doublet ground state is characterized by a deficit of one electron specifically in the 7b$_1$ orbital, compared to the anionic singlet ground state. The presence of bonding interactions between the $4d_{x^2-y^2}$ orbital of Nb and the 3p orbitals of Si atoms in the 7b$_1$ orbital leads to the elongation of Nb-Si bonds as the cluster transitions from the anionic ground state to the neutral ground state. The A-NbSi$_5$ isomer displays an excited state denoted as $^4B_2$ in C_{2v} symmetry, with a calculated relative energy of 0.95 eV. In this excited state, the Nb-Si bond lengths are determined to be 2.532 and 2.612 Å, while the Si-Si bond lengths measure 2.471, 2.386, and 2.618 Å. Additionally, the B-NbSi$_5$ isomer exhibits the ^2A and ^4A states, which possess relative energies of 0.25 and 0.99 eV, respectively. Moreover, the $^2A''$ and $^4A''$ states of C-NbSi$_4$ isomer are higher in energy than the neutral ground state by 0.27 and 1.20 eV, respectively.

Table 2. Relative energies (REs) and vibrational frequencies of the electronic states of neutral NbSi$_5$ clusters as obtained with the BP86 functional

state	sym.	vibrational frequency (cm^{-1})	RE (eV)
A-NbSi$_5$			
$^2B_1$	C_{4v}	146, 147, 162, 212, 228, 304, 305, 310, 337, 338, 355, 413	0.00
$^4B_1$	C_{2v}	68, 124, 161, 186, 204, 284, 295, 337, 357, 356, 372, 433	0.95
B-NbSi$_5$ (C_1)			
^2A	C_1	96, 105, 160, 222, 228, 274, 312, 322, 344, 414, 342, 447	0.25
^4A	C_1	78, 129, 136, 210, 214, 271, 288, 319, 336, 409, 425, 456	0.99
C-NbSi$_5$(C_s)			
$^2A''$	C_s	56, 173, 187, 232, 267, 287, 309, 335, 348,388, 418, 514	0.27
$^4A''$	C_s	47, 154, 156, 197, 254, 275, 287, 319, 324, 349, 405, 523	1.20

Our findings align with previous calculations that propose a doublet state as the neutral ground state, providing consistency in the results (Lu et al., 2016). However, a discrepancy arises in the orientation of the cluster on the Cartesian coordinate system. In our calculations, we designate the doublet ground state as $^2B_1$, while the previous study favors the notation $^2B_2$ for the identical state.

Figure 4 illustrates the normal modes and vibrational frequencies of the neutral $^2B_1$ ground state of the A-NbSi$_5$ isomer, as calculated using the BP86 functional. In C_{4v} symmetry, this state exhibits twelve vibrational modes, which can be categorized into three A$_1$, six E, two B$_1$, and one B$_2$ irreducible representations. The frequencies of the A$_1$ modes are determined to be 212, 355, and 413 cm^{-1}. The doubly degenerate E modes possess frequencies of 146 and 147, 304 and 305, and 337 and 338 cm^{-1}. The doubly degenerate E modes exhibit frequencies that differ by 1 cm^{-1} since the calculations were conducted in a C_{2v} point group. The B$_1$ modes exhibit frequencies of 162 and 310 cm^{-1}, while the B$_2$ mode has a frequency of 228 cm^{-1}. It is essential to highlight that only the totally symmetrical A$_1$ modes are allowed based on the vibrational selection rules of photoelectron spectroscopy.

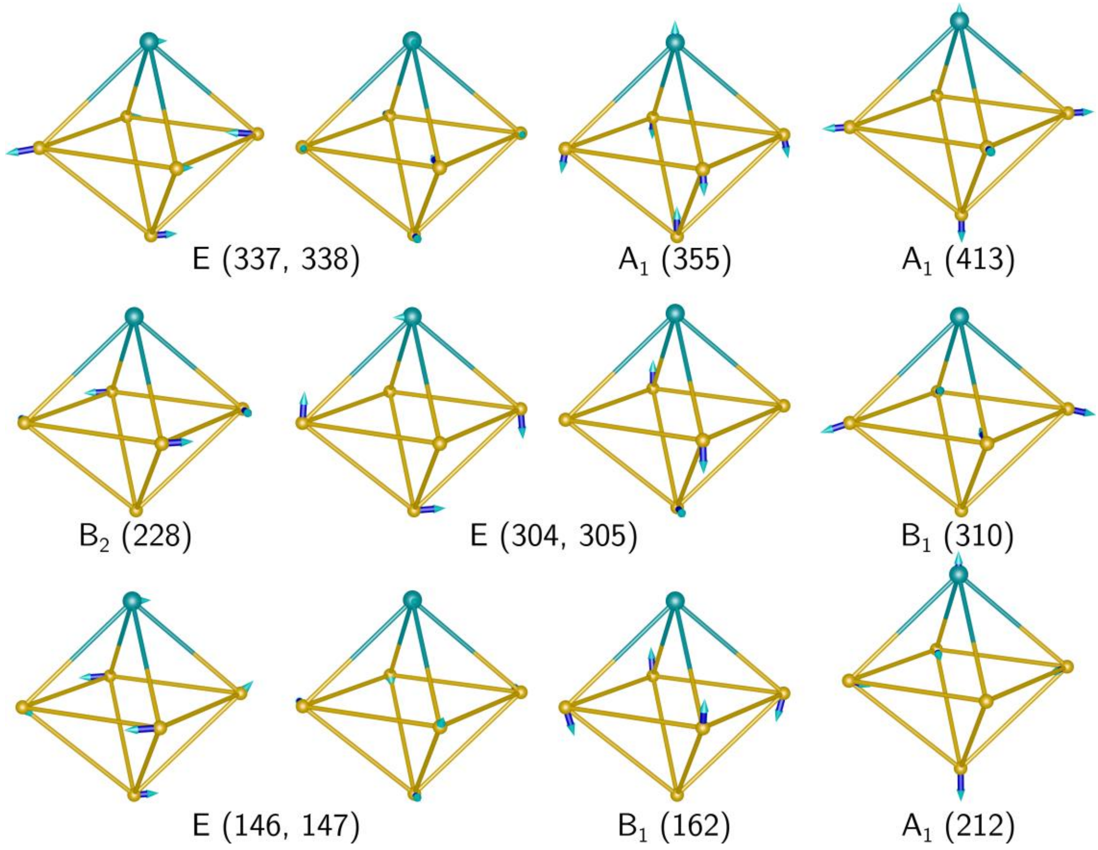


Figure 4. Vibrational frequencies and normal modes of the neutral $^2B_1$ ground state of A-$NbSi_5$ isomer as computed with the BP86 functional

3.3. Electron Detachment Energy

Table 3 presents the electron detachment energies of the anionic $^1A_1$ ground state of the $NbSi_5^-$ isomer, as computed using the CASPT2 method.

Table 3. Vertical detachment energies (VDEs) of the transitions from the anionic $^1A_1$ ground state to the neutral low-lying states as obtained in the CASPT2 calculations

state	leading configuration	orbital	VDE (eV)$^{(a)}$	
			CASPT2	expt.
A-$NbSi_5^-$				
$^1A_1$	$18a_1^2 19a_1^2 12e^4 13e^4 7b_1^2 3b_2^2$ (82%)			
A-$NbSi_5$				
$^2B_1$	$18a_1^2 19a_1^2 12e^4 13e^4 7b_1^1 3b_2^2$ (79%)	7b1	2.74 (2.72)	2.74 (2.50)
1^2A_1	$18a_1^2 19a_1^1 12e^4 13e^4 7b_1^2 3b_2^2$ (77%)	$19a_1$	3.10	3.13
1^2E	$18a_1^2 19a_1^2 12e^4 13e^3 7b_1^2 3b_2^2$ (43%)	13e	3.32	3.35
2^2E	$18a_1^2 19a_1^2 12e^4 13e^4 7b_1^2 3b_2^2$ (43%)	12e	3.77	3.7-4.3
2^2A_1	$18a_1^1 19a_1^2 12e^4 13e^4 7b_1^2 3b_2^2$ (48%)	$18a_1$	4.67	

(a) Values in parentheses are the adiabatic electron detachment energies (ADEs).

The photoelectron spectrum of the $NbSi_5^-$ cluster exhibits four distinct peaks (Lu et al., 2016). The first three peaks are centered at binding energy values of 2.74, 3.13, and 3.35 eV, while the fourth peak falls within the range of 3.7-4.3 eV. The starting point of the first peak is determined to be 2.50 eV. By utilizing the calculated electron detachment energies of the anionic ground state, we can interpret the photoelectron spectrum of the $NbSi_5^-$ cluster. In particular, the first peak at 2.74 eV corresponds to the transition to the $^2B_1$ state, which has an ADE and VDE of 2.72 and 2.74 eV, respectively. The second peak at 3.13 eV is attributed to the transition to the 1^2A_1 state, characterized by a VDE of 3.10 eV. The third peak at 3.35 eV arises from the transition to the 1^2E state, with a VDE of 3.32 eV. The fourth peak within the range of 3.7-4.3 eV is explained by the transition to the 2^2E state, which possesses a VDE of 3.77 eV. It is important to note that the transitions to the 2^2A_1 states with VDEs of 4.67 eV is observed in the spectrum due to the limited photon energy of 266 nm used for electron detachment.

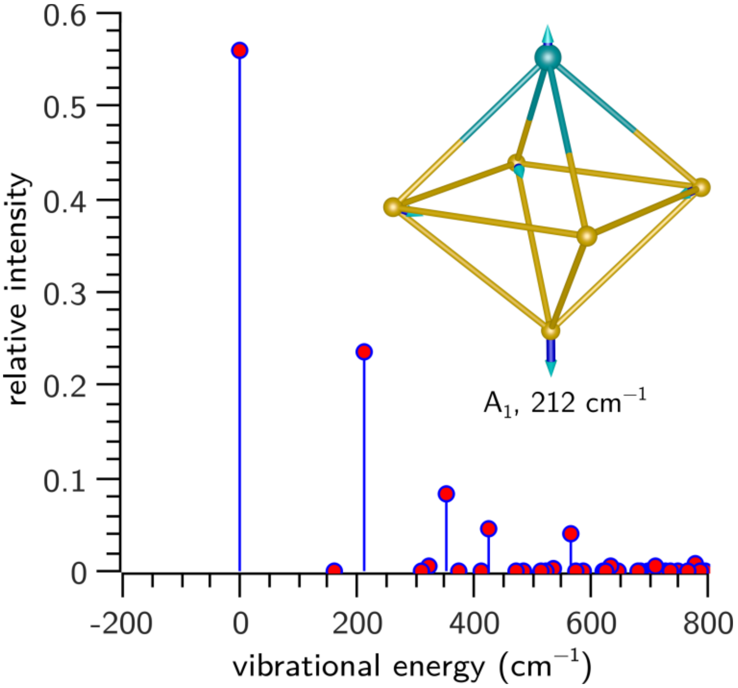


Figure 5. Vibrational progression of the transition from the anionic $^1A_1$ ground state to the neutral $^2B_1$ ground state as obtained in the Franck-Condon factor simulation for the totally symmetric modes

To gain insight into the vibrational characteristics of the first peak at 2.74 eV, a simulation of the multidimensional Franck-Condon factor was performed for the transition to the $^2B_1$ ground state. The results, depicted in Figure 5, reveal a vibrational progression exhibiting approximately three peaks at a frequency of 212 cm^{-1}. The inset in Figure 5 highlights that the vibrational normal mode associated with this frequency belongs to the totally symmetric A_1 irreducible representation. Due to the presence of a low-frequency vibrational progression in the transition to the $^2B_1$ state, the first feature in the spectrum appears as an unresolved broad band. To accurately resolve the fine structure of this band, it is recommended to employ a higher-resolution photoelectron spectrometer.

4. Conclusion

This study reports on the geometrical and electronic structures of $NbSi_5^{-/0}$ clusters as determined through DFT and CASPT2 calculations. Three isomers are observed for the studied clusters, including the tetragonal bipyramidal A-$NbSi_5^{-/0}$ and the face-capped triangle bipyramidal B-$NbSi_5^{-/0}$ and C-$NbSi_5^{-/0}$ isomers. The ground state of the anionic cluster is identified as the $^1A_1$ state of A-$NbSi_5^-$ isomers, with the ^1A state of B-$NbSi_5^-$ and $^1A'$ state of C-$NbSi_5^-$ being 0.35 and 0.69 eV higher in energy, respectively. The neutral ground state is determined to be the $^2B_1$ state of A-$NbSi_5$ isomer, while the ^2A state of B-$NbSi_5$ and $^2A''$ state of C-$NbSi_5$ are found to be 0.25 and 0.27 eV higher in energy, respectively. The ADE of the transitions from the anionic ground state to the neutral $^2B_1$ ground state is estimated to be 2.72 eV. A Franck-Condon factor simulation for the transition to the neutral ground state reveals a vibrational progression with three peaks at a frequency of 212 cm^{-1}. The VDEs of the transitions to $^2B_1$, 1^2A_1, 1^2E, 2^2E, and 2^2A_1 states are evaluated to be 2.74, 3.10, 3.32, 3.77, and 4.67 eV, respectively. The computational results proposed that the four peaks at 2.74, 3.13, 3.35, and 3.7-4.3 eV in the photoelectron spectrum correspond to transitions to the $^2B_1$, 1^2A_1, 1^2E, and 2^2E states.

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