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Theoretical study of the electronic states of Nb₄, Nb₅ clusters and their anions (Nb₄⁻, Nb₅⁻)

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ABSTRACT

Geometries and energy separations of the various low-lying electronic states of Nb_n and Nb_n⁻ (n = 4, 5) clusters with various structural arrangements have been investigated. The complete active space multi-configuration self-consistent field (CASMCSCF) method followed by multi-reference singles and doubles configuration interaction (MRSDCI) calculations that included up to 52 million configuration spin functions have been used to compute several electronic states of these clusters. The ground states of both Nb₄ (¹A', pyramidal) and Nb₄⁻ (²B_{3g}, rhombus) are low-spin states at the MRSDCI level. The ground state of Nb₅ cluster is a doublet with a distorted trigonal bipyramid (DTB) structure. The anionic cluster of Nb₅ has two competitive ground states with singlet and triplet multiplicities (DTB). The low-lying electronic states of these

clusters have been found to be distorted due to *Jahn-Teller* effect. On the basis of the energy separations of our computed electronic states of Nb₄ and Nb₅, we have assigned the observed photoelectron spectrum of Nb_n⁻ (*n* = 4, 5) clusters. We have also compared our MRSDCI results with density functional calculations. The electron affinity, ionization potential, dissociation and atomization energies of Nb₄ and Nb₅ have been calculated and the results have been found to be in excellent agreement with the experiment.

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I. INTRODUCTION

The advent of gas-phase experimental methods of small transition metal clusters has opened up a new and exciting research area that affords the opportunity to study the electronic states and changes in metal chemistry as a function of size. The low-lying electronic states of transition metal clusters pose considerable challenge to the quantum chemists due to large electron correlation effects and the existence of several low-lying electronic states of different spatial symmetries and spin multiplicities. Small niobium clusters are among the most thoroughly studied transition metal clusters by experiment. Extensive gas phase investigations have been carried out on these clusters concerning their chemical reactivity, photoelectron spectroscopy and physical properties that include ionization potentials (IPs), electron affinities (EAs) and atomization energies (AEs).¹⁻⁶ Theoretical studies of these clusters can not only provide interpretation of such experimental results but also facilitate a tractable platform to understand the metal-metal bonding and reactivity of small molecules on the metal surface. Due to complex nature of electron correlation effects, the relative order of the electronic states and their structural properties change significantly as a function of theoretical treatment. Furthermore, the results of computational studies on small metal clusters provide a link between the molecular and solid states.

Niobium clusters of various sizes have been produced by pulsed laser vaporization of compressed niobium powder^{1,7,8} and a series of experiments on the reactivity of niobium clusters have been conducted using fast flow reactor techniques,⁹⁻¹¹ flow tube¹² and guided ion beam measurements.⁵ Armentrout and his co-workers^{5,6} have measured the stepwise dissociation energies of Nb_n ($n = 2 - 6$) and Nb_n^+ ($n = 2 - 11$)

clusters using a collision induced dissociation (CID) technique. They have found that the dissociation energies (D_e) of Nb_n do not change monotonically with respect to the cluster size. The D_e value of Nb_3 is the lowest among these clusters ($n= 2 - 6$) and Nb_4 is the most stable one ($D_e = 5.9$ eV). The D_e values of all these clusters are larger than 4.0 eV indicating that these clusters are strongly bound. The D_e values of Nb_n^+ clusters⁵ also follow the same trend.

The Nb_n clusters are quite reactive analogous to their cationic counterparts. Berces and co-workers² have studied the reaction of Nb_n clusters with nitrogen and deuterium using a flow tube reactor with a laser vaporization cluster source and time of flight mass spectrometer detector. Recently Pederson and his co-workers¹³ have observed through their photoionization studies that the CO molecule adsorbs dissociatively on the Nb_3 surface. The niobium carbides, Nb_nC_m , have been the topic of extensive theoretical and experimental research.¹⁴⁻¹⁶

Earlier theoretical studies of small niobium clusters (neutral and anionic) have been focussed mainly at the density functional (DFT) level. Fowler and co-workers¹⁷ have studied the neutral Nb_3 and Nb_4 clusters at the DFT level. They have predicted that the equilibrium ground state structures of Nb_3 and Nb_4 clusters are isosceles triangle (2B_1 , C_{2v}) and tetrahedral (1A_1 , T_d) respectively. Earlier density functional studies by Salahub and co-workers¹⁸ on Nb_n ($n = 2 - 7$) have also confirmed similar structures for Nb_3 and Nb_4 clusters. They have further observed that the neutral clusters, in their ground states, always tried to remain in their lowest possible spin state. More recent DFT studies by Grönbeck and co-workers¹⁹ on the neutral and ionic Nb_n ($n = 8 - 10$) clusters have indicated that the ground states of the larger clusters are always in their lowest possible

spin states. The ground states of these clusters are competitive in nature, as the various isomers of these clusters are in very close in energy.¹⁹ Such closely spaced energy spectrum some times changes the behavior of such metal clusters. This was observed both theoretically and experimentally in the IP values of the Nb₉ cluster.¹⁹

Kietzmann and co-workers³ have studied the photoelectron spectra (PES) of small niobium cluster anions [Nb_n⁻ (*n* = 3 – 8)] using a laser vaporization technique. The authors have inferred by comparison of experiment with their local spin density calculations (LSD) that the Nb_n⁻ clusters are in their lowest possible spin states. They have also inferred that although for Nb₃⁻ and Nb₅⁻ the singlet states (D_{3h} symmetry) are the lowest in energies, the triplet states (in C_{2v} and C_s symmetries for the trimer and pentamer, respectively) were more suitable candidates to interpret the experimental data. Fournier and co-workers²⁰ have carried out LSD calculations on the anionic clusters to assign the ground and excited states of the neutral Nb_n clusters from the observed PES. They have used a scaling technique on the calculated virtual orbital energies to assign the excited states of the neutral clusters. The technique was used to locate the excited states in the spectra, although such studies need to be validated at higher levels since electron correlation effects appear to change the relative orderings of these states. Moreover, all of the techniques that haven been used up to now are based on single reference wavefunctions, while we consider for the first time multireference treatments.

It is well known that the wave functions are usually multireference in character for small transition metal clusters, and consequently, there could be several low-lying electronic states close to the ground state making the spectra of these clusters extremely complicated. In our previous paper,²¹ we have carried out a detailed high level *ab initio*

calculations on the Nb_3 and Nb_3^- at the *complete active space multi-configuration self-consistent field* (CASMCSCF) and *multireference singles and doubles configuration interaction* (MRSDCI) levels. It was evident from our studies that these clusters, like their cationic analogues, are multireference in characters in their ground and low-lying electronic states, and most of these low-lying electronic structures undergo *Jahn-Teller* distortion. The last feature is not best revealed at the previous single reference level of theories. Apart from Nb_3 and Nb_3^- , there is no information on the nature of the excited electronic states of Nb_n ($n \geq 4$) at the multireference level of theory. Such theoretical investigations, on the other hand, are crucial to interpret the observed electronic properties of the Nb_n ($n \geq 4$) clusters.

The present paper deals with the structural and electronic properties of Nb_4 , Nb_5 and their anionic clusters. These clusters are not only important due to their complicated PES, but also because of their structural distortion in various electronic states due to the *Jahn-Teller* effect.²²⁻²⁴ First we report here the results of electronic structure calculations and the energy separations of the various low-lying electronic states of these clusters. We have used our energy separations to assign five observed peaks in the PES of Nb_4^- , and Nb_5^- .

Our previous studies on the niobium trimer have indicated that the low-lying electronic states of this cluster have *Jahn-Teller* distorted triangular (C_{2v}) geometries. That is, if a D_{3h} structure of the electronic state belongs to E' or E'' representation, it would be distorted due to the $E \otimes e$ Jahn-Teller coupling.^{23,24} It could be seen from our present energy calculations that most of the low-lying electronic states of Nb_4 and Nb_5 undergo *Jahn-Teller* distortion. The calculation of IP, EA, dissociation energy (D_e) and

the AE of the Nb₄ and Nb₅ are then presented together with a comparison of these results with experiment. Finally, a detailed analysis on the orbital and the charge distribution characteristics of different low-lying electronic states of Nb₄, Nb₅ and their anions are made.

II. METHODS OF COMPUTATION

The computations have been carried out using the complete active space multi-configuration self-consistent field (CASMCSCF) followed by multireference singles and doubles configuration interaction (MRSDCI) computations on the various electronic states of these metal clusters. Full geometry optimizations were carried out for each of the electronic states of these metal clusters at the CASMCSCF level using a quasi Newton-Raphson²⁵ technique. The geometries of these clusters were also optimized at the density functional (DFT) level of theory²⁶ to seek insight into their stable geometries at different spin multiplicities. However, the results must be considered cautiously since the electronic states of these clusters are multireference in character. The DFT calculations have used Becke's three parameter functional²⁷ with local correlation part provided by Vosko *et al*²⁸ and the non-local part by Lee, Yang and Parr²⁹ (in short B3LYP). This DFT/B3LYP technique has been further used to compute the vibrational frequencies of the low-lying electronic states of these clusters.

The various possible geometries of Nb₄ and Nb₅ that we have considered here are shown in Fig.1. Tetragonal (rhombus and square) and pyramidal (tetrahedral and distorted tetrahedral) geometries were considered to be the starting points for Nb₄. The calculations for the pyramidal structures were carried out in the C_s group, whereas the tetragonal structures were considered in the C_{2v} group. The tetragonal and the pyramidal

structures can have special bent structural arrangements in the C_{2v} and D_2 groups. These structural arrangements were considered in the DFT/B3LYP calculations to compare with the previous DFT results of Fowler and co-workers.¹⁷ The various geometries considered for the Nb_5 cluster include a regular trigonal bipyramid (D_{3h}), a distorted trigonal bipyramid (C_{2v}), a tetragonal pyramid (C_{4v}), a distorted tetragonal pyramid (C_{2v}), an edge-capped tetrahedron (C_{2v}), and a distorted edge-capped tetrahedron (C_s). The calculations for the edge-capped tetrahedron were carried out in the C_s group, whereas the calculations for all other clusters were made in the C_{2v} group. Relativistic effective core potentials (RECP) that replaced all but the outer $4s^2 4p^6 4d^4 5s^1$ shells by core potentials³⁰ were used in the present study. The corresponding optimized Gaussian basis set ($5s5p4d$) was contracted to ($5s3p2d$), with three large coefficients of p and d functions contracted. This choice of basis set is based on our previous study on the Nb_n^+ ($n=3-5$),³¹ Nb_3 , and Nb_3^- clusters.²¹ However, the calculation of EA needs extended basis sets. We have carried out the EA calculation by augmenting the basis sets with $4f$ ($\zeta = 0.45$) functions (at the CASMCSCF, MRSDCI and DFT/B3LYP levels) and $5g$ ($\zeta = 0.5505$) functions (at the DFT/B3LYP level). These f and g function's ζ values are optimized for energy. We have also included diffuse s ($\zeta = 0.0148$), p ($\zeta = 0.0081$) and d ($\zeta = 0.035$) functions in the basis set at the DFT/B3LYP level. Thus the final basis sets for the EA calculations, at this level, are ($6s6p5d1f//6s4p4d1f$) and ($6s6p5d1f1g//6s4p4d1f1g$) including f and g functions respectively. It is to be mentioned in this connection that although all-electron basis sets are desirable for the *ab initio* calculations, it is not practical to use such basis sets for heavy transition metal clusters. The effective core potential approach offers an alternate way to carry out such calculations by keeping the important valence space

electrons of the atoms for explicit treatment. Moreover the RECPs include relativistic effects such as mass-velocity and Darwin effects in a convenient manner.

The full active space of Nb_4 and Nb_4^- includes 40 orbitals and they correlate into 14 a_1 , 10 b_2 , 10 b_1 , and 6 a_2 orbitals in the C_{2v} structure and 24 a' and 16 a'' orbitals in the C_s structure. Likewise, the full active space of Nb_5 and Nb_5^- includes 50 orbitals correlating into 19 a_1 , 12 b_2 , 12 b_1 , and 7 a_2 orbitals of the structures considered in the C_{2v} group, and 31 a' and 19 a'' orbitals of the structures considered in the C_s symmetry. Inclusion of all these orbitals in the active space at the CASMCSCF level leads to too large a number of configuration spin functions (CSFs). To make the computations tractable, we have considered an alternative restricted active space approach by keeping several orbitals inactive and by reducing the number of vacant orbitals in the active space. The combinations of the active space of orbitals that produced the lowest energies were finally chosen for the calculations. Excitations were not allowed from the inactive orbitals, but they were allowed to relax.

In the case of Nb_4 and Nb_4^- 4 a_1 , 3 b_2 , 3 b_1 , and 2 a_2 orbitals were in the active space for the C_{2v} structures, while 6 a_1 , 4 b_2 , 4 b_1 , and 2 a_2 orbitals were kept inactive. For the pyramidal (C_s) structure, the total numbers of active and inactive orbitals were kept the same as the C_{2v} structure. The inactive orbitals in this case were composed of 10 a' and 6 a'' orbitals, whereas the active space consisted of 7 a' and 5 a'' orbitals. Twenty electrons (21 for Nb_4^-) were distributed among these orbitals to generate electronic states of different spin multiplicities. The final active space of Nb_5 and Nb_5^- clusters consists of 5 a_1 , 4 b_2 , 3 b_1 , and 2 a_2 orbitals in the C_{2v} symmetry while 8 a_1 , 5 b_2 , 5 b_1 , and 2 a_2 orbitals were kept inactive. The active space composition of the C_s structure (edge-

capped tetrahedron) spans 9 a' and 5 a'' orbitals, and the inactive space contained 13 a' and 7 a'' orbitals. Twenty-four (25 for Nb_5^-) electrons were distributed among the active space to generate various electronic states.

The MRSDCI method of calculations was used for different electronic states of these clusters using their CASMCSCF wave functions obtained through full geometry optimization. All configurations in the CASMCSCF calculations with absolute coefficients ≥ 0.03 were included as reference configurations. For the EA calculations, a smaller cut-off limit (≥ 0.02) was chosen. The CASMCSCF calculations included up to 13,680 CSFs while the MRSDCI included up to 52 million CSFs. The effect of unlinked quadruple clusters for the MRSDCI was estimated through a multireference Davidson correction³² (MRSDCI+Q).

In our previous calculations on the Nb_n^+ ($n=3-5$) and Nb_3 clusters, the accuracy of the contracted ($5s3p2d$) Gaussian basis set was tested against the original uncontracted ($5s5p4d$) basis set as well as extended ($6s6p5d1f/6s4p4d1f$) basis set. The geometries and energy separations of the various electronic states were found to be quite satisfactory using the ($5s3p2d$) basis set. We have further verified the choice of the ($5s3p2d$) basis set in the energy calculation of the anionic electronic states by calculating the energy separation of the different electronic states of Nb_4^- using the ($5s3p2d1f$) basis set at the MRSDCI and MRSDCI+Q levels. The agreement between the energy separations of the different electronic states in these two basis sets was quite satisfactory (discussed in details in section IIICa). The B3LYP calculations were carried out using the GAUSSIAN 98³³ program. The CASMCSCF computations were made by GAMESS³⁴ and a modified

version of ALCHEMY II³⁵ to include RECPs.³⁶ The MRSDCI calculations were carried out using ALCHEMY II.

III. RESULTS AND DISCUSSION

A. Geometries of the different electronic states of Nb₄ and Nb₅

The main objective is to determine the ground state geometries and the low-lying electronic states of these clusters. This is important to ascertain their spectroscopic properties. The analysis of the bonding characteristics of the various low-lying electronic states of Nb₄ and Nb₅ is another important objective of our studies. The equilibrium geometries and energy separations (ΔE) of the low-lying electronic states of these clusters are shown in Tables I – IV at the various level of theories.

a. Nb₄: The optimized geometries of the different electronic states of Nb₄ are listed in Table I at the CASMCSCF, MRSDCI and MRSDCI+Q levels. The structure calculations were carried in C_{2v} (rhombus or square) and C_s (pyramidal) symmetries (Fig. 1). While the MRSDCI and MRSDCI+Q results indicate that the pyramidal ¹A' to be the ground state, the CASMCSCF calculations favor the ³A' state to be the ground state. The ⁵A' and ⁵A'' states are very close to this ground state (³A') at the CASMCSCF level. The electronic states arising from the rhombus geometries (D_{2h}) are quite high at the CASMCSCF level while the MRSDCI and MRSDCI+Q calculations show a different trend (Table I). Since the CASMCSCF calculations were carried out in a restricted active space, and does not include dynamic-correlation effects, the ΔE values at the CASSCF level should not be considered quite accurate. The ΔE values at the MRSDCI level are more reliable as this method included dynamical electron correlation effects. Moreover

the energy separations of the various electronic states at the MRSDCI and MRSDCI+Q levels follow a similar trend. This gives further confidence in the assignment of the various electronic states using the MRSDCI level of theory.

The DFT/B3LYP optimized geometries of the various low-lying electronic states of Nb₄ are presented in Table II. Although the ¹A' state is the ground state, it is actually a tetrahedral structure with the T_d (¹A₁) symmetry. The ³A' state in the C_s symmetry (pyramidal) is the next low-lying electronic state. Fowler and co-workers¹⁷ have also carried out similar DFT calculations on Nb₄ using a different ECP basis set. They have also found that the ¹A₁ state (T_d) to be the ground state with the Nb–Nb bond lengths (2.541 Å) comparable to our results (2.538 Å). The earlier DFT calculations of Salahub¹⁸ and Anderson *et al*³⁷ gave similar results for the ground state of Nb₄, although Anderson *et al*³⁷ found a slightly distorted C_{3v} structure.

The low-lying excited states in Fowler et al.'s calculation¹⁷ are ³B₁ (C_{2v}, ΔE: 0.44 eV), ³A_u (D_{2h}, ΔE: 0.66 eV), ³A_g (C_{2h}, ΔE: 1.00 eV), ⁵A₁ (C_{2v}, ΔE: 1.2 eV) and ⁵B₁ (C_{2v}, 1.38 eV) at the LSD level. A close examination of the geometries presented in Table II reveals that the ³A' and ¹A'' states are actually of C_{2v} symmetry. The ΔE and the geometry of ³A' are similar to the ³B₁ state in Fowler et al.'s¹⁷ calculation. But as per our orientation it is a ³B₂ state. The ³B₁ and ³B₂ states in C_{2v} calculations exhibit accidental degeneracy (Table II) and are higher in energy than the ³A' state. These C_{2v} structures (³B₁ and ³B₂) have actually been encompassed into local minima during geometry optimization and are become with high-energy geometries. The ³A_g state has a similar ΔE value compared to Fowler et al.'s result¹⁷ while ³A_u could not be identified in the low-energy region in our calculation (Table II). The ¹A'' state that actually has a C_{2v} structure

(1B_1) is 0.68 eV above the ground state. All the other singlet C_{2v} states are higher in energy (Table II).

We have identified a few other low-lying excited states viz., $^5A (D_2)$, $^1A (D_2)$ (Fig. 1) and $^1A_u (D_{2h})$ within 1.2 eV energy separation of the ground state. These low-lying excited states were not reported in the previous DFT calculations¹⁷. The 5A_1 structure (C_{2v}) in our calculation is higher in energy than that of Fowler et al.'s calculation¹⁷ and we have not identified the higher energy $^5B_1 (C_{2v})$ state in our calculation. Thus the main features of our DFT excited states are similar to those of Fowler et. al.¹⁷ The differences, which are observed regarding the assignments of a few higher energy states, could arise from the use of different ECP basis set in our calculations.

The ΔE values obtained for the different electronic states at the MRSDCI and MRSDCI+Q levels exhibit remarkable differences from those obtained at the DFT/B3LYP level. The C_s structures obtained at the CASMCSCF/MRSDCI level are mostly distorted. We shall show in the next section that these structural distortions occur due to the *Jahn-Teller* effect. The other factor is the multireference nature of the wavefunctions of the different electronic states at CASMCSCF/MRSDCI level. The correlation effect arising from this multireference character is not accountable in the single reference treatment, and the observed ΔE values in the MRSDCI calculations are mostly the result of this effect.

The first excited low-lying electronic state in the DFT/B3LYP calculation is $^3A'$. This electronic state is 1.28 eV above the ground state at the MRSDCI (1.60 eV in MRSDCI+Q) level. The leading electronic configurations of the $^3A'$ state ($36\%|1a'^2 \dots 15a'^2 16a'^1 17a'^1 1a''^2 \dots 9a''^2 10a''^2 \rangle + 22\%|1a'^2 \dots 15a'^2 16a'^2 17a'^2 1a''^2 \dots 9a''^1 10a''^1 \rangle + \dots$)

show that this state is arising from the $^1A''$ ($67\%|1a'^2 \dots 15a'^2 16a'^2 17a'^1 1a''^2 \dots 9a''^2 10a''^1 \rangle$) state through excitation of $16a'$ (or $9a''$ for second leading configuration) electron. Now, the $^1A''$ state is the higher energy *Jahn-Teller* component of the $^1A'$ ground state. Thus the $^3A'$ state has quite a high ΔE value.

The first low-lying 1A_g excited state at the CASMCSCF/MRSDCI level ($\Delta E = 0.67$ eV) is quite high at the DFT/B3LYP level. The 1A_g electronic state is highly multireference in nature ($43\%|1a_g^2 \dots 7a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 1b_{3g}^2 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2 \rangle + 18\%|1a_g^2 \dots 7a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 1b_{3g}^2 2b_{3g}^2 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 \rangle + 10.3\%|1a_g^2 \dots 6a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 5b_{2u}^2 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2 \rangle + 4.4\%|1a_g^2 \dots 7a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 1b_{3g}^2 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2 \rangle + \dots$). The high correlation effect arising from the multireference effect gives the 1A_g state enhanced stability over the other states. This effect could not be noticed in any single reference calculations.

b. Nb₅: The optimized geometries and energy separations for the various electronic states of the Nb₅ cluster in distorted tetragonal pyramid (DTP), distorted trigonal bi-pyramid (DTB) and distorted edge-capped tetrahedron (DECT) structures are shown in Table V at the CASMSCF, MRSDCI and MRSDCI+Q levels. The optimized minimum energy geometry of each cluster is shown in Fig. 2. The important feature of the trigonal bipyramid and tetragonal pyramid structures is that the structures do not retain perfect D_{3h} and C_{4v} symmetries during geometry optimization. The edge-capped tetrahedral structure also distorts from its ideal C_{2v} structure. So the various electronic states of the DTP and DTB structures are assigned in the C_{2v} symmetry, whereas the electronic states of the DECT structure are assigned in the C_s symmetry. The 2A_2 state of the DTB

structure was found to be the minimum at the MRSDCI level. This is not an unambiguous ground state, as the ${}^2A''$ electronic state of the DECT structure is just 0.08 eV (0.31 eV at the MRSDCI+Q level) above the 2A_2 ground state (Table III).

The triangular base formed by the Nb₁, Nb₂ and Nb₃ atoms (Fig. 1d) of the DTB structure constitutes an isosceles triangle. Thus we have two different types of axial-equatorial distances (distances c and d in Fig. 1f) due to isosceles triangular arrangement of the base. As seen from Table V, there is considerable difference between the two equal sides of the isosceles triangle relative to the third side. This, together with energy separations presented in Table V, suggests that the Jahn-Teller distortion is considerable in these structures. The MRSDCI energy separations indicate that electronic states of the DTB structure are lower in energy (Table III).

The energies of the various electronic states of the DTP structure (Table III) indicate that apart from the 4A_1 , 6A_2 , 2B_1 states, all other electronic states are higher in energy. The geometries of the different electronic states of the DTP structure indicate that although the distances among four Nb atoms forming the tetragonal base are the same, they are not in the same plane. That is, they form a puckered structure to avoid steric strain (Fig. 1e). This makes the distances a and b unequal for all the electronic states of the DTP structure presented in Table III. If the distortion of the structures is too high, they could be converted into the DTB structure during optimization, if the corresponding DTB electronic state is lower in energy. Thus all four electronic states (viz., nA_1 , nB_2 , nB_1 , and nA_2) in a particular spin state n ($n = 2, 4, 6$) could not be found in the DTB or DTP structures. Table V also contains the geometries and ΔE of the various electronic states of the DECT structure of Nb₅ at the CASMCSF, MRSDCI, and MRSDCI+Q

levels. The results indicate that the ${}^2A''$, ${}^4A''$ and ${}^2A'$ states are the low-lying excited states (within ΔE of 1.1 eV), whereas the ${}^6A''$, ${}^4A'$, and ${}^6A'$ electronic states of this cluster are considerably higher.

The earlier DFT calculations of Salahub and co-workers¹⁸ pointed that a doublet trigonal bipyramid structure is the ground state of Nb₅. They did not suggest any assignment for the electronic state and found that the ionization of the cluster leads to a *Jahn-Teller* distorted trigonal bipyramid. The results of our DFT/B3LYP calculations on the different electronic states of Nb₅ are presented in Table IV. The results indicate that a 2B_1 state with the DTB geometry as the ground state. The 2A_2 (DTB) state is assigned as ground state at the MRSDCI and MRSDCI+Q levels while the ${}^2A'$ (DECT) state is nearly degenerate. As would be seen in the next section, the 2A_2 (DTB) state undergoes *Jahn-Teller* distortion and the MRSDCI calculation predicts the state to be lower energy *Jahn-Teller* component of the ${}^2E''$ state. In the present DFT/B3LYP calculation, the observed *Jahn-Teller* energy separation between the 2B_1 and 2A_2 components is quite low and the 2B_1 state is the lower energy component. The MRSDCI wave function of the 2A_2 (DTB) state is highly multireference in character ($66\%|1a_2\dots 13a_1^2 1b_2^2\dots 9b_2^2 1b_1^2\dots 7b_1^2 1a_2^2\dots 3a_2^2 4a_2^1\rangle + 2.3\%|1a_2\dots 13a_1^2 1b_2^2\dots 9b_2^2 1b_1^2\dots 7b_1^1 8b_1^1 1a_2^2\dots 3a_2^2\rangle + 1.44\%|1a_2\dots 14a_1^2 1b_2^2\dots 8b_2^2 1b_1^2\dots 7b_1^2 1a_2^2\dots 3a_2^2 4a_2^1\rangle + 1\%|1a_2\dots 13a_1^2 14a_1^1 1b_2^2\dots 8b_2^2 9b_2^1 1b_1^2\dots 6b_1^2 7b_1^1 1a_2^2\dots 4a_2^1\rangle + \dots$). The 2B_1 (DTP) structure, on the other hand, has only two dominant configurations ($67\%|1a_2\dots 13a_1^2 1b_2^2\dots 9b_2^2 1b_1^2\dots 7b_1^2 8b_1^1 1a_2^2\dots 3a_2^2\rangle + 1.44\%|1a_2\dots 14a_1^2 1b_2^2\dots 8b_2^2 1b_1^2\dots 7b_1^2 8b_1^1 1a_2^2\dots 3a_2^2\rangle + \dots$). Apart from the higher stabilization due to electron correlation effect in the 2A_2 state, the 2B_1 state could be thought to be an excited state through excitation from $4a_2$ to $8b_1$ orbitals. In fact the *Jahn-*

Teller stabilization of the 2A_2 state is quite large at the MRSDCI level. The DFT/B3LYP results further show that the 2A_1 and 4B_1 states of the DTB structure are low-lying electronic states. The results are similar to those of the MRSDCI and MRSDCI+Q, although their ΔE s differ.

B. Nature of geometric distortions in the low-lying electronic states of Nb₄ and Nb₅

Most of the electronic states of Nb₄ undergo distortions from ideal tetrahedral structures (T_d) including the ground state (${}^1A'$) at the CASMCSCF/MRSDCI level (Table I). The ${}^1A'$ ground state has the same electronic configuration ($1a'^2 \dots 17a'^2 1a''^2 \dots 9a''^2$) at the DFT/B3LYP and CASMCSCF/MRSDCI levels. But this state has the ideal tetrahedral structure with the T_d (1A_1) symmetry at the DFT/B3LYP level is. The leading configuration contributes only 69% to the total wave function at the CASMCSCF/MRSDCI level. Thus the multireference character of the wave function plays important role for the distortion of the ${}^1A'$ state.

To verify the nature of distortion at the CASMCSCF/MRSDCI level, we have optimized the geometry of the ${}^1A'$ state in a perfect T_d symmetry. The leading configuration of this state in the T_d group ($\dots a_1^2 a_1^2 t_2^4 t_2^4 e^4 t^2 e^2$) shows that this electronic state is 1E . Thus the 1E state would undergo Jahn-Teller distortion into the ${}^1A'$ and ${}^1A''$ states that we have calculated at the CAMCSCF/MRSDCI level. This is also true for the other electronic states of Nb₄ in the C_s symmetry. We have further checked this case by calculating the energy of the 1E state from both ${}^1A'$ and ${}^1A''$ states and the energies differ only by 0.05 eV at the MRSDCI and 0.03 eV at the MRSDCI+Q level (Table V). Evidently the ${}^1A'$ and ${}^1A''$ states (T_d symmetry) correlate into the 1E state and the energy of the 1E state is higher than either of the ${}^1A'$ (ground state) and ${}^1A''$ states in the C_s

symmetry. This is an ideal example of geometric distortion occurring through $T \otimes e$ *Jahn-Teller* effect as discussed in Bersuker's review.²³

The discrepancy between the DFT/B3LYP and CASMCSCF/MRSDCI results needs to be discussed further. Table V contains the energies of the optimized geometries of the 1E state together with the ${}^1A'$ and ${}^1A''$ states at the DFT/B3LYP level. The results indicate that the energy of the 1E state is higher than the ${}^1A'$ and ${}^1A''$ states. Note that the A' (C_s) state correlates with the A_1 and E states in T_d symmetry. Likewise the A'' representation correlates into the A_2 and E states. The computed energy values indicate that 1E is a higher root at the DFT/B3LYP level. Since this state is really multireference in character, it appears to become a lower root at the CASMCSCF/MRSDCI level due to the electron correlation effects. Thus the ground state of Nb_4 is an undistorted T_d structure (1A_1) at the DFT/B3LYP level. The planar structures of Nb_4 in their different electronic states are all D_{2h} in nature at both the DFT/B3LYP and CASMCSCF/MRSDCI levels. These structures are distorted from their ideal D_{4h} (square) structures. The distortions of the B_{2u} , B_{3u} , B_{3g} , and B_{2g} states of the D_{4h} structure fall under the $E \otimes b_1$ type *Jahn-Teller* coupling. This is a special case $E \otimes (b_1 + b_2)$ distortion,²³ where the b_1 distortion transforms a square into rhombus. The structural distortions of the rest of the electronic states are not of *Jahn-Teller* origin.

The ground state of Nb_5 (2A_2 , DTB) is a distorted structure from an ideal D_{3h} symmetry at the CASMCSCF/MRSDCI level. This state competes for the ground state at the DFT/B3LYP level. The ground state at the DFT/B3LYP level (2B_1) is only 0.07 eV lower and both the states have distorted D_{3h} structures. The ideal D_{3h} structure of 2A_2 has the $e''^2 a_1''^1$ electronic configuration at the CASMCSCF/MRSDCI level. This means that

this state in D_{3h} symmetry is ${}^2E''$. Thus, the 2A_2 state is distorted due to the *Jahn-Teller* effect ($E \otimes e$ type *Jahn-Teller* effect²³). The DFT/B3LYP results also show that the 2B_1 and 2A_2 states are *Jahn-Teller* components. Table V contains the energies of these two states (2B_1 and 2A_2) together with the energy of the ${}^2E''$ (D_{3h}) state at the DFT/B3LYP level. The energy separation between the two *Jahn-Teller* components is very small. It has been shown in the previous section that the electron correlation effects due to multireference nature of these two states increase the energy separation between them at the MRSDCI and MRSDCI+Q levels. Since the reaction coordinate separating the geometries between the DTB and DTP structures is the simple bending mode containing the plane Nb₂-Nb₄-Nb₃-Nb₅ (Fig. 1d and 1e), the higher energy 2B_1 is distorted to the DTP structure. The distortions of the other electronic states of the DTP and the DTB structures could be similarly explained.

C. Electronic structures of Nb₄⁻ and Nb₅⁻ in their ground and excited states

We have computed the properties of the anions to facilitate the assignment of the observed PES³. The energy separations of the different electronic states of Nb₄⁻ have been determined using two different basis sets of Nb ($5s5p4d1f/5s3p2d1f$) and $5s5p4d//5s3p2d$) at the MRSDCI and MRSDCI+Q levels. This facilitates to calibrate the accuracy of our calculations.

a. Nb₄⁻: The optimized geometries and the energy separations of the different low-lying electronic states of Nb₄⁻ are shown in Table VI at the CASMCSCF, MRSDCI and MRSDCI+Q levels. Since the CASMCSCF energy separations in the restricted active space calculations are not reliable (discussed in the previous section), the ΔE values are presented at the MRSDCI and MRSDCI+Q levels only. The results in Table IV indicate

that the ground state of Nb_4^- has a rhombus structure (${}^2\text{B}_{3g}$). The energy separations of the various low-lying electronic states are similar in the smaller ($5s5p4d//5s3p2d$) and larger ($5s5p4d1f//5s3p2d1f$) basis sets. Only for the ${}^2\text{A}''$ and ${}^2\text{A}'$ states of the C_s structure, the larger basis set calculations yield higher energy separations. But both the basis sets do not yield these electronic states as the ground states at the MRSDCI and MRSDCI+Q levels. However, the results of the DFT/B3LYP calculations (Table VII) differ from those of the MRSDCI and MRSDCI+Q results. Although the DFT/B3LYP calculations predict the rhombus structures as the low-lying electronic states, the ground state is a pyramidal (C_s , ${}^2\text{A}'$) structure at the DFT level. The previous local spin density (LSD) calculations by Fournier and co-workers²⁰ have also predicted that the ground state of Nb_4^- is a pyramidal doublet structure.

The ${}^2\text{B}_{3g}$ ground state structure of Nb_4^- is a *Jahn-Teller* distorted structure ($\text{E} \otimes \text{b}_1$ type²³) and is of multireference character ($73\%|1a_g^2 \dots 7a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 1b_{3g}^2 2b_{3g}^1 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2 \rangle + 2.3\%|1a_g^2 \dots 7a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 1b_{3g}^2 2b_{3g}^1 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^1 2a_u^1 \rangle + \dots$). The ${}^2\text{A}'$ state is also multireference character ($60\%|1a'^2 \dots 16a'^2 17a'^2 1a''^2 \dots 10a''^2 \rangle + 16\%|1a'^2 \dots 16a'^2 17a'^2 1a''^2 \dots 10a''^2 11a''^1 \rangle + \dots$) at the CASMCSCF/MRSDCI level. Thus electron correlation stabilization effects are important for both the electronic states. The extra stabilization of the ${}^2\text{B}_{3g}$ state could be explained from the ease of formation of the Nb_4 ground state through electron detachment. An examination of the leading electronic configuration of the ${}^1\text{A}'$ ground state of Nb_4 ($1a'^2 \dots 16a'^2 17a'^2 1a''^2 \dots 9a''^2$) shows that it cannot be formed from the ${}^2\text{A}'$ state through a simple electron detachment from a' or a'' orbitals. This process more likely results in the ${}^1\text{A}''$ state of Nb_4 , which is 1.08 eV above the Nb_4

ground state ($^1A'$). On the other hand, the leading electronic configuration of the ground state of Nb_4^- ($^2B_{3g}$) shows that it correlates with the $1a'^2...16a'^217a'^2 1a''^2...10a''^1$ configuration in the C_s symmetry. The $^1A'$ state is easily formed through this state by an electron detachment to the $10a''$ (b_{3g}) orbital and thus the 3B_g state should have higher stabilization with respect to the $^2A'$ state.

b. Nb_5^- : The geometries and the energies of the various low-lying electronic states of Nb_5^- are presented in Table VIII at the CASMCSCF, MRSDCI and MRSDCI+Q levels. The optimized geometries are at the CASMCSCF level while the ΔE values are presented at the MRSDCI and MRSDCI+Q levels. The ground state of Nb_5^- varies as a function of level of theory. The 3B_1 and 1A_1 states of the DTB structure compete as a candidate for the ground state. The DFT/B3LYP results of the different electronic states of Nb_5^- (Table IX) also show that the ground state of the anion is sensitive to the level of theory. Here three electronic states of the DTB structure, viz., 1A_1 , 3A_2 , and 1A_2 compete for the ground state. The 3A_2 and 1A_2 electronic states are low-lying states at the MRSDCI and MRSDCI+Q levels, but their energy separations are slightly higher (Table IX). The 3B_1 state at the DFT/B3LYP level has a DTP structure and its energy is slightly higher. At the CASMCSCF/MRSDCI level both the 3B_1 and 3A_2 states exhibit DTB equilibrium structures and undergo *Jahn-Teller* distortion. The 3B_1 state in this case is the lower energy component of the $^3E''$ (D_{3h}) state.

The CASMCSCF/MRSDCI leading electronic configurations of the 3B_1 ($1a_1^2...14a_1^2 1b_2^2...8b_2^29b_2^11b_1^2...8b_1a_2^2...3a_2^24a_2^1$) and 1A_1 ($1a_1^2...13a_1^21b_2^2...9b_2^21b_1^2...7b_1a_2^2...4a_2^2$) electronic states of Nb_5^- indicate that the generation of the Nb_5 ground state (2A_2 , $1a_1^2...13a_1^21b_2^2...9b_2^21b_1^2...7b_1 1a_2^2...3a_2^24a_2^1$) through electron detachment is more

feasible from the 1A_1 ground state. Thus the preferred ground state of Nb_5^- should be 1A_1 . The present DFT/B3LYP results and the previous LSD calculations by Fournier and co-workers²⁰ also support this ground state assignment.

D. Vibrational frequencies of the Nb_n and Nb_n^- ($n=4, 5$) clusters

Tables II, IV, VII, and IX list the vibrational frequencies of the different electronic states of Nb_4 , Nb_4^- , Nb_5 , and Nb_5^- respectively. The calculated frequencies of most of the low-lying electronic states are all positive and thus confirming that the calculated geometries are true minima on the energy surfaces. There are few cases for which one of the frequencies has a low imaginary value. Since the available PES of Nb_n clusters³ are not vibrationally resolved, the calculated vibrational spectra of the Nb_n and Nb_n^- ($n=4, 5$) cannot be compared with any experimental values.

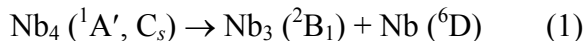
Fournier and co-workers²⁰ have previously calculated the vibrational frequencies (ν) of the Nb_n^- ($n=4, 5$) clusters using the LSD technique and have found that the frequencies of the anionic clusters are not much different than the neutral clusters. Our present DFT/B3LYP calculations show that the symmetric stretching frequencies of Nb_4 and Nb_5 are around 360-373 and 328-335 cm^{-1} respectively. In our previous work on Nb_n^+ ($n=3-5$) clusters,³¹ it was found that the symmetric stretching modes of the ground electronic states roughly correlate with their dissociation energies. The calculated ground state symmetric stretching modes of Nb_4^+ ($^2A'$) and Nb_4 ($^1A'$) are 361 and 373 cm^{-1} respectively. Similar values for the Nb_5^+ (3A_1 , DTP) and Nb_5 (2A_2 , DTB) are 356 and 345 cm^{-1} . The experimental dissociation energies^{5,6} (De) of Nb_4^+ , Nb_4 , Nb_5^+ , and Nb_5 are 5.9, 5.64, 5.5, and 5.35 eV respectively. These results show that the relative stabilities of the cationic and neutral clusters cannot be predicted solely from their symmetric stretching

modes. This was also the case for the Nb₃ and Nb₃⁺ clusters. But if we compare the symmetric stretching modes of the Nb₃ (ν : 326 cm⁻¹; D_e: 5.01 eV), Nb₄, and Nb₅ with their experimental dissociation energies,^{5,6} it is evident that the relative stabilities of the Nb_n (n= 3-5) clusters could be correlated with their respective stabilities.

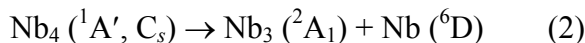
E. Dissociation energy (D_e), atomization energy (AE), ionization potential (IP), and electron affinity (EA) of Nb₄ and Nb₅

Armentrout and co-workers^{5,6} have measured the IP and D_e of Nb₄ and Nb₅ clusters through a collision induced dissociation (CID) technique. The calculated and the experimental values of these quantities are compared in Table X. The PES of Nb₄⁻ and Nb₅⁻ have yielded the vertical EA³ of Nb₄ (1.15 eV) and Nb₅ (1.65 eV).

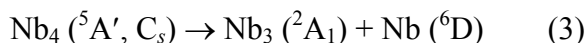
a. D_e of Nb₄: The dissociation energy of Nb₄ is computed at the MRSDCI level from the reaction (1).



Since the ground state of Nb₃ at the MRSDCI+Q level is ²A₁, the D_e of Nb₄ at the MRSDCI+Q level is calculated as follows:



The calculations are carried out in a stepwise manner. Initially the dissociation energy (D_e') is calculated for the following supermolecular system.



The D_e' for the reaction (3) was computed through a supermolecular approach by placing the apex Nb atom of the pyramid (C_s) structure of Nb₄ at 10 Å separation from the base atoms. The optimized structure of Nb₃ (²A₁) at the CASMCSCF/MRSDCI level²¹ was used for the triangular base structure to compute the energy of the supermolecular

system. The energy difference between the $^5A'$ state of Nb₄ and the supermolecular $^5A'$ state gives the value of D_e' (MRSDCI: 4.79 eV, MRSDCI+Q: 4.99eV). The actual D_e values of Nb₄ are then calculated at the MRSDCI and MRSDCI+Q levels by the use of reactions (1) and (2) and by the following adjustments of energies with respect to the ground states of Nb₃ and Nb₄.

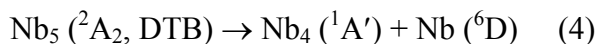
$$D_e (\text{MRSDCI}) = D_e' - \Delta E (^2A_1, \text{Nb}_3) + \Delta E (^5A', \text{Nb}_4)$$

$$D_e (\text{MRSDCI+Q}) = D_e' + \Delta E (^5A', \text{Nb}_4)$$

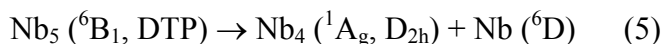
Thus the calculated D_e values at the MRSDCI and MRSDCI+Q levels are 6.01 and 6.79 eV respectively, in agreement with the experimental value quite well^{5,6} (Table X).

The D_e of Nb₄ at the DFT/B3LYP level has been computed directly from the reaction (1) using $(6s6p5d1f//6s4p4d1f)$ and $(6s6p5d1f1g//6s4p4d1f1g)$ basis sets. The D_e value is calculated as $D_e (\text{Nb}_4) = E (\text{Nb}_4, ^1A') - E (\text{Nb}_3, ^2B_1) - E (\text{Nb}, ^6D)$. The D_e values thus calculated using the two basis sets (6.07 eV and 6.10 eV, Table IX) are consistent with the MRSDCI and MRSDCI+Q results and experiment.^{5,6}

b. D_e of Nb₅: The dissociation energy of Nb₅ at the MRSDCI and MRSDCI +Q levels is computed in a stepwise manner as follows:



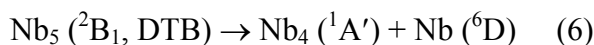
Initially the dissociation energy (D_e'') is calculated for the following system:



The D_e'' for the reaction (5) was calculated as supermolecular approach by placing the apex Nb atom of the DTP structure at 10 Å separation from the four Nb atoms of the base. The optimized geometry of the 1A_g state (Table I) of Nb₄ was used to compute the energy of the supermolecular system. The energy difference between the 6B_1 state and the

supermolecular 6B_1 state gives the value of D_e'' (MRSDCI: 4.68 eV, MRSDCI+Q: 5.04 eV). The actual D_e for the reaction (4) is the calculated by the adjustments of energies with respect to the ground states of Nb_4 (${}^1A'$, C_s) and Nb_5 (2A_2 , DTB) [$D_e = D_e'' + \Delta E$ (${}^6B_1, Nb_5$) - ΔE (${}^1A_g, Nb_4$)]. The D_e of Nb_5 , thus calculated at the MRSDCI (5.58 eV) and MRSDCI+Q (6.25 eV) levels, agree with experiment^{5,6} very well (Table X).

The D_e of Nb_5 at the DFT/B3LYP level has been computed directly by the use of the $(6s6p5d1f//6s4p4d1f)$ and $(6s6p5d1f1g//6s4p4d1f1g)$ basis sets as follows.



The D_e value is calculated as $D_e(Nb_5) = E(Nb_5, {}^2B_1) - E(Nb_4, {}^1A') - E(Nb, {}^6D)$. The D_e value thus calculated using both the basis sets (5.51 eV and 5.53 eV, Table IX) is consistent with the MRSDCI and MRSDCI+Q results and experiment.^{5,6}

The AEs of Nb_4 and Nb_5 have been calculated from the stepwise D_e values of Nb_n clusters at the MRSDCI and MRSDCI +Q levels. Balasubramanian and Zhu³⁸ have calculated the D_e of Nb_2 to be 3.95 and 4.28 eV respectively at the MRSDCI and MRSDCI+Q levels. In our previous paper, we have calculated the D_e of Nb_3 at the MRSDCI (4.76 eV) and MRSDCI+Q (4.46 eV) levels. Combining these results, the AE/atom of Nb_4 comes out to be 3.68 and 3.88 eV/atom respectively at the MRSDCI and MRSDCI+Q levels. The AE/atom of Nb_5 could be similarly calculated using the stepwise D_e values of Nb_2 , Nb_3 , Nb_4 , and Nb_5 . The values thus computed are 4.06 and 4.36 eV/atom respectively at the MRSDCI and MRSDCI+Q levels. The calculated AE/atom of Nb_4 and Nb_5 clusters at the DFT/B3LYP level are 4.32 and 4.56 eV respectively. All these results are in good agreement with the experimental AE/atom values of Nb_4 and Nb_5 , obtained from the experimental D_e values^{5,6} (Table X) of the Nb_n clusters.

c. EA of Nb₄ and Nb₅: The EA of Nb₄ has been calculated as the adiabatic energy difference between the optimized geometries of the ground states of Nb₄ and Nb₄⁻. The DFT/B3LYP level of calculation used the (6s6p5d1f//6s6p4d1f) and (6s6p5d1f1g//6s6p4d1f1g) basis sets and the energy separation was calculated between the ¹A' and the ²A' electronic states of Nb₄ and Nb₄⁻ for the calculation of EA. The EA of Nb₄ was calculated at the MRSDCI and MRSDCI+Q levels using the (5s5p4d1f//5s3p2d1f) basis set. Higher order basis set (*cf.* DFT/B3LYP calculation) could not be used, as the number of configurations in the CI calculation becomes enormously high. The energy difference between the ¹A' (Nb₄) and ²B_{3g} (Nb₄⁻) electronic states was calculated at these two levels to estimate the EA of Nb₄. Considering the adiabatic nature of the calculated EA, the calculated results (Table X)) are in agreement with experiment³ (1.15 eV). The MRSDCI+Q method predicts a slightly higher value (1.42 eV), but considering the uncertainty in the measured value of EA from the PES, this calculated value is also quite accurate.

The EA of Nb₅ was calculated at the DFT/B3LYP level using the energy difference of the ground states of Nb₅ (²A₂) and Nb₅⁻ (¹A₁). Both the (6s6p5d1f//6s6p4d1f) and (6s6p5d1f1g//6s6p4d1f1g) basis sets were employed to calculate EA at this level. The calculated value (1.31 eV) (Table X) is somewhat lower than the experiment³ (1.65 eV). However it is well recognized that the computation of the adiabatic EAs of these species is extremely difficult.

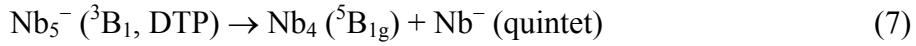
The calculation of the EA of Nb₅ could not be carried out in a straightforward way at the MRSDCI and MRSDCI+Q levels due to a large number of configurations. For accurate calculations, at least 0.02 cutoffs of configurations are needed even with the use

of the (*5s5p4d//5s3p2d*) basis set, and the total configuration becomes enormously high. Consequently, the EA of Nb₅ was computed using the following thermodynamic cycle.

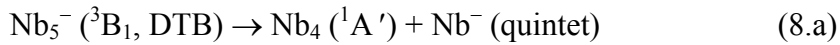
$$EA(Nb_5) = D_e^I(Nb_5^-) - D_e(Nb_5) + EA(Nb_4) \quad (I)$$

$D_e^I(Nb_5^-)$ involves the dissociation energy of Nb₅⁻ for the reaction Nb₅⁻ (³B₁, DTB) → Nb₄⁻ (²B_{2g}) + Nb (⁶D). The quantities $D_e(Nb_5)$ and $EA(Nb_4)$ have already been calculated (Table X). The $D_e^I(Nb_5^-)$ cannot be calculated in straightforward way through a supermolecular approach, as Nb₅⁻ dissociates as Nb₄ and Nb⁻ at the MRSDCI level. Thus the D_e^I value is calculated in a stepwise manner.

Initially the dissociation energy D_e^{II} is calculated for the following reaction:



The calculation is done through a supermolecular approach by placing the apex Nb atom of a tetragonal pyramid structure at 10 Å separations from four base Nb atoms. The ⁵B_{1g} (D_{2h}) structure of Nb₄ (Table I) is used for the base structure. The dissociation energy D_e^{II} is then calculated by taking the energy difference between the ³B₁ (DTP) state of Nb₅⁻ and the ³B₁ state of supermolecule. The adjustment of energy separations with respect to the ground states of Nb₅⁻ (³B₁, DTB) and Nb₄⁻ (¹A') gives the dissociation energy (D_e^{II}) for the reaction (8a) from the relation (8b).



$$D_e^{III} = D_e^{II} + \Delta E (^3B_1, DTP) - \Delta E (^5B_{1g}) \quad (8.b)$$

Since the ground state of Nb₅ at the MRSDCI+Q level is ¹A₁, the energy adjustments are made with respect to this state during D_e^{III} calculation at this level. The calculated D_e^{III} at the MRSDCI (6.77 eV) and MRSDCI+Q (7.13 eV) levels are used in the energy cycle (8c) to calculate the dissociation energy $D_e^I(Nb_5^-)$.

$$D_e^I(\text{Nb}_5^-) = D_e^{\text{III}} + \text{EA}(\text{Nb}_4) - \text{EA}(\text{Nb}) \quad (8.c)$$

We have calculated the electron affinity of Nb atom at the DFT/B3LYP level to be 2.14 eV using the $(6s6p5d1f//6s6p4d1f)$ basis set. Since all the parameters on the right side of (8c) are now known, the calculation of $D_e^I(\text{Nb}_5^-)$ at the MRSDCI (5.87 eV) and MRSDCI+Q (6.41 eV) is quite straightforward. We have checked these numbers against our DFT/B3LYP (6.01 eV), using the $(6s6p5d1f//6s6p4d1f)$ basis set) and the previous LSD²⁰ (6.32 eV) results. Our calculated $D_e^I(\text{Nb}_5^-)$ is quite satisfactory with respect to these values. The electron affinity of Nb₅ can now be calculated from relation (8b). The calculated EA of Nb₅ at the MRSDCI (1.54 eV) and MRSDCI+Q (1.58 eV) levels are in excellent agreement with the experiment³ (1.65 eV, Table X).

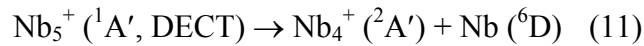
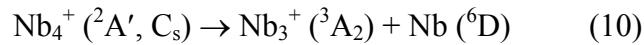
c. IP of Nb₄ and Nb₅: The IPs of Nb₄ and Nb₅ at the DFT/B3LYP level have been calculated by taking the energy difference of the ground states of cationic and neutral clusters. The calculations have been carried out using both the $(6s6p5d1f//6s4p4d1f)$ and $(6s6p5d1f1g//6s4p4d1f1g)$ basis sets. In the case of Nb₄ IP calculation, the energy difference was taken between the ¹A' (Nb₄) and ²A' (Nb₄⁺) electronic states while for the IP calculation of Nb₅ the energy difference was calculated between the ²B₁ (Nb₅, DTB) and ³A₁ (Nb₅⁺, DTP) electronic states. The calculated IP values of Nb₄ (5.43 eV) and Nb₅ (5.22 eV) are in very good agreement with the experiment^{5,39} (Table X). It is to be noted further from Table X, that the use of g function in the basis set does not change the IP significantly.

The calculation of the IP values of Nb₄ and Nb₅ at the MRSDCI and MRSDCI+Q levels turned out to be more challenging than the DFT/B3LYP technique. This way of calculation the IP needs a bigger basis set. The minimum basis set for this purpose should

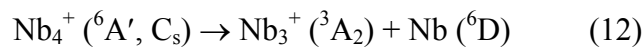
use and extra d and f function together with sp diffuse functions:[(6s6p4d1f//6s4p3d1f) type]. The MRSDCI calculation using such basis set is intractable even for Nb_4^+ . The use of lower order basis sets of the type (5s5p4d1f//5s3p2d1f), and (6s6p4d//6s4p3d) does not produce any reliable results (Table X). Thus the IP calculations at the MRSDCI and MRSDCI+Q levels have been carried out using a thermodynamic cycle. The following thermodynamic cycle relation is used for the calculations of IPs.

$$\text{IP}(\text{Nb}_n) = \text{IP}(\text{Nb}_{n-1}) - D_e(\text{Nb}_{n-1}^+ - \text{Nb}) + D_e(\text{Nb}_{n-1} - \text{Nb}) \quad (n = 4, 5) \quad (9)$$

Thus the calculation of IP values need accurate measures of the dissociation energies of Nb_n and Nb_n^+ . Since our computed D_e values Nb_4 and Nb_5 are quite accurate (Table X), and we have previously calculated the D_e values³¹ of Nb_4^+ (6.70 eV) and Nb_5^+ (6.08 eV), we can use these results to compute the IP. Although these values are within the range of the experimental data, they are not precise enough for the IP calculations through equation (9). Thus we have first recalculated the D_e values of Nb_4^+ and Nb_5^+ using larger CI and basis set calculations to maintain consistency. The following dissociation reactions are used for the calculation of D_e values of Nb_4^+ and Nb_5^+ respectively.



The same supermolecular approach as described in our previous paper³¹ has been used for the calculation of the D_e values. In the case of Nb_5^+ , the only difference is that we have used much bigger CI calculations. In the case of Nb_4^+ we have calculated the D_e value in a stepwise manner. The D_e' value is first computed for the following dissociation process in a supermolecular scheme.



This step is different from our previous approach where we have initially dissociated the ${}^4A'$ (C_s) state of Nb_4^+ instead of the ${}^6A'$ state. The measurement of D_e' is done in the same supermolecular approach as described in our previous paper.³¹ The actual D_e is obtained through adjustment of the ground state energies of Nb_3^+ and Nb_4^+ from the following relation:

$$D_e = D_e' + \Delta E ({}^6A') - \Delta E ({}^3A_2) \quad (13)$$

Our calculated D_e values of Nb_4^+ (MRDCI: 6.01 eV, MRSDCI+Q: 6.64 eV) and Nb_5^+ (MRSDCI: 5.43 eV, MRSDCI+Q: 5.76 eV) are in very good agreement with the experiment^{5,6} (Table X). The IP values could now be calculated from the relation (9), as all the parameters needed have been determined with sufficient accuracy (Table X). The calculated IP values of Nb_4^+ (MRSDCI: 5.60 eV, MRSDCI+Q: 5.76 eV) and Nb_5^+ (MRSDCI: 5.39 eV, MRSDCI+Q: 5.71 eV) are in excellent agreement with the experiment.^{5,39}

F. Assignment of the photoelectron spectrum of Nb_4^- and Nb_5^-

Kietzmann and coworkers³ have measured the PES of Nb_4^- and Nb_5^- through a laser vaporization technique. The spectra yielded the EAs of these two clusters and the positions of the various low-lying electronic states of the neutral Nb_n ($n = 4, 5$). Since the spectrum was not vibrationally resolved, the excitation energies measured from the spectra would be vertical in nature. Fournier and coworkers²⁰ have used a scaling technique for the virtual orbital energies of Nb_n^- ($n = 4, 5$) to match the locations of the excited states in the spectra. Their scaling method was quite successful in predicting the

excitation energies of the various excited states of the Nb_n ($n = 4, 5$) clusters observed in the spectrum. But this technique gives no information on the nature of the excited states. Our present calculations provide the geometries, symmetries and the energy separations of the ground and low-lying excited states of Nb_4 and Nb_5 . Since our calculations are based on the optimized geometries of the respective states, the excitation energies of the electronic states are all adiabatic. The assignments presented here are based upon our MRSDCI results on Nb_4 (Table I) and Nb_5 (Table III), as the MRSDCI method gives the most reliable energy separations of the various electronic states and predict the EAs of the Nb_n ($n = 4, 5$) clusters very accurately (Table X).

The PES³ of Nb_4^- has four intense peaks at 1.15, 1.6, 2.0, and 3.0 eV respectively (Table I). The first intense peak corresponds to the electron affinity of Nb_4 . Our MRSDCI results assign the formation of this peak from the $^2\text{B}_{3g}$ state of Nb_4^- (Table VI) to the ground state of Nb_4 ($^1\text{A}'$) through electron detachment. The feasibility of this process has already been discussed in section III Ca. The calculation of the EA of Nb_4 (section III Eb) would further justify this assignment. The first low-lying excited state is 0.45 eV above the ground state. On the basis of the MRSDCI ΔE (Table I), the $^1\text{A}_g$ state ($\Delta E = 0.67$ eV) is a possible candidate for this state. The third intense peak in the PES is at 0.85 eV relative to the ground state of Nb_4 . The possible candidate for this peak is $^3\text{B}_{3u}$ ($\Delta E = 0.82$ eV, Table I). The fourth intense peak is at an energy separation of 1.75 eV from the ground state and according to our MRSDCI results, the $^5\text{A}'$ ($\Delta E = 1.44$ eV) and $^5\text{B}_{1g}$ ($\Delta E = 1.40$ eV) are suitable candidates for this state. This peak is actually broad at 1.85 eV, where we find a cluster of electronic states. According to our MRSDCI results the $^5\text{A}''$

($\Delta E = 1.84$ eV), ${}^3B_{1g}$ ($\Delta E = 1.88$ eV), and ${}^5B_{3g}$ ($\Delta E = 1.88$ eV) states are likely candidates for this peak.

There is a weak peak at 2.5 eV in the PES, which suggests a state at 1.35 eV from the ground state. According to our MRSDCI calculation, four electronic states of Nb₄ [${}^1A''$ ($\Delta E = 1.08$ eV), ${}^3B_{2u}$ ($\Delta E = 1.12$ eV), ${}^1B_{2g}$ ($\Delta E = 1.22$ eV), and ${}^3A'$ ($\Delta E = 1.28$ eV)] lie in this region. Finally, there is another peak at the higher energy range (3.4 eV peak) in the PES, which corresponds to an electronic state with an energy separation of 2.25 eV. Three electronic states viz., ${}^1B_{1g}$ ($\Delta E = 1.99$ eV), ${}^1B_{2u}$ ($\Delta E = 2.23$ eV), and ${}^3A''$ ($\Delta E = 2.24$ eV) are probable candidates for this peak.

The PES³ of Nb₅⁻ has three intense peaks at 1.65, 2.4, and 3.2 eV respectively (Table III). The first intense peak corresponds to the electron affinity of Nb₅. Our MRSDCI results assign the formation of this peak to originate from the 1A_1 (DTB) state of Nb₅⁻ (Table VIII) to the ground state of Nb₅ (2A_2 , DTB) through electron detachment. We have already discussed in section IIICb that out of the two competing ground states for Nb₅⁻ (3B_1 and 1A_1 , Table VIII), the formation of the 2A_2 state of Nb₅ is more feasible from the 1A_1 state of Nb₅⁻. The calculation of the EA of Nb₅ (section IIIEc) would further justify this assignment. The first low-lying excited state is 0.35 eV from the ground state and this appears as a shoulder on the first intense peak in the PES (at 2.0 eV region). According to the MRSDCI ΔE values (Table III), both the 4A_1 ($\Delta E = 0.41$ eV) and 4B_1 ($\Delta E = 0.43$ eV) states of the DTB structure are the possible candidates for this state. Apart from these two states, the ${}^2A''$ state of the DECT structure is also a probable candidate. Although the MRSDCI results ($\Delta E = 0.08$ eV) suggest that this may be a potential candidate for the ground state, the MRSDCI+Q results ($\Delta E = 0.31$ eV) place it

around the shoulder peak (2.0 eV region) of the PES. The second intense peak in the PES is at 0.75 eV energy from the ground state of Nb₅. The possible candidates for this peak are ⁴A₁ (DTP, ΔE = 0.73 eV), ²A₁ (DTB, ΔE = 0.87 eV), and ⁶B₂ (DTB, ΔE = 0.91 eV) (Table III). However ⁴A₁ (DTP) should be considered as a more probable candidate for this peak.

The third intense peak of the PES of Nb₅⁻ is at 3.2 eV³ (energy separation of 1.55 eV) with a shoulder at around 2.9 eV (separation 1.25 eV). The MRSDCI results (Table III) assign the ⁶A₁ (DTB, ΔE = 1.20 eV) and ⁶A₂ (DTP, ΔE = 1.25 eV) states as candidates for the shoulder peak at 2.9 eV. On the basis of our MRSDCI results, only ⁶B₁ state of the DTP structure (ΔE = 1.57 eV) could be assigned for the intense peak at 3.2 eV. Apart from these peaks in PES of Nb₅⁻, there lies a weak peak at 3.4 eV³ (energy separation of 1.75 eV). The MRSDCI results in Table III suggest that the ⁶A'' (DECT, ΔE = 1.78 eV), ⁴B₂ (DTP, ΔE = 1.69 eV), and the ²B₂ (DTP, ΔE = 1.74 eV) states are candidates for this peak. It is to be noted that the excitation energies of the observed PES are vertical in nature. In view of the uncertainty in the measurement of peak positions, our assignment of the spectra at the MRSDCI level is quite consistent.

G. The nature of bonding in Nb_n and Nb_n⁻ (n = 4, 5): Electronic configurations, orbital composition and Mulliken populations.

The leading configurations of the low-lying electronic states of Nb_n and Nb_n⁻ (n = 4, 5) at the CASMCSCF/MRSDCI level reveal their multireference characters. Most of the electronic states of these clusters have less than 80% contributions from the leading configurations. However, for most of the electronic states the dominant configurations at the CASMCSCF/MRSDCI level are the same as those at the DFT/B3LYP level. Thus the

calculated geometries and the energy separations at both the levels are similar. The correlation effects originating due to multireference nature of the wavefunctions in the CASMCSCF/MRSDCI calculations are different than those of the DFT/B3LYP level. Thus in most of the cases some differences are observed in the geometric and energetic features of different electronic states at these two levels. In few cases this difference is quite appreciable. One such case is the difference in the geometry and the observed energy separation between the two *Jahn-Teller* components, ${}^1A'$ and ${}^1A''$ states of Nb_4 at the CASMCSCF/MRSDCI and DFT/B3LYP levels. The origin of these differences has been attributed to the multireference characters of these two states and has already been discussed in details (section IIIB). The other interesting differences, which are originating due to multireference nature of these electronic states, have been discussed in the sections IIIA and IIIC.

a. Nb_4 and Nb_4^- : The leading electronic configuration of the ${}^1A'$ ground state of Nb_4 (Table I) is $1a'^2 \dots 17a'^2 1a''^2 \dots 9a''^2$ (69%). The higher energy *Jahn-Teller* component of this electronic state (${}^1A''$) is actually formed through excitation of the electron from the doubly occupied a' orbital of the ${}^1A'$ ground state to the lowest vacant a'' orbital [$1a'^2 \dots 16a'^2 17a'^1 1a''^2 \dots 9a''^2 10a''^1$ (67%)]. The first low-lying excited state (1A_g) has also a closed shell structure and has the $1a_g^2 \dots 7a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 1b_{3g}^2 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2$ (43%) dominant configuration. It has already been discussed in section IIIC that the ground state ${}^3B_{3g}$ of Nb_4^- generates the ${}^1A'$ state through electron detachment. Although the 1A_g state is highly stabilized through electron correlation effects (section IIIA), the electron detachment of the ${}^3B_{3g}$

state of Nb_4^- does not lead to the 1A_g state of Nb_4 . Thus the ${}^1A'$ state is stabilized over the 1A_g state by electron correlation effects.

The next low-lying electronic state of Nb_4 (${}^3B_{3u}$) is formed by the excitation of the electron of the doubly occupied a_u orbital of the 1A_g state to the vacant b_{3g} orbital [$1a_g^2 \dots 7a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 1b_{3g}^2 2b_{3g}^1 1b_{3u}^2 \dots 5b_{3u}^2 \quad 1b_{2g}^2 \quad 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^1$ (66%)]. Thus ${}^3B_{3u}$ is slightly higher ($\Delta E = 0.82$ eV) than the 1A_g state. The ${}^2B_{2u}$ is the excited state of ${}^3B_{3u}$ ($\Delta E = 1.12$ eV) and is formed by a double excitation of electrons from the a_g and b_{2u} orbitals to the a_u and b_{3g} orbitals [$1a_g^2 \dots 6a_g^2 7a_g^1 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 3b_{2u}^2 4b_{2u}^1 1b_{3g}^2 2b_{3g}^2 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2$ (58%)]. The ${}^1B_{2g}$ excited state is formed from the ${}^3B_{3u}$ state by excitation of an electron of the doubly occupied b_{1g} orbital to the singly occupied a_u orbital [$1a_g^2 \dots 7a_g^2 \quad 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 \quad 1b_{3g}^2 \quad 2b_{3g}^1 \quad 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^1 1a_u^2$ (58%)], while the ${}^1B_{2u}$ state is formed from the ${}^3B_{2u}$ state by a double excitation of electrons from the b_{1u} and b_{3g} orbitals to the a_g and b_{2u} orbitals [$1a_g^2 \dots 7a_g^2 1b_{1u}^2 2b_{1u}^2 \quad 3b_{1u}^1 \quad 1b_{2u}^2 \quad \dots 3b_{2u}^2 4b_{2u}^2 1b_{3g}^2 2b_{3g}^1 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2$ (41%)].

The leading configuration of the ground state of Nb_4^- (${}^2B_{3g}$) is $1a_g^2 \dots 7a_g^2 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 1b_{3g}^2 2b_{3g}^1 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2$ (73%). The first low-lying excited state (${}^4B_{1u}$) is formed from the ${}^2B_{3g}$ ground state by the excitation of the electron of the doubly occupied a_g orbital to the vacant b_{2u} orbital [$1a_g^2 \dots 6a_g^2 7a_g^1 1b_{1u}^2 \dots 3b_{1u}^2 1b_{2u}^2 \dots 4b_{2u}^2 5b_{2u}^1 1b_{3g}^2 2b_{3g}^1 1b_{3u}^2 \dots 5b_{3u}^2 1b_{2g}^2 2b_{2g}^2 1b_{1g}^2 \dots 3b_{1g}^2 1a_u^2$ (76%)]. The ${}^2A'$ and ${}^2A''$ states of the C_s structure are higher energy states and are nearly degenerate. Both the states are highly multireference in character [${}^2A'$: $45\%|1a'^2 \dots 16a'^2 17a'^1 1a''^2 \dots 10a''^2\rangle + 16\%|1a'^2 \dots 16a'^2 17a'^1 1a''^2 \dots 9a''^2 10a''^1 11a''^1\rangle + \dots$; ${}^2A''$: $53\%|1a'^2 \dots 17a'^2 1a''^2$

... $9a''^2 10a''^1 > + 19\% |1a'^2 \dots 16a' 1a''^2 \dots 10a''^2 11a''^1 > + \dots$]. The two states are nearly degenerate due to the counterbalancing electron correlation effects from the two leading configurations contributing to these states. The relative stabilities of all the low-lying electronic states of Nb₄ and Nb₄⁻ could be similarly explained from the properties of their leading electronic configurations.

b. Nb₅ and Nb₅⁻: The leading configuration of the ground state of the Nb₅ cluster (²A₂, DTB, Table III) is $1a_1^2 \dots 13a_1^2 1b_2^2 \dots 9b_2^2 1b_1^2 \dots 7b_1^2 1a_2^2 \dots 3a_2^2 4a_2^1$ (66%). The first two low-lying excited states ⁴A₁ (DTB) [$1a_1^2 \dots 13a_1^2 1b_2^2 \dots 8b_2^2 9b_2^1 1b_1^2 \dots 7b_1^2 8b_1^1 1a_2^2 \dots 3a_2^2 4a_2^1$ (67%)] and ⁴B₁ (DTB) [$1a_1^2 \dots 13a_1^2 14a_1^1 1b_2^2 \dots 8b_2^2 9b_2^1 1b_1^2 \dots 7b_1^2 1a_2^2 \dots 3a_2^2 4a_2^1$ (66%)] are formed from the ²A₂ (DTB) ground state through the excitation of the $9b_2$ electron into the vacant $8b_1$ orbital (⁴A₁) or the $14a_1$ (⁴B₁) orbital. Thus these two low-lying states are almost degenerate. The next higher electronic state ²A₁ (DTB) is also an excited state of the ²A₂ ground state. This state is formed from the excitation of the doubly occupied $13a_1$ orbital of the ground state into the $4a_2$ singly occupied orbital [$1a_1^2 \dots 12a_1^2 13a_1^1 1b_2^2 \dots 9b_2^2 1b_1^2 \dots 7b_1^2 1a_2^2 \dots 4a_2^2$ (69%)].

The ⁴A₁ and ⁴B₂ electronic states of the DTP structure are Jahn-Teller components with the ⁴B₂ state being higher ($\Delta E = 1.69$ eV, Table III). The leading configuration of the ⁴B₂ state is $1a_1^2 \dots 13a_1^2 14a_1^1 1b_2^2 \dots 8b_2^2 1b_1^2 \dots 7b_1^2 8b_1^1 1a_2^2 \dots 3a_2^2 4a_2^1$ (64%). It is formed from the ⁴A₁ state [$1a_1^2 \dots 13a_1^2 1b_2^2 \dots 8b_2^2 9b_2^1 1b_1^2 \dots 7b_1^2 8b_1^1 1a_2^2 \dots 3a_2^2 4a_2^1$ (66%)] by promoting a $9b_2$ electron into the vacant $14a_1$ orbital. The lowest energy electronic state of the DECT structure is ²A'' [$\Delta E = 0.08$ eV, $1a'^2 \dots 21a'^2 1a''^2 \dots 11a''^2 12a''^1$ (69%)]. The ²A' electronic state [$\Delta E = 1.06$ eV,

$1a'^2 \dots 20a'^2 21a'^1 1a''^2 \dots 12a''^2$ (67%) is formed from the ${}^2A''$ state through excitation of the doubly occupied a' orbital into the singly occupied $12a''$ orbital.

The Nb_5^- cluster has two nearly degenerate ground states, 3B_1 and 1A_1 (Table VIII) of the DTB structure. We have discussed in section IIIC that the 1A_1 state is the more favored ground state at higher levels. The first low-lying 1B_1 excited state (DTB) has a similar leading configuration [$1a_1'^2 \dots 14a_1'^2 1b_2'^2 \dots 8b_2'^2 9b_2'^1 1b_1'^2 \dots 7b_1'^2 1a_2'^2 \dots 3a_2'^2 4a_2'^1$ (45%)] to the 3B_1 state. The only difference is that the 3B_1 state has more α electrons in the b_2 and a_2 orbitals ($9b_2'^1 4a_2'^1$). Thus the 3B_1 state acquires enhanced stability owing to maximization of spin exchange energy (Hund's rule). The 3A_2 ($\Delta E = 0.19$ eV) and the 3B_2 ($\Delta E = 0.19$ eV) states are excited states. The 3A_2 (DTB) state [$1a_1'^2 \dots 13a_1'^2 14a_1'^1 1b_2'^2 \dots 9b_2'^2 1b_1'^2 \dots 7b_1'^2 1a_2'^2 \dots 3a_2'^2 4a_2'^1$ (36%)] and the 3B_2 state (DTB) [$1a_1'^2 \dots 13a_1'^2 14a_1'^1 1b_2'^2 \dots 8b_2'^2 9b_2'^1 1b_1'^2 \dots 7b_1'^2 1a_2'^2 \dots 4a_2'^2$ (72%)] are formed from the 3B_1 state by the excitation of electron of the doubly occupied $14a_1$ orbital into singly occupied $9b_2$ (3A_2) or $4a_2$ (3B_2) orbitals. In fact, the 3B_1 and 3A_2 states are the results of Jahn-Teller distortion, and the 3A_2 state is the higher energy component. The energy ordering of the rest of the electronic states of Nb_5 and Nb_5^- clusters could be similarly explained from their leading electronic configurations.

c. Orbital compositions: The compositions of the natural orbitals in the MRSDCI wave function of the ground ${}^1A'$ (C_s) and the first excited 1A_g (D_{2h}) electronic states of Nb_4 are qualitatively represented below. Only a few representative orbitals are expanded in this manner. Fig.2 shows the pictures of a few selected active space orbitals of these electronic states presented below.

Nb₄ (¹A'):

$$\psi(15a') = (\text{Nb}_1 + \text{Nb}_2 - \text{Nb}_3) (5s) - (\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3) (5p_y) + (\text{Nb}_2 + \text{Nb}_2 + \text{Nb}_4) (5p_x + 4d_{x^2+y^2-2z^2}) + (\text{Nb}_1 - \text{Nb}_2) (5p_z) - (\text{Nb}_1 + \text{Nb}_2 - \text{Nb}_4) (4d_{xy}) + (\text{Nb}_3) (4d_{x^2-y^2})$$

$$\psi(16a') = -(\text{Nb}_1 + \text{Nb}_2) (5s + 4d_{x^2+y^2-2z^2}) + (\text{Nb}_1 - \text{Nb}_2) (5p_z - 4d_{xz} + 4d_{yz}) - (\text{Nb}_4) (4d_{x^2+y^2-2z^2})$$

$$\psi(17a') = -(\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3) (4d_{x^2+y^2-2z^2}) - (\text{Nb}_1 - \text{Nb}_2) (4d_{xy}) + (\text{Nb}_1 - \text{Nb}_2) (4d_{xz} + 4d_{yz}) + (\text{Nb}_4) (5p_x)$$

$$\psi(7a'') = -(\text{Nb}_1 - \text{Nb}_2) (5s + 5p_x - 5p_y - 4d_{x^2+y^2-2z^2}) - (\text{Nb}_1 + \text{Nb}_2) (5p_z) + (\text{Nb}_3 + \text{Nb}_4) (4d_{xz}) - \text{Nb}_3 (4d_{yz})$$

$$\psi(8a'') = (\text{Nb}_1 - \text{Nb}_2) (4d_{x^2+y^2-2z^2} + 4d_{xy}) - (\text{Nb}_3 - \text{Nb}_4) (4d_{xz} - 4d_{yz}) + (\text{Nb}_4) (5p_z)$$

$$\psi(9a'') = (\text{Nb}_1 + \text{Nb}_2) (5p_z) + (\text{Nb}_1 - \text{Nb}_2) (4d_{xy}) + (\text{Nb}_3) (4d_{xz}) + (\text{Nb}_3 - \text{Nb}_4) (4d_{yz})$$

Nb₄ (¹A_g):

$$\psi(6a_g) = -(\text{Nb}_1 - \text{Nb}_2) (5p_y) + (\text{Nb}_3 + \text{Nb}_4) (5s) - (\text{Nb}_3 - \text{Nb}_4) (5p_x) + (\text{Nb}_1 + \text{Nb}_2 - \text{Nb}_3 - \text{Nb}_4) (4d_{x^2-y^2})$$

$$\psi(7a_g) = (\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3 + \text{Nb}_4) (5p_z) + (\text{Nb}_1 - \text{Nb}_2) (4d_{yz}) + (\text{Nb}_3 - \text{Nb}_4) (4d_{xz})$$

$$\psi(3b_{1u}) = (\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3 + \text{Nb}_4) (5s - 4d_{x^2+y^2-2z^2}) - (\text{Nb}_3 - \text{Nb}_4) (5p_x)$$

$$\psi(4b_{2u}) = (\text{Nb}_1 - \text{Nb}_2) (5s + 4d_{x^2+y^2-2z^2}) - (\text{Nb}_3 + \text{Nb}_4) (5p_y) - (\text{Nb}_3 - \text{Nb}_4) (4d_{xy})$$

$$\psi(4b_{3u}) = (\text{Nb}_1 + \text{Nb}_2 - \text{Nb}_3 - \text{Nb}_4) (5p_x) + (\text{Nb}_1 - \text{Nb}_2) (4d_{xy}) - (\text{Nb}_3 - \text{Nb}_4) (5s + 4d_{x^2+y^2-2z^2})$$

$$\psi(2b_{2g}) = -(\text{Nb}_1 + \text{Nb}_2 - \text{Nb}_3 - \text{Nb}_4) (4d_{xz}) + (\text{Nb}_3 - \text{Nb}_4) (5p_z)$$

$$\psi(3b_{1g}) = -(\text{Nb}_1 + \text{Nb}_2) (5p_x) - (\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3 + \text{Nb}_4) (4d_{xy}) - (\text{Nb}_3 - \text{Nb}_4) (5p_y)$$

$$\psi(1a_u) = -(\text{Nb}_1 + \text{Nb}_2) (4d_{xz}) - (\text{Nb}_3 - \text{Nb}_4) (4d_{yz})$$

As can be seen from above, considerable 5s-4d overlap is observed in most of the orbitals presented here except for the $1a_u$ orbital (1A_g), which is composed of pure d orbitals. The orbital compositions further reveal that there is considerable p orbital mixings in the most of the orbitals presented for the $^1A'$ and 1A_g electronic states of Nb_4 . The compositions thus indicate that apart from the σ orbital interaction, there is considerable π overlap between the Nb atoms in these orbitals. Thus it could be expected that there would be considerable s and p electron donation and back donation between the atoms to facilitate Nb-Nb bonding.

The natural orbital compositions of a few representative orbitals (at the MRSDCI level) of the 2A_2 (DTB) ground state and the low-lying $^2A''$ are shown below together with the pictures of the $13a_1$, $9b_2$, $7b_1$, $4a_2$ (2A_2), $21a'$, and $12a''$ in Fig.3. These compositions also show a similar Nb-Nb bonding trend.

Nb₅ (DTB, 2A_2):

$$\begin{aligned} \psi(12a_1) = & -(\text{Nb}_1) (4d_{x^2-y^2}) + (\text{Nb}_2 + \text{Nb}_3) (5s) - (\text{Nb}_2 - \text{Nb}_3) (5p_x) + (\text{Nb}_2 + \text{Nb}_3 + \text{Nb}_4 \\ & + \text{Nb}_5) (4d_{x^2+y^2-2z^2}) - (\text{Nb}_4 - \text{Nb}_5) (4d_{yz}) \end{aligned}$$

$$\begin{aligned} \psi(13a_1) = & (\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3 - \text{Nb}_4 - \text{Nb}_5) (5s) - (\text{Nb}_1) (4d_{x^2-y^2}) - (\text{Nb}_2 + \text{Nb}_3) \\ & (4d_{x^2+y^2-2z^2}) - (\text{Nb}_2 - \text{Nb}_3 - \text{Nb}_4 + \text{Nb}_5) (4d_{yz}) - (\text{Nb}_4 - \text{Nb}_5) (5p_y) \end{aligned}$$

$$\begin{aligned} \psi(8b_2) = & -(\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3 + \text{Nb}_4 + \text{Nb}_5) (5p_y) - (\text{Nb}_2 - \text{Nb}_3) (4d_{xy}) + (\text{Nb}_4 - \text{Nb}_5) \\ & (5s + 4d_{x^2+y^2-2z^2}) + (\text{Nb}_4 + \text{Nb}_5) (4d_{yz}) \end{aligned}$$

$$\begin{aligned} \psi(9b_2) = & (\text{Nb}_1 - \text{Nb}_2 - \text{Nb}_3) (5p_y) - (\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3) (4d_{yz}) - (\text{Nb}_4 - \text{Nb}_5) \\ & (5s + 4d_{x^2+y^2-2z^2}) - (\text{Nb}_4 + \text{Nb}_5) (4d_{yz}) \end{aligned}$$

$$\psi(7b_1) = (\text{Nb}_1 - \text{Nb}_4 - \text{Nb}_5) (4d_{xz}) - (\text{Nb}_2 - \text{Nb}_3) (5s + 4d_{x^2+y^2-2z^2}) - (\text{Nb}_4 - \text{Nb}_5) (4d_{xy})$$

$$\psi(4a_2) = (\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3 + \text{Nb}_4 + \text{Nb}_5) (4d_{xy}) - (\text{Nb}_2 - \text{Nb}_3) (5p_y) + (\text{Nb}_4 + \text{Nb}_5) (5p_x + 4d_{xz})$$

Nb₅ (DECT, ²A''):

$$\psi(21a_1) = - (\text{Nb}_1 + \text{Nb}_5) (5s + 4d_{x^2+y^2-2z^2} - 4d_{xy})$$

$$\psi(12a_1) = - (\text{Nb}_1 + \text{Nb}_2 + \text{Nb}_3) (5p_z) - (\text{Nb}_2 - \text{Nb}_3) (5s - 5p_y) + (\text{Nb}_4 + \text{Nb}_5) (4d_{yz}) + (\text{Nb}_5) (4d_{xz})$$

The orbital compositions seem to influence the relative stabilities of the various electronic states. It has already been found that the D_e values of Nb_n ($n = 4, 5$) clusters are quite high and it is almost close to the Nb_n^+ ($n = 4, 5$) clusters (Table X). The $4d^45s^1$ ground state configuration of the Nb atom indicates that the principal bonding features of Nb_3 are governed by the s - s and d - d overlaps. This is supported by the orbital compositions of the Nb_4 and Nb_5 clusters as discussed in this section. The $5s$ orbital has four radial nodes compared to one of the $4d$ orbital. These characteristics of the $5s$ orbital together with the relativistic mass-velocity effect^{40,41} allow it to penetrate the core more than the $4d$ orbital. The Mulliken populations (section III Fd) reveal that the $5s$ and $4d$ orbitals involve substantial exchange of electrons with the $5p$ orbitals. In the case of the ¹A' electronic state of Nb_4 , the total s and d orbital populations are 12.49 and 15.36 respectively (see, section III Fd). Considering the total population of $4s$ for all 4 atoms to be 8, the total $5s$ population of ¹A' is 4.49 (gain of electron 0.49e). The total $4d$ orbital population for all four Nb atoms is smaller (loss of 0.64e) than the total number of electrons (16). This suggests that the exchange of electron density with the $5p$ orbital results in Nb-Nb bonds that are not purely σ type. Similar conclusions could be deduced

from the Mulliken population results on the ground state (2A_2) of Nb₅ (Section III Gd). The penetration of the 5s orbital into the core leads to the possibility of substantial *d-d* overlap. The orbital compositions of Nb₄ and Nb₅ reveal that there is substantial π overlap of the 4*d* and 5*p* orbitals. These π overlaps facilitate the formation of multiple bonds between the Nb atoms and shortening of the Nb-Nb bonds. The average Nb-Nb bonding distances in the ground state of Nb₄ (${}^1A'$) and Nb₅ (2A_2) are 2.59 Å, and 2.65 Å respectively. When compared with the covalent radius of Nb atom (1.34 Å), these average bond lengths show that the Nb-Nb bonds are actually shortened, and they correlate well with the observed dissociation energy of Nb₄ and Nb₅. These Nb–Nb bonding features could be analyzed more clearly through the Mulliken population analysis. The Mulliken population analysis is one of a number of choices to partition electron density. Although Mulliken populations are basis set dependent, it seems that for transition metal clusters, relative s, p and d populations in a given basis set provide considerable insight into the extent of hybridization, charge transfer and back transfer.

d. Mulliken Population: The Mulliken populations analyses considered here are derived from the MRSDCI natural orbitals of the different electronic states of the Nb_{*n*} and Nb_{*n*}[−] (*n* = 4, 5) clusters. The gross Mulliken populations show that the orbital populations of the different atoms of the ${}^1A'$ (C_s) state of Nb₄ are Nb_{1/2} ($4d^{3.89}5s^{0.91}5p^{0.06}$), Nb₃ ($4d^{3.77}5s^{1.32}5p^{0.10}$) and Nb₄ ($4d^{3.70}5s^{1.34}5p^{0.06}$). Here Nb₄ is the apex Nb atom while Nb_{1/2} and Nb₃ refers to the base Nb atoms of the pyramidal Nb₄ cluster (Fig. 1c). Throughout this section, we will refer to the symmetric Nb atoms of any cluster as Nb_{*i/j*} (*i, j* are integers). Considering the $4d^45s^1$ configuration of the Nb atom, these populations reveal that the 4*d* orbitals are electron deficient at both the apex and base Nb sites of Nb₄. The

5s orbitals of the Nb_{1/2} atoms are also electron deficient while the 5s orbitals of Nb₃ and Nb₄ orbitals have excess electrons. The 5p orbitals have also gained electronic charge relative to the neutral atoms. Thus an electron donation and back donation process is operative in the formation of the Nb–Nb bonds. It is to be noted further from the population data that the Nb_{1/2} atom is slightly positively charged (0.14e) while the Nb₃ (-0.19e) and Nb₄ (-0.10e) atoms are slightly negatively charged. Thus the Nb–Nb bond would be weakly polar. The calculated low dipole moment of the ¹A' state (μ = 0.87 D) also supports this fact.

The higher energy *Jahn-Teller* component of the ¹A' state of Nb₄ (¹A'', Table I) has a charge distribution pattern of Nb_{1/2}: 4d^{3.72}5s^{1.05}5p^{0.26}, Nb₃: 4d^{3.93}5s^{0.77}5p^{0.25}, Nb₄: 4d^{3.68} 5s^{1.21} 5p^{0.09}. The charges on the different orbitals of Nb atoms indicate that the charge transfer is similar to that of the ¹A' state. The only difference is that here, instead of the Nb_{1/2} atoms, the s orbital of the Nb₃ atom is losing electron. The net charges on the Nb atoms (Nb_{1/2}: -0.06e, Nb₃: 0.15e, Nb₄: -0.02e) and the dipole moment (0.83D) show that the Nb–Nb bonds are weakly polar. The populations of higher energy electronic states of the pyramidal (C_s) structure, viz., ³A' (Nb_{1/2}: 4d^{3.58}5s^{1.12}5p^{0.28}, Nb₃: 4d^{4.29}4s^{1.98}5s^{0.00}5p^{0.84}, Nb₄: 4d^{3.65}5s^{0.89}5p^{0.42}) and ⁵A' (Nb_{1/2}: 4d^{3.58}5s^{1.12}5p^{0.28}, Nb₃: 4d^{4.29}4s^{1.96}5s^{0.00}5p^{0.86}, Nb₄: 4d^{3.63}5s^{0.90}5p^{0.42}) reveal that the electron transfer process is similar to ¹A'' state. The only difference is that the s orbitals are more electron-deficient in these electronic states. Consequently, the Nb–Nb bonds of these electronic states are slightly more polar than those of the ¹A' and ¹A'' states. This effect, combined with the higher geometric distortions, makes the dipole moment of these two electronic states higher (³A': μ = 2.75 D, ⁵A': μ = 2.70 D).

The population data of the first low-lying excited state of Nb₄ (¹A_g, D_{2h}, Nb_{1/2}: 4d^{3.49}5s^{0.97}5p^{0.45}, Nb_{3/4}: 4d^{3.46}5s^{1.31}5p^{0.33}) shows that the 4*d* orbitals of the Nb atoms are electron deficient and the 5*p* orbitals have gained electron density. The *s* orbitals of the Nb_{1/2} atoms (Fig. 1a) are electron deficient, while these orbitals of Nb_{3/4} atoms have gained electrons. Thus the nature of Nb–Nb bonding is similar to that of the C_s structure. The net charges on the Nb atoms (Nb_{1/2}: 0.09e, Nb_{3/4}: 0.10e) show that the Nb-Nb bond is slightly more polar than the ¹A' ground state. This effect will, of course, not be reflected in the magnitude of the dipole moment (μ), as for all the electronic states of D_{2h} structure μ is zero by symmetry. The populations of the other low-lying electronic states of the D_{2h} structure (³B_{3u}: Nb_{1/2}: 4d^{3.44}5s^{1.06}5p^{0.39}, Nb_{3/4}: 4d^{3.41}5s^{1.40}5p^{0.30}, ³B_{2u}: Nb_{1/2}: 4d^{3.51}5s^{1.03}5p^{0.37}, Nb_{3/4}: 4d^{3.42}5s^{1.37}5p^{0.30}, ¹B_{2g}: Nb_{1/2}: 4d^{3.45}5s^{1.05}5p^{0.41}, Nb_{3/4}: 4d^{3.40}5s^{1.40}5p^{0.29}, and ⁵B_{1g}: Nb_{1/2}: 4d^{3.49}5s^{0.89}5p^{0.50}, Nb_{3/4}: 4d^{3.50}5s^{1.27}5p^{0.36}) show similar bonding characteristics of the Nb atoms.

The ground state of Nb₄⁻ (²B_{3g}, D_{2h}, Table VI) has the population Nb_{1/2}: 4d^{3.55}5s^{1.29}5p^{0.62}, Nb_{3/4}: 4d^{3.40}5s^{1.19}5p^{0.45}. The populations reveal that the net charges on the Nb_{1/2} and Nb_{3/4} are -0.46e and -0.04e respectively. This means that the excess electron density is localized on the Nb₁ and Nb₂ atoms. The low-lying ²B_{1u} state exhibits a similar charge distribution pattern (Nb_{1/2}: 4d^{3.63}5s^{1.11}5p^{0.68}, Nb_{3/4}: 4d^{3.57}5s^{1.10}5p^{0.41}). The low-lying excited states ⁴B_{2g} and ⁴B_{1u} have a different charge distribution patterns. The populations (⁴B_{2g}: Nb_{1/2}: 4d^{3.45}5s^{1.21}5p^{0.61}, Nb_{3/4}: 4d^{3.52}5s^{1.11}5p^{0.61}, ⁴B_{1u}: Nb_{1/2}: 4d^{3.46}5s^{1.16}5p^{0.64}, Nb_{3/4}: 4d^{3.39}5s^{1.34}5p^{0.51}) indicate that the excess electronic charges are evenly distributed over all the Nb atoms. The ²A' excited state population (Nb_{1/2}: 4d^{3.59}5s^{1.03}5p^{0.53}, Nb₃: 4d^{4.38}5s^{0.004}5p^{1.16}, Nb₄: 4d^{3.51}5s^{1.09}5p^{0.55}) of the C_s structure shows

that the excess electronic charge is more localized on the Nb₃ atom. The orbital populations of different electronic states further reveal that the Nb–Nb bonding properties of the anion are similar to those of the neutral cluster.

The population analyses presented above clearly show that there is considerable *5p*-orbital participation in the formation of the Nb-Nb bonds apart from the *5s-4d* mixings. The difference density plot of the ¹A' electronic state of Nb₄ (Fig. 4a and 4b) is consistent with this charge donation and back-donation scheme through orbital mixings. The contour map is drawn as the difference of Nb₄ charge densities with respect to the separated Nb atoms. The map clearly shows charge depletion near the *d* orbital regions and the enhancement of charge density around the *s* and *p* orbital regions of the Nb atoms. As a result of such orbital mixings, the Nb-Nb bonds would not be purely of σ type. There is also considerable π overlap (due to the *p*- and *d*-orbital participation) resulting in multiple bonds between the Nb atoms.

The populations of the ground state of Nb₅ (Table III) cluster (²A₂, DTB, Nb₁: 4d^{3.92} 5s^{0.98} 5p^{0.24}, Nb_{2/3}: 4d^{3.74} 5s^{1.18} 5p^{0.28}, Nb_{4/5}: 4d^{3.64} 5s^{0.97} 5p^{0.12}) reveal that the *d* orbitals of all the Nb atoms are electron deficient. The *5s* orbital of the Nb_{2/3} atoms (Fig. 1d) and all the *5p* orbitals have excess electrons, while the *5s* orbitals of Nb₁ and Nb_{4/5} are electron deficient. Analogous to the Nb₄ cluster, there is considerable electron donation and back donation during the formation of the Nb-Nb bonds. The net charges on the Nb atoms (Nb₁: -0.14e, Nb_{2/3}: -0.2e, and Nb_{4/5}: 0.27e) indicate that the Nb–Nb bonds are slightly polar. The low dipole moment (0.18 D) of this electronic state is not indicative of the low bond polarity, as the dipole moment of the DTB structure would be in general very low due to its symmetry. The first two low-lying excited states of the DTB structure,

4A_1 (Nb₁: $4d^{4.01}5s^{0.67}5p^{0.30}$, Nb_{2/3}: $4d^{3.68}5s^{1.22}5p^{0.24}$, Nb_{4/5}: $4d^{3.54}5s^{1.08}5p^{0.25}$, $\mu = 1.31$ D) and 4B_1 (Nb₁: $4d^{3.81}5s^{0.78}5p^{0.60}$, Nb_{2/3}: $4d^{3.39}5s^{1.22}5p^{0.28}$, Nb_{4/5}: $4d^{3.68}5s^{1.04}5p^{0.31}$, $\mu = 0.02$ D), have similar electron donation and back-donations. The populations of the other low-lying excited states viz., 2A_1 (DTB, Nb₁: $4d^{3.83}5s^{1.10}5p^{0.30}$, Nb_{2/3}: $4d^{3.80}5s^{0.87}5p^{0.43}$, Nb_{4/5}: $4d^{3.65}5s^{0.95}5p^{0.18}$), 4A_1 (DTP, Nb₁: $4d^{3.72}5s^{0.89}5p^{0.48}$, Nb_{2/3}: $4d^{3.64}5s^{0.93}5p^{0.42}$, Nb_{4/5}: $4d^{3.65}5s^{1.07}5p^{0.25}$), and $^2A''$ (DECT, C_s: Nb₁: $4d^{3.32}5s^{1.29}4p^{0.05}$, Nb_{2/3}: $4d^{3.56}5s^{1.04}5p^{0.55}$, Nb₄: $4d^{3.45}5s^{1.25}5p^{0.23}$, Nb₄: $4d^{3.49}5s^{1.28}5p^{0.25}$), reveal that the bonding characteristics are similar to those of ground electronic states (2A_2 , DTB).

The charge distribution pattern of the 3B_1 (DTB) ground state of the Nb₅⁻ (Table VIII)) is Nb₁: $4d^{3.92}5s^{0.47}5p^{0.80}$, Nb_{2/3}: $4d^{3.38}5s^{1.18}5p^{0.60}$, Nb_{4/5}: $4d^{3.86}5s^{0.87}5p^{0.51}$. The results indicate that the Nb–Nb bond is formed through exchange of electronic density between the *5s*, *4d*, and *5p* orbitals, where the *4d* and *5s* (except Nb_{2/3}) orbitals shed electronic charge, while *5p* gains electronic density. The involvement of the *5p* orbitals further shows that the Nb-Nb bonds have some π character. The calculated net charges on the different Nb atoms (Nb₁: -0.19e, Nb_{2/3}: -0.16e, Nb_{4/5}: -0.24e) indicate that the excess electronic charge in this electronic state is more or less evenly distributed over the Nb atoms. The low-lying excited states 1B_1 (DTB, Nb₁: $4d^{3.89}5s^{0.49}5p^{0.82}$, Nb_{2/3}: $4d^{3.38}5s^{1.17}5p^{0.60}$, Nb_{4/5}: $4d^{3.86}5s^{0.87}5p^{0.51}$), and the competitive ground state 1A_1 (DTB, Nb₁: $4d^{4.25}5s^{0.71}5p^{0.60}$, Nb_{2/3}: $4d^{3.53}5s^{1.28}5p^{0.44}$, Nb_{4/5}: $4d^{3.85}5s^{0.64}5p^{0.46}$) have similar bonding characteristics with respect to the 3B_1 state. In the case of the 1A_1 state the net charges on the Nb atoms (Nb₁: -0.56e, Nb_{2/3}: -0.25e, Nb_{4/5}: 0.03e) indicate that the excess charge is mostly localized on the Nb₁, and Nb_{2/3} atoms. The slightly higher excited states 3A_2 (DTB, Nb₁: $4d^{3.83}5s^{0.73}5p^{0.81}$, Nb_{2/3}: $4d^{3.40}5s^{1.19}5p^{0.56}$, Nb_{4/5}: $4d^{3.83}5s^{0.90}5p^{0.45}$),

and ${}^3A''$ (DECT, Nb₁: $4d^{3.62}5s^{0.79}5p^{0.77}$, Nb_{2/3}: $4d^{3.51}5s^{0.83}5p^{0.76}$, Nb₄: $4d^{3.56}5s^{1.11}5p^{0.41}$, Nb₄: $4d^{3.41}5s^{1.40}5p^{0.74}$) have similar charge localization properties.

The orbital populations of Nb₅ and Nb₅⁻ clusters on their different electronic states establish that like Nb₄ and Nb₄⁻ clusters, the Nb-Nb bonding involves the electron donation and back-donation. The $4d$ orbitals of the Nb atoms mostly lose electron density while the $5p$ orbitals gain electronic density. The $5s$ electrons are involved both in electronic gain and loss. These sharing of electrons are depicted in the difference density plots of the 2A_2 (DTB) state for the Nb₅ cluster (Fig. 5). The contour plots are drawn in a manner similar to those of the Nb₄ cluster i.e., by taking the density difference of Nb₅ with respect to the separated Nb atoms. The picture reveals the charge depletion regions (around s and d orbitals) of the Nb atom, while electron density gain is observed around the Nb p orbitals. The involvement of the p -orbitals in the electron exchange indicates the Nb atoms exhibit multiple bonds.

IV. CONCLUSIONS

Large-scale CASMCSCF, MRSDCI as well as DFT/B3LYP calculations have been carried out on the different electronic states of Nb_{*n*} and Nb_{*n*}⁻ ($n = 4, 5$). We have predicted the geometric and electronic properties of the low-lying electronic states of these clusters that assisted to interpret the observed in the PES³ of Nb_{*n*}⁻. The electronic states of the Nb₄ and Nb₄⁻ clusters have been studied for the tetragonal (both C_{2v} and D_{2h} type) and pyramidal (C_s) structures. The electronic states of the Nb₅ and Nb₅⁻ have been studied for the various geometrical arrangements. They include regular and distorted

trigonal bipyramid, regular and distorted tetragonal pyramid, and edge-capped tetrahedron. The studies have expounded on the Nb–Nb bonding characteristics and have revealed considerable involvement of both the $5s$ and $4d$ orbitals together with the $5p$ orbital of the Nb atom in the bond. The current study has not only aided understanding of the experimental findings on the PES³ of Nb_n^- ($n = 4, 5$), but also predicted properties such as EA, IP and D_e of Nb_n ($n = 4, 5$), which compare very well with the available experimental^{5,6,39} data. This gives confidence to our findings on the geometric and electronic properties of the different electronic states of Nb_n and Nb_n^- ($n = 4, 5$).

The CASMCSF/MRSDCI energy calculations and the analysis of the electronic configurations have shown that the ground ($^1A'$, C_s) and the low-lying electronic states of Nb_4 exhibit $T \otimes e$ *Jahn-Teller*²³ distortion. Although our present DFT/B3LYP calculations and the earlier DFT calculations¹⁷ agree on the energy ordering of the low-lying electronic states of Nb_4 , the Jahn-Teller effect of the ($^1A'$) electronic states of Nb_4 could not be explained through this method. The DFT/B3LYP method calculates the E state of the T_d structure as a higher root and thus fails to yield proper *Jahn-Teller* description of the electronic states. For the D_{2h} structure, of course, both the DFT/B3LYP and CASMCSF/MRSDCI results agree on the $E \otimes b_1$ type *Jahn-Teller* distortion²³ of the B_{2u} , B_{3u} , B_{3g} , and B_{2g} states.

The ground state of the Nb_5 (2A_2 , DTB) cluster has been found to undergo $E \otimes e$ *Jahn-Teller*²³ distortion. Both the CASMCSF/MRSDCI and DFT/B3LYP calculations support such a distortion. The only difference is that, while the DFT/B3LYP method predicts the energy separations of the two *Jahn-Teller* components, viz., 2A_2 and 2B_1 to be nearly degenerate ($\Delta E = 0.07$ eV), the CASMCSF/MRSDCI predicts the energy

separation of these two electronic states to be considerably higher ($\Delta E = 1.47$ eV). The CASMCSCF/MRSDCI method also predicts higher geometric distortion of the 2B_1 state. The present DFT/B3LYP and CASMCSCF/MRSDCI results are a bit different from the earlier DFT¹⁸ studies. The earlier DFT calculations predicted the ground state to be a doublet state with a trigonal bipyramid structure. Structural distortions were not predicted in the previous studies.

We have suggested tentative assignments of the observed PES³ of Nb_n^- ($n = 4, 5$) on the basis of our computed energy separations. Our CASMCSCF/MRSDCI results based on the ${}^1A'$ ground state (1.15 eV peak) of Nb_4 assign the first two strong peaks of the observed spectra at 1.6 eV and 2.0 eV as the 1A_g and the ${}^3B_{3u}$ states. The ${}^5A'$ (C_s) and ${}^5B_{1g}$ (D_{2h}) states have been assigned for the peak at 2.9 eV. This peak is actually very broad (extending beyond 3.0 eV). Three different electronic states viz., ${}^5A''$, ${}^3B_{1g}$, and ${}^5B_{3g}$ could be assigned to this peak. Two weak peaks of Nb_4^- at 2.5 and 3.4 eV were assigned tentatively to the ${}^1A''$, ${}^3B_{2u}$, ${}^1B_{1g}$, ${}^3A'$ (for 2.5 eV), ${}^1B_{1g}$, ${}^1B_{2u}$ and ${}^3A''$ (for 3.4 eV).

The PES³ of Nb_5^- has three peaks at 1.65, 2.4 (with a shoulder at 2.0 eV) and 3.2 eV. On the basis of the CASMCSCF/MRSDCI ground state of Nb_5 (2A_2 , DTB, 1.65 eV peak), the 2.0 eV shoulder peak has been assigned to the 4A_1 (DTB) and 4B_1 (DTB) states. The intense peak at 2.4 eV has been attributed to the 4A_1 (DTP), 2A_1 (DTB), and 6B_2 (DTB) states. According the MRSDCI+Q energy separation, the ${}^2A''$ (DECT) state is also a possible candidate for this peak. The 6B_1 (DTP) state has been assigned as the probable candidate for the peak at 3.2 eV. Apart from these intense peaks, the PES of Nb_5^- has a shoulder peak at 2.9 eV and a weak peak at 3.4 eV. The electronic states 6A_1

(DTB), 6A_2 (DTP) have been assigned for the shoulder peak (2.9 eV), while the ${}^6A''$ (DECT), 4B_2 (DTP), and 2B_2 (DTP) states are potential candidates for the 3.4 eV peak.

The PES³ predict the vertical EA of Nb₄ and Nb₅ as 1.15 eV and 1.65 eV respectively. The DFT/B3LYP and MRSDCI results predict the ground state of Nb₄⁻ as ${}^2A'$ (C_s) and ${}^2B_{3g}$ respectively. According to the CASMCSCF/MRSDCI calculations, the ground state of Nb₅⁻ has two competitive ground states (3B_1 , and 1A_1) for the DTB structure. The DFT/ B3LYP level of calculation also suggests two competitive ground states (1A_1 , and 3A_2 , DTB). Our calculated adiabatic EA values based on these ground states of Nb₄⁻ and Nb₅⁻ agree with the experimental results very well (Table X). The computed IP, D_e and the AE of the Nb₄ and Nb₅ clusters are all in excellent agreement with the experiment.^{5,6,39}

The dipole moments of the various low-lying electronic states of Nb₄ and Nb₅ suggest that these clusters are weakly polar in these states, consistent with their Mulliken populations. The orbital compositions, Mulliken populations and the difference density plots further suggest that there is considerable electron donation and back-donation in the formation of the Nb–Nb bonds in different electronic states. The involvement of the 5*p* orbitals of Nb in the Nb–Nb bonding indicates that there is considerable multiple-bond character and it imparts high stability to the Nb₄ and Nb₅ clusters. The calculated and the experimental D_e values of Nb₄ and Nb₅ are in agreement with this observation. The population analysis has also been carried out on the low-lying electronic states of Nb₄⁻ and Nb₅⁻ clusters. The results suggest that the bonding nature of these clusters in their ground and the low-lying electronic states are similar to their corresponding neutral clusters.

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TABLE I. Bond lengths (a, b, c...),^a and energy separations (ΔE) of the electronic states of Nb₄ at the CASMCSCF, MRSDCI, and MRSDCI+Q levels. The experimental ΔE values (peak positions) from the observed PES are included.

Structure	State	a	b	c	d	$\Delta E_{\text{CASMCSCF}}$	ΔE_{MRSDCI}	$\Delta E_{\text{MRSDCI+Q}}$	Expt. ΔE (peak position) ^{b,c}
		(Å)	(Å)	(Å)	(Å)	(eV)	(eV)	(eV)	(eV)
Pyramid (C _s)	¹ A'	2.713	2.483	2.601	2.568	0.10	0.00	0.00	0.0 (1.15)
	¹ A''	2.614	2.738	2.671	2.616	1.03	1.08	0.75	
	³ A'	2.454	3.283	3.169	2.498	0.00	1.28	1.60	
	⁵ A'	2.458	3.307	3.210	2.506	0.06	1.44	1.80	
	⁵ A''	2.446	3.331	3.234	2.647	0.47	1.84	2.12	
	³ A''	2.447	3.149	3.172	2.508	1.49	2.24	2.21	
Rhombus (D _{2h})	¹ A _g	2.507	2.847	4.128		0.69	0.67	0.64	0.45 (1.60)
	³ B _{3u}	2.410	2.771	3.943		1.03	0.82	0.87	0.85 (2.00)
	³ B _{2u}	2.433	2.747	4.017		1.20	1.12	1.19	1.35 (2.50 ^d)
	¹ B _{2g}	2.410	2.766	3.947		1.85	1.22	1.10	
	⁵ B _{1g}	2.556	2.969	4.161		0.85	1.40	1.47	1.75 (2.90) ^d
	³ B _{1g}	2.376	2.697	3.914		1.87	1.88	2.01	1.85 (3.00) ^d
	⁵ B _{3g}	2.500	2.858	4.103		2.00	1.88	1.92	
	⁵ B ₁	2.458	2.877	3.986		1.82	1.89	1.85	
	¹ B _{1g}	2.376	2.697	3.913		1.97	1.99	2.12	2.25 (3.40) ^d
	¹ B _{2u}	2.436	2.744	4.026		2.30	2.23	2.17	
	⁵ A _g	2.624	3.001	4.305		1.58	2.49	2.54	
	³ A _g	2.484	2.768	4.125		2.23	2.51	2.58	

^aRefer to Fig. 1 for the definition of the bond lengths (a, b, c...) of different structures.

^bRef. 3. ^cThe values within parentheses indicate the actual peak positions in the PES.

^dAlternate assignments are discussed in the text.

TABLE II. Bond lengths (a, b, c...),^a bond angles (θ), energy separations (ΔE), and vibrational frequencies (ν) of the electronic states of Nb₄ at the DFT/B3LYP level.

Structure	State	a	b	c	d	θ (Deg.)	ΔE (eV)	ν (cm ⁻¹)
		(Å)	(Å)	(Å)	(Å)			
Pyramid (C _s)	¹ A' (T _d) ^b	2.538	2.538	2.538	2.538		0.00	162, 162, 253, 253, 253, 373
	³ A'	2.495	2.884	2.495	2.555		0.46	88, 142, 217, 227, 245, 364
	¹ A''	2.497	2.822	2.497	2.551		0.68	-63, 139, 204, 228, 233, 365
Rhombus (D _{2h})	¹ A _u	2.370	2.693	3.900			0.97	81, 136, 199, 220, 273, 331
	³ A _g	2.389	2.690	3.948			1.09	-28, 137, 185, 194, 273, 324
	⁵ B _{2g}	2.413	2.785	3.941			1.52	97, 102, 188, 235, 259, 310
	³ B _{3u}	2.351	2.710	3.842			1.53	106, 158, 177, 218, 281, 335
	¹ A _g	2.344	2.705	3.830			1.71	-215, 191, 211, 254, 258, 331
	³ B _{1g}	2.736	2.405	3.955			2.49	130, 188, 219, 262, 296, 316
	³ B _{2u}	2.346	2.675	3.855			2.58	91, 159, 191, 257, 280, 340
	¹ B _{1g}	2.404	2.729	3.959			2.59	-85, 181, 229, 257, 303, 318
	¹ B _{2u}	2.350	2.676	3.863			2.61	91, 163, 168, 193, 273, 336
	⁵ A _g	2.444	2.720	4.060			2.68	-61, 165, 192, 222, 259, 310
	⁵ B _{3g}	2.442	2.772	4.021			3.00	67, 120, 166, 259, 299, 313
	¹ B _{2g}	2.424	2.837	3.930			3.19	-140, 189, 201, 217, 264, 298
	⁵ B _{3u}	2.455	2.743	4.074			3.45	182, 221, 242, 298, 391, 660
	⁵ B _{1g}	2.450	2.834	3.998			3.73	155, 212, 245, 264, 281, 289
	D ₂	³ A _u	2.374	2.696	3.909			4.75
⁵ A		2.473	2.841	2.473	2.841	70.1	1.00	133, 155, 192, 199, 200, 353
C _{2v}	¹ A	2.520	2.568	2.833	2.568	68.4	1.22	116, 146, 208, 236, 261, 354
	¹ B ₂	2.417	2.797	3.904		107.7	1.59	31, 183, 248, 251, 255, 296
	¹ A ₁	2.345	2.753	3.700		104.2	1.50	82, 149, 203, 259, 285, 324
	³ B ₁	2.405	2.952	3.491		93.1	1.56	60, 104, 143, 187, 238, 313
	³ B ₂	2.405	2.953	3.491		93.0	1.57	60, 104, 144, 187, 238, 313
	⁵ A ₁	2.429	3.114	3.114		79.7	1.58	-40, 67, 68, 124, 144, 333
	³ A ₁	2.383	2.932	3.539		95.9	1.92	97, 173, 200, 264, 299, 320
	⁵ A ₂	2.473	2.767	4.076		111.0	2.07	84, 95, 178, 204, 268, 303
	⁵ B ₂	2.398	3.144	3.282		81.9	2.12	127, 139, 165, 250, 272, 309

^aRefer to Fig. 1 for the definition of the bond lengths (a, b, c...) and bond angles (θ) of the different structures.

^bThe electronic state is actually ¹A₁ in T_d symmetry.

TABLE III. Bond lengths (a, b, c...),^a and energy separations (ΔE) of the electronic states of Nb₅ at the CASMCSCF, MRSDCI, and MRSDCI+Q levels. The experimental ΔE values(peak positions) from the observed PES are included for comparison.

Structure	State	a	b	c	d	e	f	$\Delta E_{\text{CASMCSCF}}$	ΔE_{MRSDCI}	$\Delta E_{\text{MRSDCI+Q}}$	Expt. ΔE (peak positions) ^{b,c}
		(Å)	(Å)	(Å)	(Å)	(Å)	(Å)	(eV)	(eV)	(eV)	(eV)
DTB (C _{2v})	² A ₂	2.661	2.617	2.663	2.661	4.359		0.21	0.00	0.00	0.00 (1.65)
	⁴ A ₁	2.556	2.654	2.662	2.775	4.583		0.36	0.41	0.63	0.35 (2.00) ^d
	⁴ B ₁	2.846	2.388	2.582	2.794	4.405		0.26	0.43	0.63	
	² A ₁	2.666	2.881	2.804	2.547	4.142		0.89	0.87	0.90	
	⁶ B ₂	2.507	2.513	2.784	2.791	4.765		1.17	0.91	1.20	
DECT (C _s)	⁶ A ₁	2.581	2.451	2.742	2.835	4.770		0.99	1.20	1.58	1.25 (2.90) ^d
	² A''	2.663	2.376	2.981	2.971	3.981	2.363	0.00	0.08	0.31	
	⁴ A''	2.489	3.040	3.055	2.803	3.985	2.398	0.90	1.04	1.37	
	² A'	3.001	2.373	2.845	3.234	4.265	2.415	0.01	1.06	1.42	
	⁶ A''	2.540	3.474	3.051	2.793	4.010	2.352	1.32	1.78	2.25	
DTP (C _{2v})	⁴ A'	2.927	2.588	2.870	3.177	4.243	2.426	1.16	2.12	2.42	
	⁶ A'	3.137	2.350	3.046	3.111	4.204	2.402	2.70	3.96	4.41	
	⁴ A ₁	2.878	2.788	2.554	2.921	4.125		1.08	0.73	0.70	0.75 (2.40) ^d
	⁶ A ₂	3.087	2.677	2.558	2.873	4.234		0.71	1.25	1.63	
	² B ₁	2.857	2.668	2.572	2.909	4.201		1.14	1.47	1.80	
	⁶ B ₁	2.967	2.511	2.647	3.015	4.352		1.21	1.57	1.85	1.55 (3.20)
	⁴ B ₂	3.085	2.656	2.545	2.833	4.229		1.75	1.69	1.77	1.75 (3.40) ^d
² B ₂	2.831	2.613	2.543	2.885	4.158		1.61	1.74	1.80		
⁴ A ₂	2.933	2.654	2.547	2.907	4.172		2.22	2.07	2.17		

^aRefer to Fig. 1 for the definition of the bond lengths (a, b, c...) of different structures.

^bFrom the PES of ref. 3. ^cThe values within parentheses indicate the actual peak position the PES.

^dThe alternate assignments of the peaks are discussed in the text.

TABLE IV. Bond lengths (a, b, c...),^a energy separations (ΔE), and vibrational frequencies (ν) of the electronic states of Nb₅ at the DFT/B3LYP level.

Structure	State	a	b	c	d	e	f	ΔE (eV)	ν (cm ⁻¹)
		(Å)	(Å)	(Å)	(Å)	(Å)	(Å)		
DTB (C _{2v})	² B ₁	2.644	2.899	2.641	2.512	3.988		0.0	54, 93, 116, 144, 202, 220, 260, 279, 345
	² A ₂	2.836	2.561	2.488	2.576	3.968		0.07	-138, 97, 118, 122, 182, 218, 264, 271, 346
	² A ₁	2.824	2.824	2.515	2.515	3.830		0.28	-165, -165, 87, 87, 201, 230, 230, 239, 338
	⁴ B ₁	2.946	2.386	2.447	2.666	4.012		0.85	-444, -340, -93, 121, 159, 203, 274, 285, 355
	⁴ A ₁	2.979	2.297	2.389	2.739	4.025		1.05	-74, 78, 145, 153, 186, 243, 269, 292, 376
	⁶ A ₁	2.906	2.365	2.413	2.716	4.069		1.25	-190, 90, 137, 153, 181, 237, 258, 351, 1857 (?)
DECT (C _s)	⁶ B ₂	2.916	2.412	2.397	2.680	3.996		1.44	52, 141, 145, 176, 261, 275, 340, 341, 368
	² A'	2.512	2.643	2.645	2.901	3.990	2.513	0.04	55, 95, 116, 144, 202, 220, 255, 280, 345
	⁴ A''	2.521	2.597	2.640	3.012	3.932	2.522	0.48	-121, 120, 137, 160, 198, 207, 213, 266, 332
	⁴ A'	2.570	2.515	2.568	2.995	4.048	2.480	0.88	-286, 113, 126, 128, 191, 213, 227, 255, 339
DTP (C _{2v})	⁶ A''	2.502	2.575	2.792	2.963	3.823	2.503	1.09	94, 103, 151, 157, 177, 200, 212, 266, 325
	² B ₂	2.785	2.550	2.516	2.926	4.077		0.42	-99, 128, 170, 172, 204, 219, 242, 248, 340
	² B ₁	2.746	2.532	2.530	3.005	4.053		0.94	-112, 126, 128, 172, 194, 214, 227, 235, 333
	⁴ A ₂	2.857	2.573	2.482	2.880	4.037		1.03	-96, 121, 188, 200, 209, 223, 240, 330, 409
	⁶ A ₂	2.692	2.553	2.587	2.869	4.216		1.07	-87, 68, 110, 121, 183, 192, 197, 209, 340
	⁶ B ₁	2.737	2.593	2.565	3.022	4.013		1.76	-127, 104, 114, 157, 177, 178, 209, 239, 330
	⁴ A ₁	2.696	2.513	2.611	3.015	4.212		1.98	-142, 57, 113, 158, 166, 183, 183, 211, 333
	⁴ B ₂	2.808	2.527	2.577	2.842	4.268		2.09	-87, 100, 108, 137, 144, 199, 207, 291, 325
² A ₂	2.707	2.502	2.589	3.022	4.169		3.46	-166, -102, 126, 166, 178, 189, 236, 335, 848	

^aRefer to Fig. 1 for the definition of the bond lengths (a, b, c...) of different structures.

TABLE V. Bond lengths (a, b, c,...)^a, relative energies (ΔE) of the $^1E'$, $^1A'$, and $^1A''$ states of Nb₄ (at the DFT/B3LYP and MRSDCI levels), and the $^2E''$, 2A_2 , and 2B_2 states of Nb₅ (DFT/B3LYP level).

Cluster	Method	State	a	b	c	d	e	ΔE
			(Å)	(Å)	(Å)	(Å)	(Å)	(eV)
Nb ₄	DFT/B3LYP	$^1A'$	2.538	2.538	2.538	2.538		0.00
		$^1A''$	2.497	2.822	2.497	2.551		0.68
		1E	2.566	2.566	2.566	2.566		2.50
	MRSDCI (MRSDCI+Q)	$^1A'$	2.713	2.483	2.601	2.568		0.00 (0.00)
		$^1A''$	2.614	2.738	2.671	2.616		1.08 (0.75)
		$^1E^b$	2.597	2.597	2.597	2.597		1.09 ^c (1.14) ^d 0.78 ^c (0.81) ^d
Nb ₅	DFT/B3LYP	2B_1	2.644	2.899	2.641	2.512	3.988	0.00
		2A_2	2.836	2.561	2.488	2.576	3.968	0.07
		$^2E''$	2.621	2.621	2.621	2.621	4.279	1.29

^aRefer to Fig. 1 for the definitions of a, b, c....

^bThe geometry of this state has been optimized at the MRSDCI level.

^c ΔE calculated from $^1A''$.

^d ΔE calculated from $^1A'$.

TABLE VI. Bond lengths (a, b, c...),^a and energy separations (ΔE) of the electronic states of Nb_4^- at the MRSDCI, and MRSDCI+Q levels. The optimized geometric parameters presented here are at the CASMCSCF level.

Structure	State	a	b	c	d	$\Delta E_{\text{MRSDCI}}^b$	$\Delta E_{\text{MRSDCI+Q}}^b$
		(Å)	(Å)	(Å)	(Å)	(eV)	(eV)
Rhombus (D_{2h})	$^2B_{3g}$	2.318	2.608	3.869		0.00 (0.00)	0.00 (0.00)
	$^4B_{1u}$	2.365	2.705	3.881		0.17 (0.42)	0.23 (0.50)
	$^4B_{2g}$	2.290	2.607	3.767		0.30 (0.28)	0.36 (0.31)
	$^2B_{1u}$	2.356	2.688	3.869		0.76 (0.62)	0.81 (0.72)
	4A_u	2.324	2.682	3.795		0.62 (1.02)	0.73 (1.12)
	$^2B_{1g}$	2.383	2.651	3.960		1.02 (1.14)	1.07 (1.19)
	$^2B_{3u}$	2.452	2.941	3.926		1.31 (1.85)	1.34 (1.77)
Pyramid (C_s)	$^2A''$	2.403	3.086	3.204	2.430	0.49 (1.57)	0.84 (2.02)
	$^2A'$	2.418	3.228	3.138	2.401	0.49 (1.60)	0.86 (2.09)
	$^4A'$	2.422	3.241	3.241	2.422	0.77 (1.82)	1.19 (2.33)
	$^4A''$	2.381	3.249	3.095	2.517	1.47 (2.50)	1.87 (3.03)

^aRefer to Fig. 1 for the definition of the bond lengths (a, b, c...) of different structures.

^bThe ΔE values within parentheses are calculated using (5s5p4d1f//5s3p2d1f) basis set while the ΔE values without parentheses were calculated using (5s5p4d//5s3p2d) basis set of Nb.

TABLE VII. Bond lengths (a, b, c...),^a energy separations (ΔE), and vibrational frequencies (ν) of the electronic states of Nb_4^- at the DFT/B3LYP level.

Structure	State	a (Å)	b (Å)	c (Å)	d (Å)	ΔE (eV)	ν (cm^{-1})
Pyramid (C_s)	$^2A'$	2.491	2.484	2.491	2.580	0.0	42, 151, 158, 232, 234, 351
	$^2A''$	2.756	2.265	2.611	2.290	0.32	-142, 120, 149, 168, 297, 362
	$^4A'$	2.648	2.435	2.489	2.407	0.41	-124, 115, 198, 240, 352, 377
	$^4A''$	2.544	2.526	2.548	2.366	0.44	
Rhombus (D_{2h})	$^2B_{1g}$	2.342	2.629	3.875		0.19	70, 110, 205, 240, 274, 325
	$^4B_{2g}$	2.324	2.639	3.825		0.26	110, 124, 201, 210, 282, 331
	$^2B_{1u}$	2.317	2.629	3.817		0.97	132, 154, 181, 207, 261, 325
	$^2B_{3g}$	2.321	2.618	3.834		1.26	125, 175, 197, 207, 279, 331
	$^4B_{1u}$	2.411	2.633	4.040		1.60	
	$^4B_{3u}$	2.359	2.665	3.893		1.94	130, 162, 248, 261, 318, 348
	$^2B_{3u}$	2.361	2.659	3.901		2.01	83, 154, 248, 257, 307, 319
	4A_u	2.413	2.875	3.876		2.06	-139, 199, 208, 291, 355, 404

^aRefer to Fig. 1 for the definition of the bond lengths (a, b, c...) of different structures.

TABLE VIII. Bond lengths (a, b, c...),^{a,b} and energy separations (ΔE) of the electronic states of Nb_5^- at the MRSDCI, and MRSDCI+Q levels. The optimized geometries presented here were calculated at the CAMCSCF level.

Structure	State	a	b	c	d	e	f	ΔE_{MRSDCI}	$\Delta E_{\text{MRSDCI+Q}}$
		(Å)	(Å)	(Å)	(Å)	(Å)	(Å)	(eV)	(eV)
DTB (C_{2v})	3B_1	2.858	2.249	2.449	2.753	4.208		0.00	0.002
	1A_1	2.746	2.867	2.315	2.746	2.867		0.04	0.00
	1B_1	2.858	2.241	2.459	2.762	4.233		0.16	0.19
	3A_2	2.879	2.226	2.464	2.771	4.238		0.19	0.21
	3B_2	2.877	2.263	2.511	2.739	4.249		0.19	0.28
	1A_2	2.877	2.224	2.454	2.773	4.241		0.22	0.25
DTP (C_{2v})	3A_1	2.741	2.943	2.294	2.741	2.943	3.983	0.19	0.17
	1B_2	2.731	3.069	2.245	2.731	3.069	4.043	0.23	0.23
DECT (C_s)	$^3A''$	2.362	2.918	2.720	2.799	4.012	2.532	0.78	0.75
	$^1A''$	2.448	2.455	2.838	2.828	4.011	2.489	1.10	1.03
	$^3A'$	2.438	2.428	3.049	2.781	4.036	2.479	1.37	1.28
	$^1A'$	2.746	2.226	2.976	2.266	4.113	2.678	1.63	1.83

^aRefer to Fig. 1 for the definition of the bond lengths (a, b, c...) of different structures.

TABLE IX. Bond lengths (a, b, c...),^a energy separations (ΔE), and vibrational frequencies (ν) of the electronic states of Nb_5^- at the DFT/B3LYP level.

Structure	State	a	b	c	d	e	f	ΔE (eV)	ν (cm^{-1})
		(\AA)	(\AA)	(\AA)	(\AA)	(\AA)	(\AA)		
DTB (C_{2v})	1A_1	2.744	2.745	2.470	2.470	3.790		0.00	77, 77, 116, 116, 242, 242, 246, 262, 328
	3A_2	2.840	2.431	2.431	2.553	3.899		0.04	-103, 116, 116, 129, 181, 218, 262, 264, 335
	1A_2	2.836	2.431	2.431	2.555	3.905		0.07	-57, 112, 129, 129, 181, 220, 264, 272, 335
	3B_2	2.852	2.453	2.352	2.583	3.840		0.23	90, 125, 177, 182, 193, 268, 283, 322, 337
	1B_1	2.926	2.350	2.366	2.617	3.866		0.66	-115, 65, 162, 171, 218, 270, 273, 335, 582
	3A_1	2.766	2.927	2.487	2.485	3.754		1.57	-283, -75, 109, 130, 215, 229, 264, 269, 315
DTP (C_{2v})	1B_2	2.599	2.655	2.455	2.797	3.892		0.28	92, 106, 118, 142, 200, 235, 269, 308, 329
	3B_1	2.672	2.577	2.457	2.871	3.934		0.55	-47, 112, 133, 142, 200, 235, 269, 308, 329
DECT (C_s)	$^1A'$	2.490	2.618	2.538	2.975	3.938	2.489	0.55	32, 73, 131, 187, 236, 239, 251, 278, 334
	$^3A'$	2.497	2.514	2.656	2.973	3.843	2.498	0.81	-20, 98, 102, 165, 164, 188, 220, 265, 326
	$^1A''$	2.567	2.442	2.568	2.938	3.960	2.371	1.26	-105, 98, 110, 121, 184, 191, 232, 257, 311

^aRefer to Fig. 1 for the definition of the bond lengths (a, b, c...) of different structures.

TABLE X. Calculated electron affinity (EA), ionization potential (IP), dissociation energy (D_e , including the value of the corresponding cation), and atomization energy (AE, per atom) of Nb_4 and Nb_5 at the various levels of theory. Experimental data are also included in the table for comparison. The parameters, if not indicated, are calculated using $(5s5p4d//5s3p2d)$ basis set of Nb.

Method	Nb_4				Nb_5				D_e (cations)	
	EA (eV)	IP (eV)	D_e (eV)	AE (eV)	EA (eV)	IP (eV)	D_e (eV)	AE (eV)	Nb_4^+	Nb_5^+
MRSDCI	1.24 ^a	5.60 ^d (4.77 ^e , 4.33 ^a)	6.02	3.68	1.54 ^d	5.39 ^d	5.58	4.06	5.85	5.79
MRSDCI + Q	1.42 ^a	5.76 ^d (4.96 ^e , 4.56 ^a)	6.79	3.88	1.58 ^d	5.71 ^d	6.25	4.36	6.64	6.30
DFT/B3LYP	0.82 ^b	5.43 ^b	6.07 ^b	4.32 ^b	1.31 ^b	5.22 ^b	5.51 ^b	4.56 ^b		
	(0.824) ^c	(5.44) ^c	(6.10) ^c		(1.32) ^c	(5.23) ^c	(5.53) ^c			
Experimental	1.15 ^f	5.64 ± 0.005 ^g	5.9 ± 0.80 ^h	3.84	1.65 ^f	5.45 ± 0.05 ^g	5.35 ± 0.2 ^h	4.14	5.900 ± 0.2 ^h	5.50 ± 0.2 ^h
		5.58 ± 0.1 ^h	6.26 ± 0.72 ⁱ	4.29		5.43 ± 0.05 ^h	5.46 ± 0.29 ⁱ	4.52	6.00 ± 0.3	5.61 ± 0.3 ⁱ
	5.45 ± 0.05	5.80 ± 0.31 ⁱ								

^aThe calculated values are using $(5s5p4d1f//5s3p2d1f)$ basis set of Nb

^bThe calculated values are using $(6s6p5d1f//6s4p4d1f)$ basis set of Nb.

^cCalculated using $(6s6p5d1f1g//6s4p4d1f1g)$ basis set of Nb.

^dCalculated using thermodynamic cycle (see the text for details).

^eCalculated using $(6s6p4d//6s4p3d)$ basis set of Nb

^fRef. 3.; ^gRef. 39; ^hRef. : ⁱRef. 6

^jCalculated using the experimental D_e values in Ref. 5 and 6.

FIGURE CAPTIONS

FIG. 1. Optimized structures of Nb₄ and Nb₅ clusters. The structures a, b, and c are the rhombus (D_{2h} , 1A_g), D_2 (5A), and pyramidal (C_s , $^1A'$) structures of Nb₄, while d, e, and f are the distorted trigonal bipyramid (C_{2v} , 2A_2), distorted tetragonal pyramid (C_{2v} , 4A_1), and distorted edge-capped tetrahedron (C_s , $^2A''$) structures of Nb₅. The optimized D_2 (b) structure is at the DT/B3LYP level, while the other optimized structures are at the CASMCSCF level. The optimized values of the structural parameters (marked as a, b, c, d...) for the various electronic states of Nb_n and Nb_n⁻ (n = 4, 5) clusters are available in Tables I - IV (Nb_n) and VI - IX (Nb_n⁻).

FIG. 2. The active space MOs of the ground ($^1A'$, C_s) and the first excited state (1A_g , D_{2h}) of Nb₄. Only a few selected MOs of these two electronic states [$16a'$, $17a'$, $7a''$ ($^1A'$), $4b_{2u}$, and $4b_{3u}$ (1A_g), calculated at the CAMCSCF/MRSDCI level, are presented here. The pictures were originally drawn keeping z as the vertical axis. Each MO picture is then rotated to have better visualization.

FIG. 3. The active space MOs of the ground (2A_2 , DTB) and the low-lying excited state ($^2A''$, C_s) of Nb₄. Only a few selected MOs of these two electronic states [$13a_1$, $9b_2$, $7b_1$, $4a_2$ (2A_2), $21a'$, and $12a''$ ($^2A''$), calculated at the CAMCSCF/MRSDCI level, are presented here. The pictures were originally drawn keeping z as the vertical axis. Each MO picture is then rotated to have better visualization.

FIG. 4. The electron density difference maps of Nb₄ (¹A') in (a) *xz*, and (b) *yz* planes. The contours are derived from the CASMCSCF natural orbitals and are drawn with respect to the separated Nb atoms. The separation between the contour lines is 0.03 electron/bohr³. The contours with no density are labeled with zeros, while solid lines indicate enhancement of electron density.

FIG. 5. The electron density difference maps of the ground state of Nb₅ (²A₂, DTB) in (a) *yz*, and (b) *xz* planes. The contours are derived from the CASMCSCF natural orbitals and are drawn with respect to the separated Nb atoms. The separation between the contour lines is 0.03 electron/bohr³. The contours with no density are labeled with zeros, while solid lines indicate enhancement of electron density.

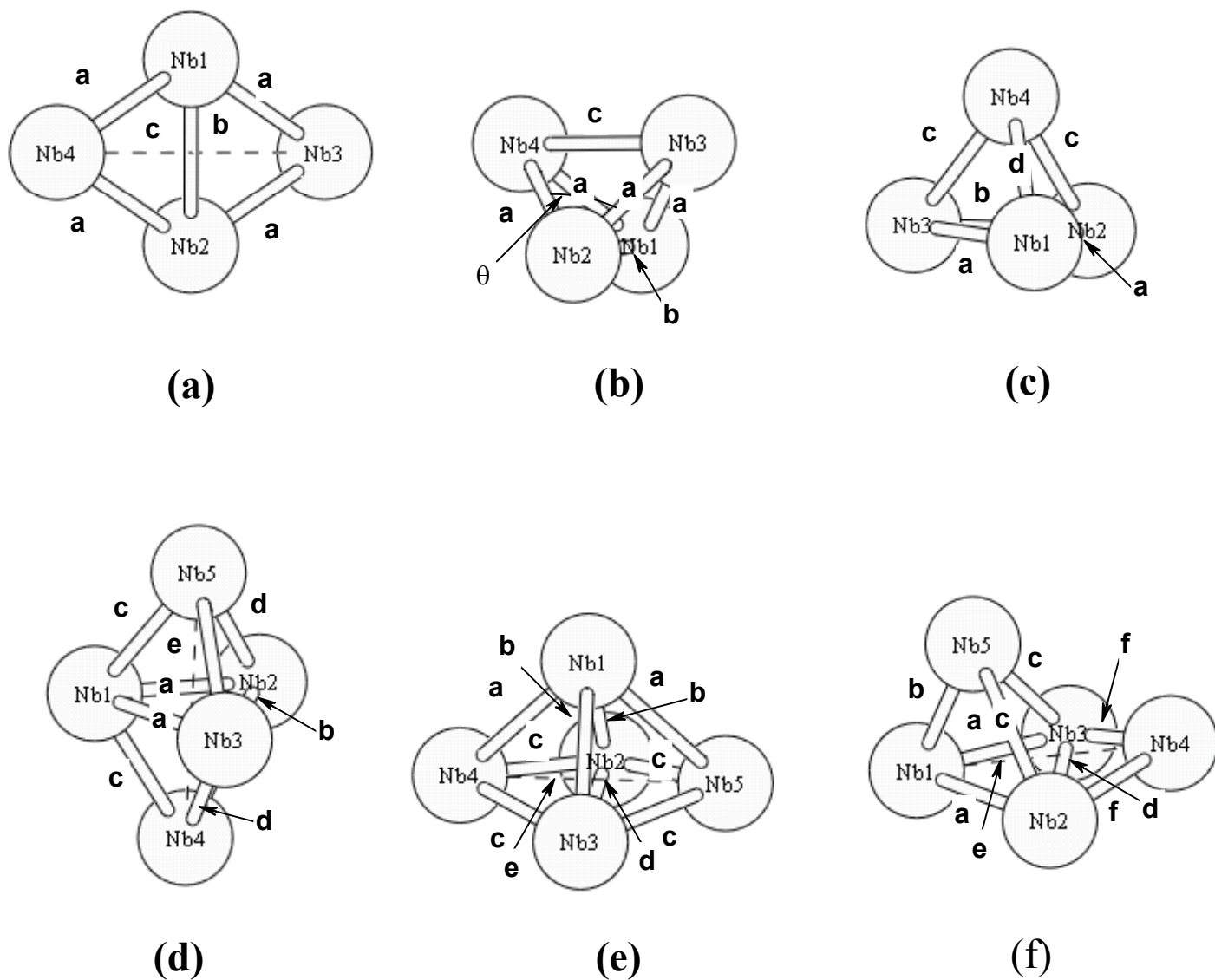
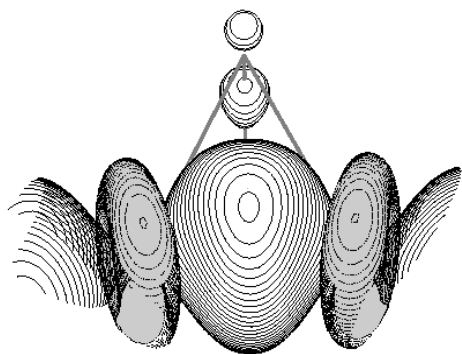
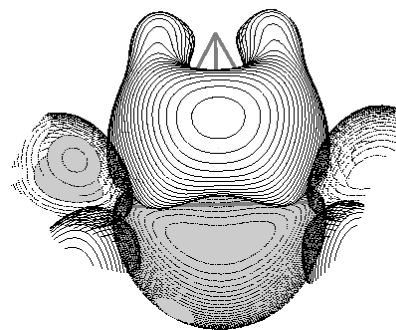


Fig. 1

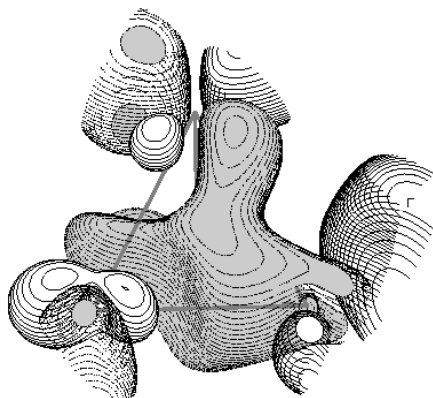
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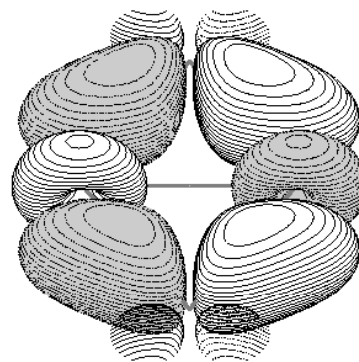
16a'



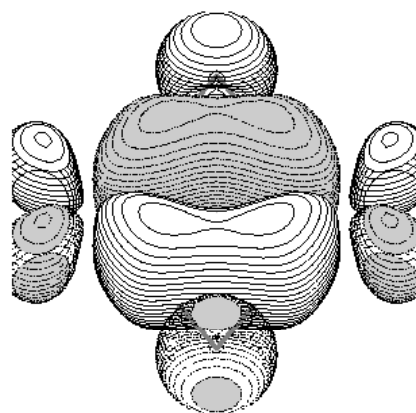
17a'



7a''



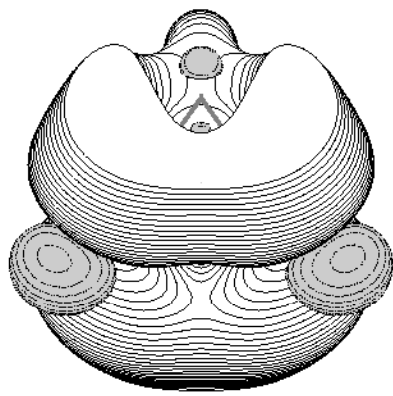
4b_{2u}



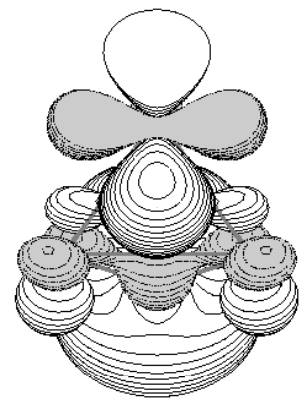
4b_{3u}

Fig. 2

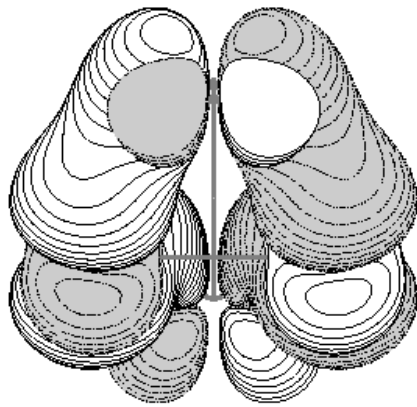
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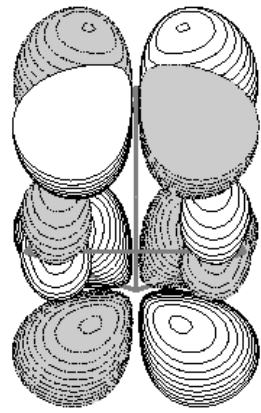
13a₁



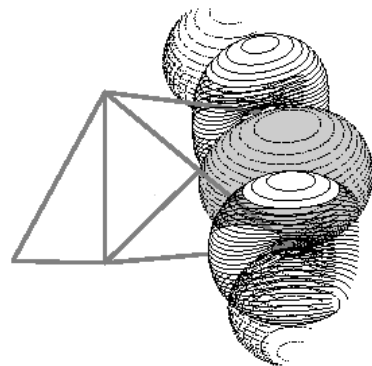
9b₂



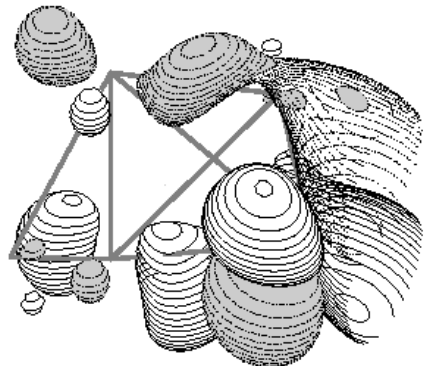
7b₁



4a₂

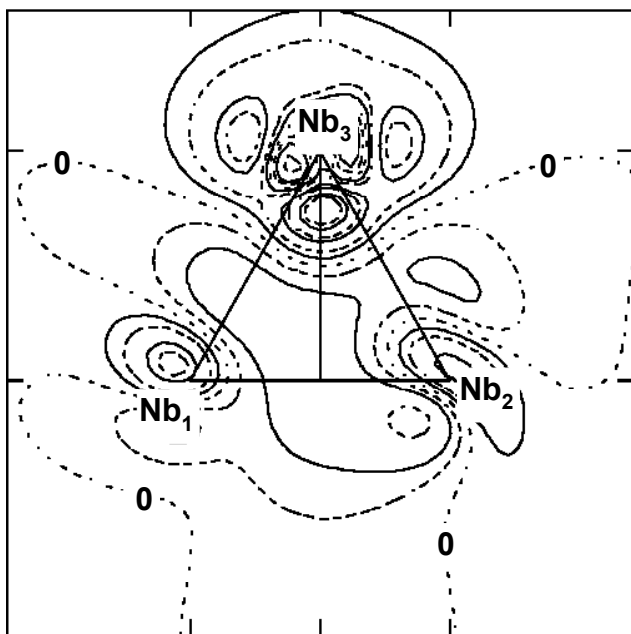


21a'

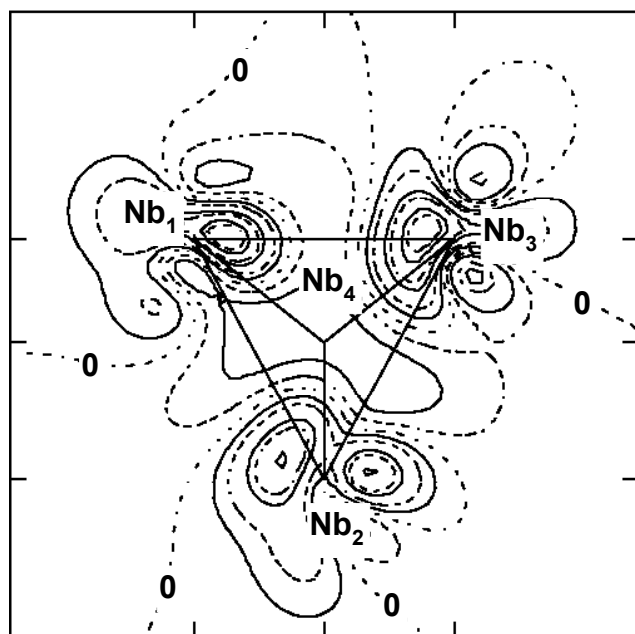


12a''

Fig. 3
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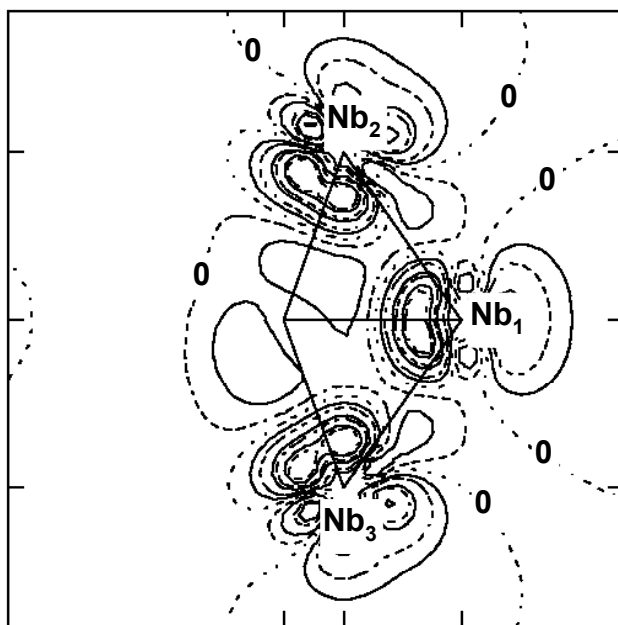


(a)

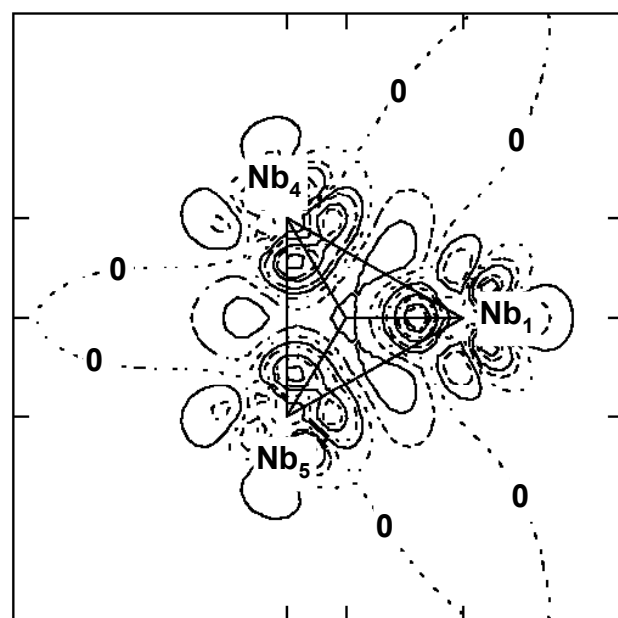


(b)

Fig. 4
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(a)



(b)

Fig. 5
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