Experimental observation of TiN$_{12}^+$ cluster and theoretical investigation of its stable and metastable isomers†

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TiN$_{n}^+$ clusters were generated by laser ablation and analyzed experimentally by mass spectrometry. The results showed that the mass peak of the TiN$_{12}^+$ cluster is dominant in the spectrum. The TiN$_{n}^+$ cluster was further investigated by photodissociation experiments with 266, 532 and 1064 nm photons. Density functional calculations were conducted to investigate stable structures of TiN$_{12}^+$ and the corresponding neutral cluster, TiN$_{12}$. The theoretical calculations found that the most stable structure of TiN$_{12}^+$ is Ti(N$_2$)$_6^+$ with O$_h$ symmetry. The calculated binding energy is in good agreement with that obtained from the photodissociation experiments. The most stable structure of neutral TiN$_{12}$ is Ti(N$_2$)$_6$ with D$_{3d}$ symmetry. The Ti–N bond strengths are greater than 0.94 eV in both Ti(N$_2$)$_6^+$ and its neutral counterpart. The interaction between Ti and N$_2$ weakens the N–N bond significantly. For neutral TiN$_{12}$, the Ti(N$_3$)$_4$ azide, the N$_2$TiN$_7$ sandwich structure and the N$_6$TiN$_6$ structure are much higher in energy than the Ti(N$_2$)$_6$ complex. The DFT calculations predicted that the decomposition of Ti(N$_2$)$_6$, N$_2$TiN$_7$, and N$_6$TiN$_6$ into a Ti atom and six N$_2$ molecules can release energies of about 139, 857, and 978 kJ mol$^{-1}$ respectively.

Due to their importance in understanding metal–nitrogen interactions, metal–nitrogen complexes have been extensively investigated by a variety of experimental techniques in recent decades. Andrews and co-workers investigated Fe–N$_2$, Se–N$_2$, Os–N$_2$, and Ru–N$_2$ complexes with matrix-isolated infrared spectroscopy12–15 and found that an Os atom can insert directly into the dinitrogen bond to form bent NOsN. Duncan and co-workers investigated In–N$_2$ and Al–N$_2$ complexes by photoionization spectroscopy,16,17 and studied Mg$^+$–N$_2$, Ca$^+$–N$_2$, Nb$^+(N_2)_n$, and V$^+(N_2)_n$ complexes using photodissociation spectroscopy.18–21 Dagdigian and co-workers studied the electronic states of an Al–N$_2$ complex with laser-induced fluorescence spectroscopy.22

Many kinds of binary azides have been prepared and characterized experimentally, and have also been investigated by theoretical calculations. B(N$_3$)$_3$ was isolated in a low-temperature argon matrix and characterized by FTIR spectroscopy;23 recently, it was also identified by a combination of VUV photoelectron spectroscopy and outer valence Green’s functional calculations.24 Binary azides of Group 4 elements (such as Ti),25 Group 5 elements (V, Nb, and Ta),26–28 Group 6 elements (Mo and W),29 Group 14 elements (Si and Ge),30–32 Group 15 and 16 elements (P, Bi, Se, and Te)33–36 were synthesized and isolated experimentally, and were characterized by NMR spectroscopy. Some of them were also examined by infrared and/or Raman spectroscopy, and verified by theoretical calculations. Gagliardi and Pyykö studied the Group 4 tetra-azides M[N$_3$]$_4$ (M = Ti, Hf, Th) by theoretical calculations.37 Li and Duan investigated the

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1 Introduction

Nitrogen-rich and all-nitrogen compounds are potential candidates for high energy density materials (HEDMs).1–6 Despite numerous theoretical and experimental efforts aimed at all-nitrogen compounds, only a few attempts, for example the synthesis of N$_6^+$ salts and the detection of N$_4$ with a lifetime of only about 1 microsecond,8 have been successful. A less challenging goal might be to produce nitrogen-rich species containing one or more other atoms. Thus, metal-doped nitrogen clusters have drawn increasing attention in recent years because of their diverse structural properties and predicted relatively high stabilities.9–11 These clusters can also be considered as good models for understanding the formation and properties of nitrogen-rich compounds at the molecular level.
structures and stabilities of a series of tri-azides M(N3)3 (M = Sc, Y, La, B, Al, Ga, In, Ti) and tetra-azides M(N3)4 (M = Ti, Zr, Hf, C, Si, Ge, Sn, Pb) using density functional theory calculations. 38

Many researchers have used theoretical chemistry to investigate species containing polynitrogen rings. The theoretical calculations of Gallagiardi and Pykkö found that ScN2 has a local minimum with C7v symmetry, 9 and that the sandwich structures of N2MN7 (M = Ti, Zr, Hf, Th) are locally stable. 39 Other species with polynitrogen rings, such as CsN7Ba 40 and MN6 (M = Ti, Zr, Hf, Th), 40 were also investigated theoretically. Theoretical calculations also predicted the possible existence of high-energy nitrogen-rich pentazole with a very large nitrogen-to-element ratio, such as [M(N5)5]− (M = Cr, Mo, W). 11 After that, Duan and Li investigated a series of polynitrogen ring species (ScN6−, TiN6−, V6N6−, Ca2N6−, and ScN6Cu) using density functional theory calculations. 41 Jin and Ding calculated the sandwich structures of [N2NM13]− and [N2MN13]+ ([M, q] = (Ni, 0), (Co, −1), (Fe, −2)) using density functional theory. 42 Very recently, an investigation of stable high pressure phases of potassium azide using the first-principles method and the evolutionary algorithm suggested that planar N4 rings may be formed in potassium azide at a pressure of 100 GPa. 43

Overall, the previous experimental and theoretical studies have shown that metal–nitrogen clusters may exist in the forms of M-(N3)n complexes, binary azides, or polynitrogen ring structures. Whether they are energy-rich or not, they are of great general interest. In this work, we investigated the TiN12+ cluster by laser ablation and photodissociation experiments coupled with density functional calculations, in order to gain an insight into the geometric and electronic properties of the most stable TiN12+ cluster, as well as its neutral counterpart. The relative stabilities of the polyazide and polynitrogen ring isomers were also investigated by density functional calculations.

2 Experimental and theoretical methods

2.1 Experimental method

The experiments were conducted on a home-built apparatus equipped with a laser vaporization cluster source and a reflectron time-of-flight mass spectrometer (RTOF-MS), which has been described elsewhere. 44 Briefly, the TiN12+ cluster ions were generated in the laser vaporization source by laser ablation of a rotating and translating disk target of a mixture of Ti and BN (13 mm diameter, Ti : BN mole ratio = 2 : 1) with the second harmonic of a nanosecond Nd:YAG laser (Continuum Surelite II-10). A typical laser power used in this work is about 10 mJ per pulse. Nitrogen gas with ~4 atm back pressure was allowed to expand into the source through a pulsed valve (General Valve Series 9) to provide nitrogen for cluster formation and to cool the formed clusters. The masses of the generated cluster ions were analyzed with the RTOF-MS. The TiN12+ cluster ions were further investigated via photodissociation experiments. During the photodissociation experiments, the TiN12+ ions were selected with a pulsed mass-gate at the first space focus point of the RTOF-MS, decelerated with a DC electric field, and then dissociated with 266, 532, and 1064 nm photons from another nanosecond Nd:YAG laser (Continuum Surelite II-10). The fragment ions and parent ions were then re-accelerated toward the reflectron zone and reflected to the microchannel plate (MCP) detector. The output from the MCP detector was amplified with a broadband amplifier and recorded with a 200 MHz digital card. The digitalized data were collected on a laboratory computer with home-made software.

2.2 Computational methods

The theoretical calculations were carried out using GAUSSIAN 09 code. 45 Geometry optimization and frequency analysis were performed at the B3LYP/6-31G* level. 46 The ionization energy of Ti and the bond length of the N2 molecule were calculated to verify the accuracy of our method. The calculated ionization energy of Ti is about 656 kJ mol−1 and the N-N bond length is about 1.10 Å, which are consistent with the experimental values of 658.8 kJ mol−1 and 1.0977 Å. 47 The binding energy is defined as (n is the number of N2 molecules):

\[ E_{b1} = -[E(TiN_{2n}) - E(Ti) - n \times E(N2)]/n \] (for neutral clusters)

\[ E_{b2} = -[E(TiN_{2n}^+) - E(Ti^+) - n \times E(N2)]/n \] (for ionic clusters)

To gain further insight into the interactions between the N2 molecules and Ti or Ti+, we performed natural bond orbital (NBO) analysis, 39 in which the electronic wave function is interpreted in terms of a set of occupied Lewis orbitals and a set of unoccupied non-Lewis delocalized orbitals. For each donor NBO (i) and acceptor NBO (j), the stabilization energy \( E_2 \) associated with charge transfer \( i \to j \) is given by

\[ E_2 = \Delta E_{ij} = q_i \left( F(i,j) \right)^2 / (\varepsilon_j - \varepsilon_i) \]

where \( q_i \) is the donor orbital occupancy, \( \varepsilon_i \) and \( \varepsilon_j \) are diagonal elements (orbital energies), and \( F(i,j) \) is the off-diagonal NBO Fock matrix element.

3 Experimental results

Fig. 1 shows a typical mass spectrum of the clusters generated in our experiments. It can be seen that the predominant mass peaks correspond to Ti+ and TiN12+. It is very interesting that there are no mass peaks due to other TiNq+ clusters. This indicates that TiN12+ may have the most stable or symmetric structure in comparison with other clusters. In addition to the mass peak of TiN12+, we also observed weak mass peaks corresponding to TiON3+, TiON4+, and Ti2O4N6+ in the mass spectrum. The detection of TiON5+ is similar to the formation of TiO+(N2)5 by gas phase clustering of N2 molecules on TiO+ reported by Daly and El-Shall. 48

The photodissociation of TiN12+ was conducted using 266, 532 and 1064 nm photons. No fragment ions were observed when TiN12+ was photodissociated by 1064 nm photons. The photodissociation mass spectra of TiN12+ at 532 and 266 nm
are shown in Fig. 2. TiN_{12}^+, TiN_{11}^+, TiN_{10}^+, TiN_{9}^+, and Ti^+ fragment ions were produced when TiN_{12} was photodissociated by 532 nm photons, and the TiN_{6}^+ fragment had the highest abundance. This indicates that TiN_{12} can lose at least 4 nitrogen atoms, and that the main dissociation channel when TiN_{12} was photodissociated by 532 nm photons was the loss of 6 nitrogen atoms. The fragment ions observed when TiN_{12} was photodissociated by 266 nm photons were TiN_{4}^+, TiN_{2}^+, and Ti^+, which shows that TiN_{12} can lose at least 8 nitrogen atoms.

![Image](image1)

**Fig. 1** Typical mass spectrum of Ti–N clusters generated by laser ablation of a Ti : BN mixture target.

**Fig. 2** Photodissociation mass spectra of the TiN_{12}^+ cluster at 532 and 266 nm.

### 4 Theoretical results

We started with one N₂ molecule bonded to Ti and Ti⁺. We calculated both the end-on linear structure and the side-on triangular structure, and found that for TiN₂ the end-on linear geometry is 0.34 eV lower in energy than the side-on geometry, while for TiN₂⁺ the two configurations are almost degenerate. The binding energies of the end-on linear configurations were calculated to be 0.25 and 0.93 eV for TiN₂ and TiN₂⁺, respectively. TiN₂ was found to have a magnetic moment of 4.0 \( \mu_B \), a Ti–N bond length of 1.94 Å, and a N–N bond length of 1.15 Å. While for TiN₂⁺, the magnetic moment is 3.0 \( \mu_B \), the Ti–N bond length is 2.18 Å, and the N–N bond length is 1.11 Å.

To investigate the stable states of TiN_{12} and TiN_{12}⁺, we selected six initial geometrical configurations consisting of one Ti and six N₂ molecules (Fig. 3, I₁–I₆), and two structures consisting of one Ti atom and four N₅ moieties (Fig. 3, I₇ and I₈). We also considered structures composed of one Ti atom, one N₂ ring and one N₁ ring (N₁TiN₂) (Fig. 3, I₉), and one Ti and two N₆ rings (N₂TiN₆) (Fig. 3, I₁₀). After full relaxation, it was found that, for the neutral cluster, the initial structures of I₁, I₃, and I₄ converged to the same structure with \( D_{3d} \) symmetry, labeled as N₁₋₃ in Fig. 3, which is the lowest energy geometrical configuration with a magnetic moment of 2.0 \( \mu_B \). While the other optimized isomers, labeled as N₅ ~ N₁₀ in Fig. 3, have much higher energies than isomer N₁₋₃. Their relative energies, calculated with respect to the lowest energy configuration, and symmetries are also given in Fig. 3. In the lowest energy geometry (N₁₋₃), the Ti–N₂ distance and N–N bond length are 2.09 and 1.12 Å, respectively. The average binding energy of each N₂ molecule with Ti in isomer N₁₋₃ is 0.79 eV, which is larger than that in TiN₂. The Ti(N₁₋₃)₆ structure with \( T₃ \) symmetry is 6.18 eV higher in energy than the most stable Ti(N₂)₆ complex. The linear Ti–N–N–N bond angles of the \( T₃ \) structure calculated in this work are in agreement with those obtained from previous theoretical calculations on free gaseous Ti(N₃)₄.\(^{37,38}\)

These bond angles were found to vary in the solid phase due to solid-state effects.\(^{25}\) The \( N₅TiN₇ \) structure has a Ti atom sandwiched by an \( η^3-N₅ \) ring and an \( η^2-N₂ \) ring, similar to that reported by Gagliardi and Pykkö.\(^{19}\) It is worth mentioning that \( η^5-η^1 \) sandwich structures were also observed in (C₅H₅)M(C₇H₇) type compounds, where M is a transition metal.\(^{52-54}\) The \( N₆TiN₆ \) structure exhibits \( D_{3d} \) symmetry, in which the two N₆ rings are distorted and only two N atoms in each N₆ ring interact directly with the Ti atom, with a shorter Ti–N distance of 1.98 Å. The \( N₅TiN₇ \) and \( N₆TiN₆ \) structures are higher in energy than the most stable \( Ti(N₂)₆ \) complex by 13.65 and 14.89 eV respectively. According to the calculated binding energies, the decomposition of Ti(N₁₋₃)₆, TiN₁₋₃, and N₆TiN₆ into a Ti atom and six N₂ molecules could release energies of 139, 857, and 978 kJ mol⁻¹ respectively.

For the cationic TiN_{12}⁺ cluster, the initial structures of I₁, I₂, I₄, and I₆ converged to one structure \( (P₁₋₀) \) with \( D₅h \) symmetry, as shown in Fig. 3. This is the lowest energy configuration of TiN_{12}⁺ with a Ti–N₂ distance and N–N bond length of 2.17 and 1.11 Å, respectively. The magnetic moment was found to be 3.0 \( \mu_B \). The
average binding energy of each N₂ with Ti in isomer P₁–₄ was calculated to be 0.94 eV. The other optimized isomers, namely P₅–₆, P₇–₈, P₉, and P₁₀ in Fig. 3, were found to be higher in energy than isomer P₁–₄ by 1.36, 9.61, 7.24 and 8.75 eV, respectively. The structure of Ti(N₃)₄⁺ has C₅ᵥ symmetry. The N₂TiN₂ and N₆TiN₆ structures of TiN₁₂⁻ are not stable. The N₂TiN₆ structure is rearranged into a N₅Ti(N₃)N₂ type of structure, while the N₆TiN₆ structure is rearranged into N₅Ti(N₂)₃ after the geometry optimizations. According to the calculated binding energies, the decomposition of Ti[N₃]³⁺, N₂Ti[N₁(N₂)]²⁺, and N₆Ti[N₂]³⁺ can release energies of 382, 156, and 301 kJ mol⁻¹, respectively.

5 Discussion

5.1 Comparison of binding energies

Based on the calculated binding energy of the most stable structure of the TiN₁₂⁻ cluster (0.94 eV), the energy of a 532 nm photon is able to dissociate two N₂ molecules from isomer P₁–₄, while the energy of a 266 nm photon is able to dissociate four N₂ molecules. This is in good agreement with our photodissociation experiment, as the experiment showed that the photodissociation of TiN₁₂⁻ at 532 nm could remove at least 4 nitrogen atoms (two N₂ molecules), and photodissociation at 266 nm could remove at least 8 nitrogen atoms (four N₂ molecules). The detection of no photofragments at 1064 nm indicates that the energy barrier for the dissociation of TiN₁₂⁻ is higher than 1.16 eV. In the experiment, the production of TiN₄⁺, TiN₅⁺, TiN₆⁺, and Ti⁺ fragments at 532 nm, and the production of TiN₅⁺ and Ti⁺ fragments at 266 nm are probably due to multiple-photon processes. The good agreement between the experiment and the theoretical calculations validates the theoretical method selected for this work and confirms that the TiN₁₂⁻ cluster detected in our experiment has the form Ti(N₆)₆⁺ with Oh symmetry. This is consistent with the matrix infrared and ultraviolet-visible spectroscopy studies of Ti(CO)₆ and Ti(N₂)₆ by Busby et al.³⁵

Although the binding energy of neutral TiN₂ (0.25 eV) is smaller than that of TiN₄⁺ (0.93 eV) by 0.68 eV, the Ti–N bond in neutral TiN₂ (1.94 Å) is actually shorter (stronger) than that in TiN₂⁺ (2.18 Å), while the N–N bond in neutral TiN₂ (1.15 Å) is longer (weaker) than that in TiN₂⁺ (1.11 Å). The decrease in the binding energy for neutral TiN₂ compared to TiN₂⁺ is due to the weakening of the N–N bond. Thus, we would like to stress that the calculated binding energies do not reflect the exact Ti–N bond strengths in the clusters. The N–N bond in TiN₂⁺ is weaker than that in the N₂ molecule; thus, the Ti–N bond strength in TiN₂⁺ would be larger than the binding energy (0.93 eV). Moreover, the Ti–N bond in neutral TiN₂ is stronger than the Ti–N bond in TiN₂⁺. Hence, we obtain the relation: BE([Ti–N]TiN₂) > BE([Ti–N]TiN₂⁺) > 0.93 eV, where BE([Ti–N]TiN₂) is the Ti–N bond energy in TiN₂ and BE([Ti–N]TiN₂⁺) is the Ti–N bond energy in TiN₂⁺. This also implies that the N–N bond in neutral TiN₂ is weaker than those in TiN₂⁺ and N₂ by at least 0.68 eV, which can be formulated as: BE([N–N]TiN₂) + 0.68 eV < BE([N–N]TiN₂⁺), BE([N–N]TiN₂), BE([N–N]TiN₂⁺), and BE([N–N]N₂) are the N–N bond energies in TiN₁₂, TiN₂⁺, and N₂, respectively.

Similarly, although the average binding energy of the most stable structure of TiN₁₂ (0.79 eV) is smaller than that of TiN₁₂⁻ (0.94 eV) by 0.15 eV, the Ti–N bonds in neutral TiN₁₂ (2.09 Å) are actually shorter (stronger) than those in TiN₁₂⁻ (2.17 Å), while the N–N bonds in neutral TiN₁₂ are longer (weaker) (1.12 Å) than those in TiN₁₂⁻ (1.11 Å). We can also conclude that the Ti–N bond energies of both TiN₁₂ and TiN₁₂⁻ are larger than 0.94 eV, BE([Ti–N]TiN₁₂) > BE([Ti–N]TiN₁₂⁻) > 0.94 eV.
It is interesting to note that the average binding energy of each N₂ with Ti in the ground state of neutral TiN₁₂ is 0.79 eV, which is much larger than that in TiN₂, while the average binding energy of each N₂ with Ti⁺ in the ground state of TiN₁₂⁺ is 0.94 eV, which is nearly the same as that in TiN₂⁺. Considering the bond lengths in TiN₂, TiN₁₂, TiN₂⁺, and TiN₁₂⁺, we can see that the Ti–N bond lengths are in the order TiN₁₂ > TiN₂ > TiN₂⁺ > TiN₁₂⁺, while the N–N bond lengths are in the order TiN₁₂ > TiN₂ > TiN₂⁺ > TiN₁₂⁺. The Ti–N and N–N distances in TiN₂⁺ and TiN₁₂⁺ are very close to each other, while those in TiN₂ and TiN₁₂ are very different from each other. The Ti–N bond in TiN₂ is much shorter than those in the other three species, and the N–N bond in TiN₂ is much longer than those in the other species. In TiN₁₂, the N–N bond is weakened significantly due to the strong Ti–N₂ interaction. This could explain why the calculated binding energies of TiN₂⁺ and TiN₁₂⁺ are similar while the binding energy of TiN₂ is much smaller than that of TiN₁₂. Overall, we have BE[(Ti–N)TiN₂] > BE[(Ti–N)TiN₁₂] > BE[(Ti–N)TiN₁₂⁺] > BE[(Ti–N)TiN₂⁺] > 0.93 eV.

5.2 NBO analyses

To further address the differences in the binding energies, we performed NBO analyses for TiN₂, TiN₂⁺, TiN₁₂ and TiN₁₂⁺ in order to understand the effects of charge and coordination number on the binding and electronic structures. The calculated results are provided in Tables S1–S4.† Based on the NBO data, we note that in neutral TiN₂, the Ti lone pairs in the spin-up channel with d-orbital components of 99.51% donate 0.64 electrons to the π-antibonding orbitals between the two N atoms, which have p-orbital components of 99.90% and 99.53%. The corresponding back donations from the N valence lone pairs in two spin channels to the valence non-Lewis lone pairs on Ti total 0.14 electrons, giving rise to the loss of approximately 0.50 electrons on the Ti site, while the N1 and N2 atoms gain 0.45 and 0.05 electrons, respectively. Thus, the Ti–N interaction is very strong and the N–N bond is weakened significantly in neutral TiN₂ because of the large charge transfer between Ti and N1. On the other hand, in TiN₂⁺, the charge donation from the lone pair on Ti to the antibonding orbital of N₂ is negligible since it is more difficult to transfer electrons from Ti⁺. Contrarily, about 0.09 electrons are transferred from the lone pair on N1 to Ti. N1 and N2 carry charges of −0.242 and +0.216 respectively, forming a dipole which strongly interacts with Ti⁺ with a charge of +1.026, resulting in a large binding energy for N₂ and Ti⁺.

On going from TiN₂ to Ti(N₂)₆, the enhanced coordination field splits the Ti 3d orbitals to form bonding orbitals between Ti and the six linking N₁ atoms in both spin-up and spin-down channels. The bonding orbitals have Ti 4s, Ti 4p and Ti 3d components of 16.66%, 49.92% and 33.34% respectively, resulting in sp²d² hybridization character, which is consistent with the octahedral ligand field where the Ti atom is located. Therefore, the bonding orbitals between Ti and N₁ give rise to a larger binding energy for the N₂ molecule in Ti(N₂)₆ compared to that in TiN₂.

Despite their different charges, TiN₁₂ and TiN₁₂⁺ share some common features: (1) bonding orbitals are formed between Ti and N₁ and Ti⁺, and between Ti⁺ and N₁; and (2) the second order perturbation analysis suggests that there are no obvious stabilization interactions associated with charge transfer between Ti and N₂. These two common features result in a reduction in the difference between the binding energies (0.79 versus 0.94 eV) of the N₂ molecules in the neutral and charged TiN₁₂.

5.3 Electronic and magnetic properties

In the lowest energy structure of cationic TiN₁₂, Ti⁺ is six-fold coordinated with Oₓₙ symmetry, in which the five d orbitals of Ti split into three-fold degenerate dₓᵧ, dₓz and dᵧz, and two-fold degenerate dₓ−y² and dₓzorbital. The former three orbitals are occupied by three spin-up electrons, while the latter two fold degenerate orbitals are empty, resulting in a magnetic moment of 3.0 μB. The energy gap between the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) is 2.8 eV, as shown in Fig. 4(b). However, compared to TiN₁₂⁺, the neutral TiN₁₂ cluster has one more electron, which would induce the Jahn–Teller effect. The symmetry changes from Oₓₙ to D₃d, and three electrons are spin-up and one electron is spin-down, leading to a total magnetic moment of 2.0 μB and an energy gap of 1.5 eV, as shown in Fig. 4(a). The three occupied spin-up orbitals, one occupied spin-down orbital, and two-fold degenerate lowest unoccupied molecular orbitals of neutral TiN₁₂ are plotted in Fig. 5(a–f), and the Ti 3d-orbital component percentages are 38.3%, 38.3%, 50.6%, 58.3%, 65% and 65%, respectively. For comparison, the three-fold degenerate HOMOs and the three-fold degenerate LUMOs of TiN₁₂⁺ are given in Fig. 5(g–i), and the Ti 3d-orbital component percentages are 41.6%, 41.6%, 41.6%, 78.0%, 78.0% and 78.0%, respectively. This suggests that the Ti 3d orbitals make a larger contribution to the frontier orbitals in the charged cluster (TiN₁₂⁺) compared with the neutral TiN₁₂.

As discussed above, TiN₁₂ and TiN₁₂⁺ have magnetic moments of 2.0 and 3.0 μB, respectively. In order to see how the magnetic moments are distributed in the clusters, spin density

![Fig. 4](image-url) Energy levels and optimized structures of TiN₁₂ (a) and TiN₁₂⁺ (b). The solid and dashed lines represent occupied and unoccupied energy levels, respectively. The blue and red colors represent spin-up and spin-down, respectively. The Fermi level is set to zero eV.
isosurfaces are plotted in Fig. 6. They clearly show that the spin density of TiN$_{12}^+$ is more symmetric, and that Ti$^+$ carries a larger net spin moment and more strongly polarizes the contacting N atoms (termed N1 atoms) antiferromagnetically. The non-contacting N atoms (named N2 atoms) are ferromagnetically polarized in both the neutral and charged clusters.

### 6 Conclusions

The TiN$_{12}^+$ cluster was generated experimentally and was further investigated by photodissociation experiments at 1064, 532, and 266 nm. The results showed that the TiN$_{12}^+$ cluster has very high abundance compared to other TiN$_n^+$ clusters. Density functional calculations were conducted to investigate the stable structures of TiN$_{12}^+$ and its corresponding neutral cluster TiN$_{12}$. The calculated binding energy of the TiN$_{12}^+$ cluster was in good agreement with the photodissociation experiment. The theoretical calculations found that the most stable structure of TiN$_{12}^+$ is Ti(N$_2$)$_6^+$ with $O_h$ symmetry and the most stable structure of neutral TiN$_{12}$ is Ti(N$_2$)$_6$ with $D_{4d}$ symmetry. The Ti-N bond strengths are greater than 0.94 eV in both Ti(N$_2$)$_6^+$ and its neutral counterpart. The interaction between Ti and N$_2$ weakens the N-N bond significantly. The C$_{2v}$ azide isomer Ti(N$_3$)$_5^+$ is higher in energy than the O$_h$ Ti(N$_3$)$_6^+$ isomer by 9.61 eV. The azide isomer Ti(N$_3$)$_5$ and the N$_2$TiN$_7$ and N$_6$TiN$_8$ structures are higher in energy than the most stable Ti(N$_3$)$_6$ complex by 6.18, 13.65 and 14.89 eV respectively, indicating that the N$_2$TiN$_7$ and N$_6$TiN$_8$ isomers are potential candidates for high energy density materials.

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