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

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$\text{TiN}_n^+$  clusters were generated by laser ablation and analyzed experimentally by mass spectrometry. The results showed that the mass peak of the  $\text{TiN}_{12}^+$  cluster is dominant in the spectrum. The  $\text{TiN}_{12}^+$  cluster was further investigated by photodissociation experiments with 266, 532 and 1064 nm photons. Density functional calculations were conducted to investigate stable structures of  $\text{TiN}_{12}^+$  and the corresponding neutral cluster,  $\text{TiN}_{12}$ . The theoretical calculations found that the most stable structure of  $\text{TiN}_{12}^+$  is  $\text{Ti}(\text{N}_2)_6^+$  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  $\text{TiN}_{12}$  is  $\text{Ti}(\text{N}_2)_6$  with  $D_{3d}$  symmetry. The Ti–N bond strengths are greater than 0.94 eV in both  $\text{Ti}(\text{N}_2)_6^+$  and its neutral counterpart. The interaction between Ti and  $\text{N}_2$  weakens the N–N bond significantly. For neutral  $\text{TiN}_{12}$ , the  $\text{Ti}(\text{N}_3)_4$  azide, the  $\text{N}_5\text{TiN}_7$  sandwich structure and the  $\text{N}_6\text{TiN}_6$  structure are much higher in energy than the  $\text{Ti}(\text{N}_2)_6$  complex. The DFT calculations predicted that the decomposition of  $\text{Ti}(\text{N}_3)_4$ ,  $\text{N}_5\text{TiN}_7$ , and  $\text{N}_6\text{TiN}_6$  into a Ti atom and six  $\text{N}_2$  molecules can release energies of about 139, 857, and 978  $\text{kJ mol}^{-1}$  respectively.

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## 1 Introduction

Nitrogen-rich and all-nitrogen compounds are potential candidates for high energy density materials (HEDMs).<sup>1–6</sup> Despite numerous theoretical and experimental efforts aimed at all-nitrogen compounds, only a few attempts, for example the synthesis of  $\text{N}_5^+$  salts<sup>7</sup> and the detection of  $\text{N}_4$  with a lifetime of only about 1 microsecond,<sup>8</sup> 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 diversiform structures and predicted relatively high stabilities.<sup>9–11</sup> These clusters can also be considered as good models for understanding the formation and properties of nitrogen-rich compounds at the molecular level.

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– $\text{N}_2$ , Sc– $\text{N}_2$ , Os– $\text{N}_2$ , and Ru– $\text{N}_2$  complexes with matrix-isolated infrared spectroscopy<sup>12–15</sup> and found that an Os atom can insert directly into the dinitrogen bond to form bent  $\text{NOsN}$ . Duncan and co-workers investigated In– $\text{N}_2$  and Al– $\text{N}_2$  complexes by photoionization spectroscopy,<sup>16,17</sup> and studied  $\text{Mg}^+-\text{N}_2$ ,  $\text{Ca}^+-\text{N}_2$ ,  $\text{Nb}^+(\text{N}_2)_n$ , and  $\text{V}^+(\text{N}_2)_n$  complexes using photodissociation spectroscopy.<sup>18–21</sup> Dagdigian and co-workers studied the electronic states of an Al– $\text{N}_2$  complex with laser-induced fluorescence spectroscopy.<sup>22</sup>

Many kinds of binary azides have been prepared and characterized experimentally, and have also been investigated by theoretical calculations.  $\text{B}(\text{N}_3)_3$  was isolated in a low-temperature argon matrix and characterized by FTIR spectroscopy;<sup>23</sup> recently, it was also identified by a combination of VUV photoelectron spectroscopy and outer valence Green's functional calculations.<sup>24</sup> Binary azides of Group 4 elements (such as Ti),<sup>25</sup> Group 5 elements (V, Nb, and Ta),<sup>26–28</sup> Group 6 elements (Mo and W),<sup>29</sup> Group 14 elements (Si and Ge),<sup>30–32</sup> Group 15 and 16 elements (P, Bi, Se, and Te)<sup>33–36</sup> 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 Pyykkö studied the Group 4 tetra-azides  $\text{M}(\text{N}_3)_4$  ( $\text{M} = \text{Ti-Hf, Th}$ ) by theoretical calculations.<sup>37</sup> Li and Duan investigated the

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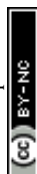
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structures and stabilities of a series of tri-azides  $M(N_3)_3$  ( $M = Sc, Y, La, B, Al, Ga, In, Tl$ ) and tetra-azides  $M(N_3)_4$  ( $M = Ti, Zr, Hf, C, Si, Ge, Sn, Pb$ ) using density functional theory calculations.<sup>38</sup>

Many researchers have used theoretical chemistry to investigate species containing polynitrogen rings. The theoretical calculations of Gagliardi and Pyykkö found that  $ScN_7$  has a local minimum with  $C_{7v}$  symmetry,<sup>9</sup> and that the sandwich structures of  $N_5MN_7$  ( $M = Ti, Zr, Hf, Th$ ) are locally stable.<sup>40</sup> Other species with polynitrogen rings, such as  $CsN_7Ba$ <sup>39</sup> and  $MN_6$  ( $M = Ti, Zr, Hf, Th$ ),<sup>40</sup> were also investigated theoretically. Theoretical calculations also predicted the possible existence of high-energy nitrogen-rich pentazolides with a very large nitrogen-to-element ratio, such as  $[M(N_5)_8]^{2-}$  ( $M = Cr, Mo, W$ ).<sup>11</sup> After that, Duan and Li investigated a series of polynitrogen ring species ( $ScN_6^-$ ,  $TiN_6$ ,  $VN_6^+$ ,  $Ca_2N_6$ , and  $ScN_6Cu$ ) using density functional theory calculations.<sup>41</sup> Jin and Ding calculated the sandwich structures of  $[N_3NiN_3]^{2-}$  and  $[N_3MN_5]^q$  [ $(M, q) = (Ni, 0), (Co, -1), (Fe, -2)$ ] using density functional theory.<sup>42,43</sup> Very recently, an investigation of stable high pressure phases of potassium azide using the first-principles method and the evolutionary algorithm suggested that planar  $N_6$  rings may be formed in potassium azide at a pressure of 100 GPa.<sup>44</sup>

Overall, the previous experimental and theoretical studies have shown that metal-nitrogen clusters may exist in the forms of  $M-(N_2)_n$  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  $TiN_{12}^+$  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  $TiN_{12}^+$  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.<sup>45</sup> Briefly, the  $TiN_{12}^+$  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  $TiN_{12}^+$  cluster ions were further investigated *via* photodissociation experiments. During the photodissociation experiments, the  $TiN_{12}^+$  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.<sup>46</sup> Geometry optimization and frequency analysis were performed at the B3LYP/6-31G\* level.<sup>47,48</sup> The ionization energy of Ti and the bond length of the  $N_2$  molecule were calculated to verify the accuracy of our method. The calculated ionization energy of Ti is about 656 kJ mol<sup>-1</sup> and the N-N bond length is about 1.10 Å, which are consistent with the experimental values of 658.8 kJ mol<sup>-1</sup> and 1.0977 Å.<sup>49</sup> The binding energy is defined as ( $n$  is the number of  $N_2$  molecules):

$$E_{b1} = -[E(TiN_{2n}) - E(Ti) - n \times E(N_2)]/n \text{ (for neutral clusters)}$$

$$E_{b2} = -[E(TiN_{2n}^+) - E(Ti^+) - n \times E(N_2)]/n \text{ (for ionic clusters)}$$

To gain further insight into the interactions between the  $N_2$  molecules and Ti or  $Ti^+$ , we performed natural bond orbital (NBO) analysis,<sup>50</sup> 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  $i \rightarrow j$  is given by

$$E_2 = \Delta E_{ij} = q_i \left[ \frac{F(i,j)^2}{\epsilon_j - \epsilon_i} \right]$$

where  $q_i$  is the donor orbital occupancy,  $\epsilon_i$  and  $\epsilon_j$  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  $TiN_{12}^+$ . It is very interesting that there are no mass peaks due to other  $TiN_n^+$  clusters. This indicates that  $TiN_{12}^+$  may have the most stable or symmetric structure in comparison with other clusters. In addition to the mass peak of  $TiN_{12}^+$ , we also observed weak mass peaks corresponding to  $TiON_8^+$ ,  $TiON_{10}^+$ , and  $TiO_2N_9^+$  in the mass spectrum. The detection of  $TiON_{10}^+$  is similar to the formation of  $TiO^+(N_2)_5$  by gas phase clustering of  $N_2$  molecules on  $TiO^+$  reported by Daly and El-Shall.<sup>51</sup>

The photodissociation of  $TiN_{12}^+$  was conducted using 266, 532 and 1064 nm photons. No fragment ions were observed when  $TiN_{12}^+$  was photodissociated by 1064 nm photons. The photodissociation mass spectra of  $TiN_{12}^+$  at 532 and 266 nm



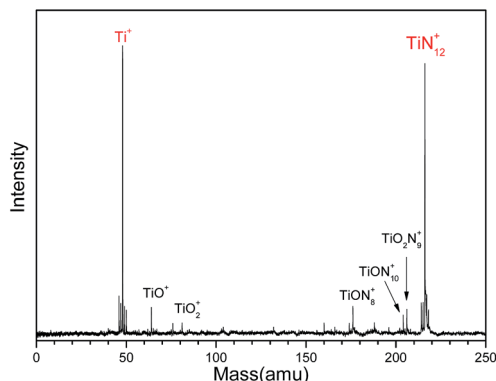


Fig. 1 Typical mass spectrum of Ti–N clusters generated by laser ablation of a Ti : BN mixture target.

are shown in Fig. 2.  $\text{TiN}_8^+$ ,  $\text{TiN}_6^+$ ,  $\text{TiN}_4^+$ ,  $\text{TiN}_2^+$  and  $\text{Ti}^+$  fragment ions were produced when  $\text{TiN}_{12}^+$  was photodissociated by 532 nm photons, and the  $\text{TiN}_6^+$  fragment had the highest abundance. This indicates that  $\text{TiN}_{12}^+$  can lose at least 4 nitrogen atoms, and that the main dissociation channel when  $\text{TiN}_{12}^+$  was photodissociated by 532 nm photons was the loss of 6 nitrogen atoms. The fragment ions observed when  $\text{TiN}_{12}^+$  was photodissociated by 266 nm photons were  $\text{TiN}_4^+$ ,  $\text{TiN}_2^+$ , and  $\text{Ti}^+$ , which shows that  $\text{TiN}_{12}^+$  can lose at least 8 nitrogen atoms.

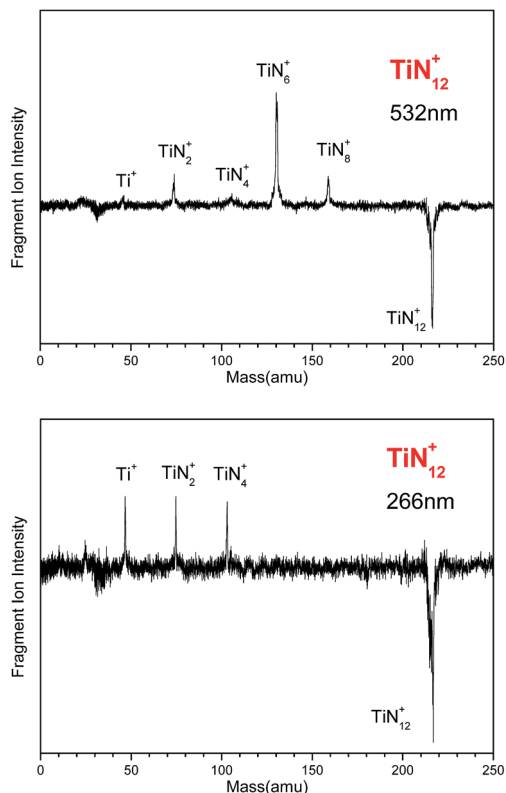


Fig. 2 Photodissociation mass spectra of the  $\text{TiN}_{12}^+$  cluster at 532 and 266 nm.

## 4 Theoretical results

We started with one  $\text{N}_2$  molecule bonded to Ti and  $\text{Ti}^+$ . We calculated both the end-on linear structure and the side-on triangular structure, and found that for  $\text{TiN}_2$  the end-on linear geometry is 0.34 eV lower in energy than the side-on geometry, while for  $\text{TiN}_2^+$  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  $\text{TiN}_2$  and  $\text{TiN}_2^+$ , respectively.  $\text{TiN}_2$  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  $\text{TiN}_2^+$ , 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  $\text{TiN}_{12}$  and  $\text{TiN}_{12}^+$ , we selected six initial geometrical configurations consisting of one Ti and six  $\text{N}_2$  molecules (Fig. 3,  $I_1$ – $I_6$ ), and two structures consisting of one Ti atom and four  $\text{N}_3$  moieties (Fig. 3,  $I_7$  and  $I_8$ ). We also considered structures composed of one Ti atom, one  $\text{N}_5$  ring and one  $\text{N}_7$  ring ( $\text{N}_5\text{TiN}_7$ ) (Fig. 3,  $I_9$ ), and one Ti and two  $\text{N}_6$  rings ( $\text{N}_6\text{TiN}_6$ ) (Fig. 3,  $I_{10}$ ). After full relaxation, it was found that, for the neutral cluster, the initial structures of  $I_1$ ,  $I_2$  and  $I_3$  converged to the same structure with  $D_{3d}$  symmetry, labeled as  $N_{1-3}$  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  $N_4 \sim N_{10}$  in Fig. 3, have much higher energies than isomer  $N_{1-3}$ . Their relative energies, calculated with respect to the lowest energy configuration, and symmetries are also given in Fig. 3. In the lowest energy geometry ( $N_{1-3}$ ), the Ti– $\text{N}_2$  distance and N–N bond length are 2.09 and 1.12 Å, respectively. The average binding energy of each  $\text{N}_2$  molecule with Ti in isomer  $N_{1-3}$  is 0.79 eV, which is larger than that in  $\text{TiN}_2$ . The  $\text{Ti}(\text{N}_3)_4$  structure with  $T_d$  symmetry is 6.18 eV higher in energy than the most stable  $\text{Ti}(\text{N}_2)_6$  complex. The linear Ti–N–NN bond angles of the  $T_d$  structure calculated in this work are in agreement with those obtained from previous theoretical calculations on free gaseous  $\text{Ti}(\text{N}_3)_4$ .<sup>37,38</sup> These bond angles were found to vary in the solid phase due to solid-state effects.<sup>25</sup> The  $\text{N}_5\text{TiN}_7$  structure has a Ti atom sandwiched by an  $\eta^5\text{-N}_5$  ring and an  $\eta^7\text{-N}_7$  ring, similar to that reported by Gagliardi and Pyykkö.<sup>10</sup> It is worth mentioning that  $\eta^5\text{-}\eta^7$  sandwich structures were also observed in  $(\text{C}_5\text{H}_5)\text{M}(\text{C}_7\text{H}_7)$  type compounds, where M is a transition metal.<sup>52–54</sup> The  $\text{N}_6\text{TiN}_6$  structure exhibits  $D_{2d}$  symmetry, in which the two  $\text{N}_6$  rings are distorted and only two N atoms in each  $\text{N}_6$  ring interact directly with the Ti atom, with a shorter Ti–N distance of 1.98 Å. The  $\text{N}_5\text{TiN}_7$  and  $\text{N}_6\text{TiN}_6$  structures are higher in energy than the most stable  $\text{Ti}(\text{N}_2)_6$  complex by 13.65 and 14.89 eV respectively. According to the calculated binding energies, the decomposition of  $\text{Ti}(\text{N}_3)_4$ ,  $\text{N}_5\text{TiN}_7$ , and  $\text{N}_6\text{TiN}_6$  into a Ti atom and six  $\text{N}_2$  molecules could release energies of 139, 857, and 978  $\text{kJ mol}^{-1}$  respectively.

For the cationic  $\text{TiN}_{12}^+$  cluster, the initial structures of  $I_1$ ,  $I_2$ ,  $I_3$  and  $I_4$  converged to one structure ( $P_{1-4}$ ) with  $O_h$  symmetry, as shown in Fig. 3. This is the lowest energy configuration of  $\text{TiN}_{12}^+$  with a  $\text{Ti}^+\text{-N}_2$  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



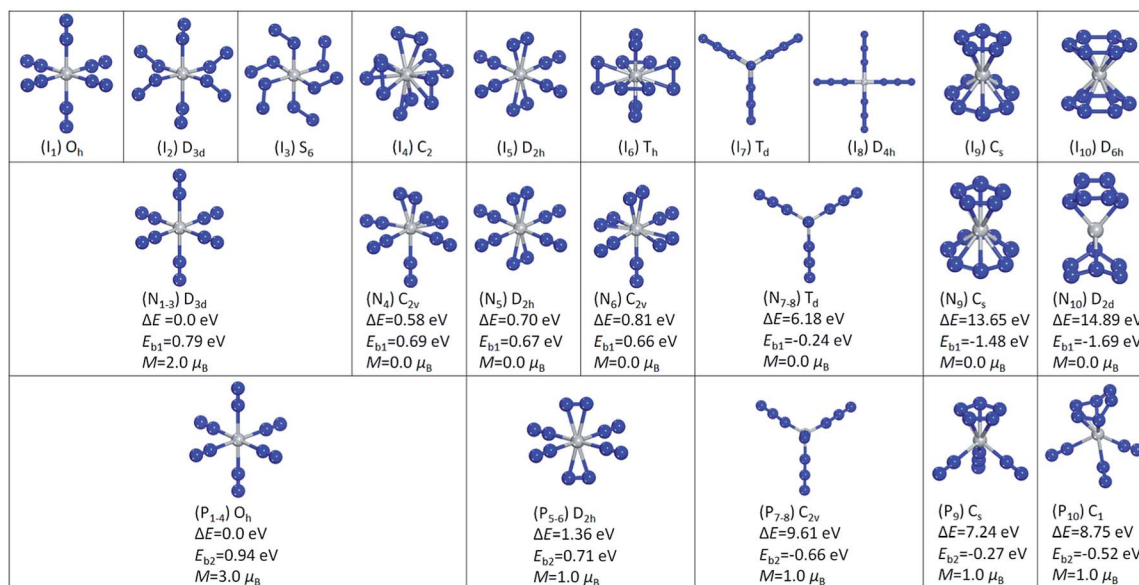


Fig. 3 Ten initial structural isomers of TiN<sub>12</sub> (I<sub>1</sub>–I<sub>10</sub>). Optimized structures and the corresponding relative energies ΔE calculated with respect to the lowest energy structures N<sub>1–3</sub> and P<sub>1–4</sub>, average binding energies E<sub>b1</sub> and E<sub>b2</sub>, and magnetic moments of the neutral TiN<sub>12</sub> (N<sub>1</sub>–N<sub>10</sub>) and TiN<sub>12</sub><sup>+</sup> (P<sub>1</sub>–P<sub>10</sub>).

average binding energy of each N<sub>2</sub> with Ti in isomer P<sub>1–4</sub> was calculated to be 0.94 eV. The other optimized isomers, namely P<sub>5–6</sub>, P<sub>7–8</sub>, P<sub>9</sub> and P<sub>10</sub> in Fig. 3, were found to be higher in energy than isomer P<sub>1–4</sub> by 1.36, 9.61, 7.24 and 8.75 eV, respectively. The structure of Ti(N<sub>3</sub>)<sub>4</sub><sup>+</sup> has C<sub>2v</sub> symmetry. The N<sub>5</sub>TiN<sub>7</sub> and N<sub>6</sub>TiN<sub>6</sub> structures of TiN<sub>12</sub><sup>+</sup> are not stable. The N<sub>5</sub>TiN<sub>7</sub> structure is rearranged into a N<sub>5</sub>Ti(N<sub>3</sub>)(N<sub>2</sub>)<sub>2</sub> type of structure, while the N<sub>6</sub>TiN<sub>6</sub> structure is rearranged into N<sub>6</sub>Ti(N<sub>2</sub>)<sub>3</sub> after the geometry optimizations. According to the calculated binding energies, the decomposition of Ti(N<sub>3</sub>)<sub>4</sub><sup>+</sup>, N<sub>5</sub>Ti(N<sub>3</sub>)(N<sub>2</sub>)<sub>2</sub><sup>+</sup>, and N<sub>6</sub>Ti(N<sub>2</sub>)<sub>3</sub><sup>+</sup> can release energies of 382, 156, and 301 kJ mol<sup>-1</sup>, respectively.

## 5 Discussion

### 5.1 Comparison of binding energies

Based on the calculated binding energy of the most stable structure of the TiN<sub>12</sub><sup>+</sup> cluster (0.94 eV), the energy of a 532 nm photon is able to dissociate two N<sub>2</sub> molecules from isomer P<sub>1–4</sub>, while the energy of a 266 nm photon is able to dissociate four N<sub>2</sub> molecules. This is in good agreement with our photodissociation experiment, as the experiment showed that the photodissociation of TiN<sub>12</sub><sup>+</sup> at 532 nm could remove at least 4 nitrogen atoms (two N<sub>2</sub> molecules), and photodissociation at 266 nm could remove at least 8 nitrogen atoms (four N<sub>2</sub> molecules). The detection of no photofragments at 1064 nm indicates that the energy barrier for the dissociation of TiN<sub>12</sub><sup>+</sup> is higher than 1.16 eV. In the experiment, the production of TiN<sub>6</sub><sup>+</sup>, TiN<sub>4</sub><sup>+</sup>, TiN<sub>2</sub><sup>+</sup> and Ti<sup>+</sup> fragments at 532 nm, and the production of TiN<sub>2</sub><sup>+</sup> and Ti<sup>+</sup> 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 TiN<sub>12</sub><sup>+</sup> cluster detected in our experiment has the form Ti(N<sub>2</sub>)<sub>6</sub><sup>+</sup> with O<sub>h</sub>

symmetry. This is consistent with the matrix infrared and ultraviolet-visible spectroscopy studies of Ti(CO)<sub>6</sub> and Ti(N<sub>2</sub>)<sub>6</sub> by Busby *et al.*<sup>55</sup>

Although the binding energy of neutral TiN<sub>2</sub> (0.25 eV) is smaller than that of TiN<sub>2</sub><sup>+</sup> (0.93 eV) by 0.68 eV, the Ti–N bond in neutral TiN<sub>2</sub> (1.94 Å) is actually shorter (stronger) than that in TiN<sub>2</sub><sup>+</sup> (2.18 Å), while the N–N bond in neutral TiN<sub>2</sub> (1.15 Å) is longer (weaker) than that in TiN<sub>2</sub><sup>+</sup> (1.11 Å). The decrease in the binding energy for neutral TiN<sub>2</sub> compared to TiN<sub>2</sub><sup>+</sup> 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 TiN<sub>2</sub><sup>+</sup> is weaker than that in the N<sub>2</sub> molecule; thus, the Ti–N bond strength in TiN<sub>2</sub><sup>+</sup> would be larger than the binding energy (0.93 eV). Moreover, the Ti–N bond in neutral TiN<sub>2</sub> is stronger than the Ti–N bond in TiN<sub>2</sub><sup>+</sup>. Hence, we obtain the relation: BE[(Ti–N)TiN<sub>2</sub>] > BE[(Ti–N)TiN<sub>2</sub><sup>+</sup>] > 0.93 eV, where BE[(Ti–N)TiN<sub>2</sub>] is the Ti–N bond energy in TiN<sub>2</sub> and BE[(Ti–N)TiN<sub>2</sub><sup>+</sup>] is the Ti–N bond energy in TiN<sub>2</sub><sup>+</sup>. This also implies that the N–N bond in neutral TiN<sub>2</sub> is weaker than those in TiN<sub>2</sub><sup>+</sup> and N<sub>2</sub> by at least 0.68 eV, which can be formularized as: BE[(N–N)TiN<sub>2</sub>] + 0.68 eV < BE[(N–N)TiN<sub>2</sub><sup>+</sup>] < BE[(N–N)N<sub>2</sub>], where BE[(N–N)TiN<sub>2</sub>], BE[(N–N)TiN<sub>2</sub><sup>+</sup>], and BE[(N–N)N<sub>2</sub>] are the N–N bond energies in TiN<sub>2</sub>, TiN<sub>2</sub><sup>+</sup> and N<sub>2</sub>, respectively.

Similarly, although the average binding energy of the most stable structure of TiN<sub>12</sub> (0.79 eV) is smaller than that of TiN<sub>12</sub><sup>+</sup> (0.94 eV) by 0.15 eV, the Ti–N bonds in neutral TiN<sub>12</sub> (2.09 Å) are actually shorter (stronger) than those in TiN<sub>12</sub><sup>+</sup> (2.17 Å), while the N–N bonds in neutral TiN<sub>12</sub> are longer (weaker) (1.12 Å) than those in TiN<sub>12</sub><sup>+</sup> (1.11 Å). We can also conclude that the Ti–N bond energies of both TiN<sub>12</sub> and TiN<sub>12</sub><sup>+</sup> are larger than 0.94 eV, BE[(Ti–N)TiN<sub>12</sub>] > BE[(Ti–N)TiN<sub>12</sub><sup>+</sup>] > 0.94 eV.



It is interesting to note that the average binding energy of each  $N_2$  with Ti in the ground state of neutral  $TiN_{12}$  is 0.79 eV, which is much larger than that in  $TiN_2$ , while the average binding energy of each  $N_2$  with  $Ti^+$  in the ground state of  $TiN_{12}^+$  is 0.94 eV, which is nearly the same as that in  $TiN_2^+$ . Considering the bond lengths in  $TiN_2$ ,  $TiN_{12}$ ,  $TiN_2^+$ , and  $TiN_{12}^+$ , we can see that the Ti–N bond lengths are in the order  $TiN_2^+ \approx TiN_{12}^+ > TiN_{12} > TiN_2$ , while the N–N bond lengths are in the order  $TiN_2^+ \approx TiN_{12}^+ < TiN_{12} < TiN_2$ . The Ti–N and N–N distances in  $TiN_2^+$  and  $TiN_{12}^+$  are very close to each other, while those in  $TiN_2$  and  $TiN_{12}$  are very different from each other. The Ti–N bond in  $TiN_2$  is much shorter than those in the other three species, and the N–N bond in  $TiN_2$  is much longer than those in the other species. In  $TiN_2$ , the N–N bond is weakened significantly due to the strong Ti– $N_2$  interaction. This could explain why the calculated binding energies of  $TiN_2^+$  and  $TiN_{12}^+$  are similar while the binding energy of  $TiN_2$  is much smaller than that of  $TiN_{12}$ . Overall, we have  $BE[(Ti-N)TiN_2] > BE[(Ti-N)TiN_{12}] > BE[(Ti-N)TiN_{12}^+] > BE[(Ti-N)TiN_2^+] > 0.93$  eV.

## 5.2 NBO analyses

To further address the differences in the binding energies, we performed NBO analyses for  $TiN_2$ ,  $TiN_2^+$ ,  $TiN_{12}$  and  $TiN_{12}^+$  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  $TiN_2$ , the Ti lone pairs in the spin-up channel with d-orbital components of 99.51% donate 0.64 electrons to the  $\pi$ -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  $TiN_2$  because of the large charge transfer between Ti and N1. On the other hand, in  $TiN_2^+$ , the charge donation from the lone pair on Ti to the antibonding orbital of  $N_2$  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  $N_2$  and  $Ti^+$ .

On going from  $TiN_2$  to  $Ti(N_2)_6$ , 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  $sp^3d^2$  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  $N_2$  molecule in  $Ti(N_2)_6$  compared to that in  $TiN_2$ .

Despite their different charges,  $TiN_{12}$  and  $TiN_{12}^+$  share some common features: (1) bonding orbitals are formed between Ti and N1, 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  $N_2$ . These two common features result in a reduction in the difference between the binding energies (0.79 versus 0.94 eV) of the  $N_2$  molecules in the neutral and charged  $TiN_{12}$ .

## 5.3 Electronic and magnetic properties

In the lowest energy structure of cationic  $TiN_{12}$ ,  $Ti^+$  is six-fold coordinated with  $O_h$  symmetry, in which the five d orbitals of Ti split into three-fold degenerate  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ , and two-fold degenerate  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. 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  $3.0 \mu_B$ . 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  $TiN_{12}^+$ , the neutral  $TiN_{12}$  cluster has one more electron, which would induce the Jahn–Teller effect. The symmetry changes from  $O_h$  to  $D_{3d}$ , and three electrons are spin-up and one electron is spin-down, leading to a total magnetic moment of  $2.0 \mu_B$  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  $TiN_{12}$  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  $TiN_{12}^+$  are given in Fig. 5(g–l), 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 ( $TiN_{12}^+$ ) compared with the neutral  $TiN_{12}$ .

As discussed above,  $TiN_{12}$  and  $TiN_{12}^+$  have magnetic moments of 2.0 and  $3.0 \mu_B$ , respectively. In order to see how the magnetic moments are distributed in the clusters, spin density

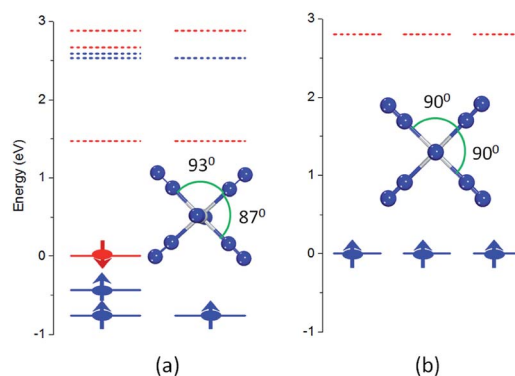


Fig. 4 Energy levels and optimized structures of  $TiN_{12}$  (a) and  $TiN_{12}^+$  (b). The solid and dashed lines represent occupied and unoccupied energy levels, respectively. The blue and red colors represent spin-up and spin-down, respectively. The Fermi level is set to zero eV.



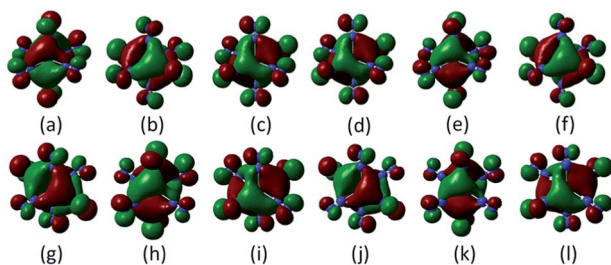


Fig. 5 Occupied orbitals and LUMOs of  $\text{TiN}_{12}$  (a–f) and  $\text{TiN}_{12}^+$  (g–l).

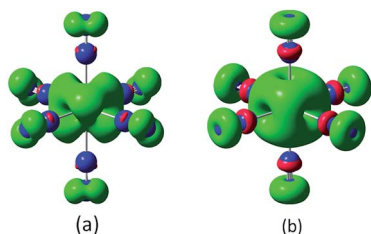


Fig. 6 Spin density distributions of  $\text{TiN}_{12}$  (a) and  $\text{TiN}_{12}^+$  (b) (isosurface value is 0.004).

isosurfaces are plotted in Fig. 6. They clearly show that the spin density of  $\text{TiN}_{12}^+$  is more symmetric, and that  $\text{Ti}^+$  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  $\text{TiN}_{12}^+$  cluster was generated experimentally and was further investigated by photodissociation experiments at 1064, 532, and 266 nm. The results showed that the  $\text{TiN}_{12}^+$  cluster has very high abundance compared to other  $\text{TiN}_n^+$  clusters. Density functional calculations were conducted to investigate the stable structures of  $\text{TiN}_{12}^+$  and its corresponding neutral cluster  $\text{TiN}_{12}$ . The calculated binding energy of the  $\text{TiN}_{12}^+$  cluster was in good agreement with the photodissociation experiment. The theoretical calculations found that the most stable structure of  $\text{TiN}_{12}^+$  is  $\text{Ti}(\text{N}_2)_6^+$  with  $O_h$  symmetry and the most stable structure of neutral  $\text{TiN}_{12}$  is  $\text{Ti}(\text{N}_2)_6$  with  $D_{3d}$  symmetry. The Ti–N bond strengths are greater than 0.94 eV in both  $\text{Ti}(\text{N}_2)_6^+$  and its neutral counterpart. The interaction between Ti and  $\text{N}_2$  weakens the N–N bond significantly. The  $C_{2v}$  azide isomer  $\text{Ti}(\text{N}_3)_4^+$  is higher in energy than the  $O_h$   $\text{Ti}(\text{N}_2)_6^+$  isomer by 9.61 eV. The azide isomer  $\text{Ti}(\text{N}_3)_4$  and the  $\text{N}_5\text{TiN}_7$  and  $\text{N}_6\text{TiN}_6$  structures are higher in energy than the most stable  $\text{Ti}(\text{N}_2)_6$  complex by 6.18, 13.65 and 14.89 eV respectively, indicating that the  $\text{N}_5\text{TiN}_7$  and  $\text{N}_6\text{TiN}_6$  isomers are potential candidates for high energy density materials.

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