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## Geometries and stabilities of chromium doped nitrogen clusters: mass spectrometry and density functional theory studies†

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Metal-doped nitrogen clusters serve as effective models for elucidating the geometries and electronic properties of nitrogen-rich compounds at the molecular scale. Herein, we have conducted a systematic study of VIB-group metal chromium (Cr) doped nitrogen clusters through a combination of mass spectrometry techniques and density functional theory (DFT) calculations. The laser ablation is employed to generate  $\text{CrN}_n^+$  clusters. The results reveal that  $\text{CrN}_8^+$  cluster exhibits the highest signal intensity in mass spectrometry. The photodissociation experiments with 266 nm photons confirm that the chromium heteroazide clusters are composed of chromium ions and  $\text{N}_2$  molecules. Further structural searches and electronic structure calculations indicate that the cationic  $\text{CrN}_8^+$  cluster possesses an X shaped geometry with  $D_2$  symmetry and exhibits robust stability. Molecular orbital and chemical bonding analyses demonstrate the existence of strong interactions between  $\text{Cr}^+$  cation and  $\text{N}_2$  ligands. The present findings enrich the geometries of metal doped nitrogen clusters and provide valuable guidance for the rational design and synthesis of novel transition metal nitrides.

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### 1 Introduction

Metal atoms, including transition metals (TMs), incorporated into nitrogen cluster nanoparticles are recognized as potential high-energy-density materials due to substantial energies released during the fragmentation reactions.<sup>1–6</sup> Compared to pure nitrogen clusters, which suffer from poor stabilization and challenging preparation processes, metal-doped nitrogen clusters exhibit distinctive properties. Normally, the nitrogen skeletons are prone to enhance their stabilities through bonding with the metal atoms and their structures show diversity, making them environmentally friendly high-energy-density

material candidates.<sup>7–10</sup> Thus, the investigations on the varied geometries and structural stabilities of metal-doped nitrogen clusters have attracted much attention. Ongoing efforts focus on understanding the distinct structural patterns and evolutions guided by different metal-doped nitrogen clusters, with the goal of elucidating the interactions and bonding mechanisms between the metal atoms and the main nitrogen ligands.

So far, researchers have conducted extensive studies on metal-doped nitrogen clusters through diverse experimental and theoretical methods. For example,  $\text{N}_4$  rings doped with alkaline earth metals ( $\text{M} = \text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ) exhibit pyramidal structures.<sup>11</sup> The syntheses of numerous binary azides, including group 4 elements (like Ti), group 5 elements (such as V, Nb and Ta),<sup>12–14</sup> group 6 elements (Mo and W),<sup>15</sup> group 15 element (Bi)<sup>16</sup> and so on, were systematically explored through experimental methods. Gagliardi *et al.*<sup>17</sup> identified a local minimum isomer with  $C_{7v}$  symmetry for  $\text{ScN}_7$  in Sc-doped N clusters and demonstrated the local stability of sandwich geometric structures in TM-doped  $\text{N}_5\text{MN}_7$  ( $\text{M} = \text{Ti, Zr, Hf, Th}$ ) clusters. In addition, the geometries and stabilities of numerous metal-doped polyazides (e.g., tri-azides  $\text{M}(\text{N}_3)_3$  ( $\text{M} = \text{Sc, Y, La, Al, Ga, In, Tl}$ )<sup>18–20</sup> of group 3 and 13, tetra-azides  $\text{M}(\text{N}_4)_3$  ( $\text{M} = \text{Ti, Zr, Hf, Th, Ge, Sn, Pb}$ )<sup>18,21</sup> of group 4 and 14, as well as novel aromatic compounds with planar  $\text{N}_6$  rings of  $\text{ScN}_6^-$ ,  $\text{VN}_6^+$ ,  $\text{Ca}_2\text{N}_6$ ,  $\text{ScN}_6$  Cu and  $\text{M}(\eta^6\text{N}_6)$  ( $\text{M} = \text{Ti, Zr, Hf, Th}$ )<sup>22,23</sup> and so on), have been extensively studied both experimentally and theoretically.

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In particular, in 2017, Zhang *et al.*<sup>2</sup> successfully synthesized the pentazolate anion cyclo- $\text{N}_5^-$ , revealing its unexpected stability and potential application in energetic polynitrogen compounds. Subsequently, Sun *et al.*<sup>24</sup> achieved a significant breakthrough in cyclo-pentazole chemistry by experimentally isolating the  $\text{AgN}_5$  of the cyclo- $\text{N}_5^-$  metal complex. Wang *et al.*<sup>25</sup> reported the synthesis of planar  $\text{N}_6^{2-}$  hexazine dianions through potassium azide ( $\text{KN}_3$ ) under high pressure. Laniel *et al.*<sup>26</sup> conducted a study on the synthesis of the  $\text{K}_9\text{N}_{56}$  compound by laser heating under high pressure and a first principles calculations. The results revealed that the  $\text{K}_9\text{N}_{56}$  compound comprises a complex arrangement of planar aromatic hexazine  $[\text{N}_6]^{4-}$  and  $[\text{N}_5]^-$  rings, along with neutral nitrogen dimers. Moreover, the diverse properties exhibited by metal-doped nitrogen clusters of varying sizes have stimulated scientists to systematically explore the size-dependent properties of these clusters. In recent years, there has been a surge of in-depth studies focusing on the alkali metal hetero-azide clusters, specifically  $\text{LiN}_n^+$  and  $\text{Li}_2\text{N}_n^{+}$ ,<sup>27-29</sup> as well as potassium heteroazide clusters ( $\text{KN}_n^+$ ),<sup>30</sup> and sodium hetero-azide clusters ( $\text{NaN}_n^+$ ).<sup>29</sup> Substantial advancements and notable progress have been achieved.

Except for the main group elements, other attentions were directed towards the TM-doped nitrogen clusters, *i.e.*  $\text{MN}_n^+$  ( $\text{M} = \text{Sc}, \text{Zr}, \text{V}, \text{Cu}, \text{Fe}, \text{Co}, \text{Ni}, \text{Ti}, \text{Zn}$ ),<sup>31-35</sup> which focus on the generations and geometries of these clusters, shedding light on their structure and electronic properties. These findings verify the imperative for further exploration of the structures and characteristics of metal-doped nitrogen clusters. A deeper comprehension of the bonding modes between metal and nitrogen atoms holds promise for the rational design of stabilizers and catalysts tailored for all-nitrogen materials. Overall, these studies reveal the profound impact of metal doping, including transition metals, in modulating the geometric and electronic properties of nitrogen clusters, unveiling unique properties distinct from their bulk materials.

Cr is the inaugural element in group 6 of the periodic table, which exhibits distinctive physical properties, presenting as a steely-grey, lustrous, hard, and brittle transition metal. The  $[\text{Ar}]3\text{d}^54\text{s}^1$  electronic configuration of Cr fosters the formation of robust d-d bonds and notably short bond lengths (1.68 Å) in its dimers.<sup>36,37</sup> Beyond its inherent electronic properties, Cr holds significance in industrial applications, engaging in interactions with non-metallic elements such as oxygen,<sup>38</sup> carbon,<sup>39</sup> and nitrogen.<sup>39-41</sup> The versatility of Cr enhances its value, making it advantageous for applications as the catalyst or the coating for hard materials. Wang *et al.*<sup>42</sup> uncovered the nitrogen-induced magnetic transition of Cr atom in their exploration of  $\text{Cr}_m\text{N}$  ( $m = 2-5$ ) and  $\text{Cr}_2\text{N}_2$ . Specifically, the neighboring Cr atom exhibited antiferromagnetic coupling to nitrogen, causing the robust Cr-N bonds. The study of Cr doped nitrogen clusters also contributes to the understanding of the structural evolution and formation mechanisms of nitrogen rich compounds at the atomic and molecular levels. Some of them are expected to serve as precursors for energy-containing materials or the synthesis of nitrogen-riched

materials. Consequently, there is an intriguing impetus to study Cr doped nitrogen clusters and explore their unconventional chemical bonding patterns. This work involves a systematic study of Cr doped nitrogen clusters using laser sputtering and photolysis techniques in combination with DFT calculations. The objective is to achieve a comprehensive understanding of the structural evolutions and stabilities of Cr doped nitrogen clusters.

## 2 Methods

The experiments were conducted employing a custom-designed laser sputtering-time-of-flight (TOF) mass spectrometer.<sup>43</sup> The apparatus comprises a Nd:YAG laser, a laser sputtering ion source, a reflectance TOF mass spectrometer, a vacuum system, a carrier gas system, and a timing system, *etc.* It was successfully applied to prepare various metal doped nitrogen clusters.<sup>28,32-34</sup> Firstly, solid samples with a diameter of 13 mm and a thickness of 2–5 mm were fabricated using a tablet press, employing a Cr/AlN mole ratio of 2:1. Subsequently, the surface of the samples underwent pulsed laser sputtering on a laser sputtering-TOF mass spectrometer to generate chromium hetero nitrogen clusters. High-purity nitrogen served as the carrier gas during this process to facilitate the formation of chromium-hybrid nitrogen clusters, while liquid nitrogen was employed to cool the clusters generated by laser bombardment. The laser system was characterized by specific operational parameters, namely a wavelength of 532 nm, a pulse energy of approximately 10 mJ, and a repetition frequency of 10 Hz. At a pressure of approximately 4 atmospheres, nitrogen was introduced into the source region through a pulse valve (General Valve Series 9) to cool the clusters formed. The synthesized Cr doped nitrogen clusters were acceleration, deflection, and focusing with the carrier gas in the high-voltage electric field acceleration region, reaching the reflection region, and finally arriving at the microchannel plate (MCP) detector of the TOF mass spectrometer after reflection. Signals from the detectors were passed through a preamplifier and recorded by a 200 MHz digital acquisition card. The acquired digital data were subsequently organized and analyzed using self-programmed software. In addition,  $\text{CrN}_8^+$  cluster, which exhibits the stronger peak in mass spectra of the generated chromium heteroazide clusters, was photolysed with a laser at a wavelength of 266 nm using a mass gate in a time-of-flight mass spectrometer, and mass spectra of the photolysed products were obtained.

The systematic search of the potential energy surfaces (PESs) of neutral and cationic  $\text{CrN}_n^{0/+}$  ( $n = 2-11$ ) were performed using the CALYPSO package.<sup>44-46</sup> The CALYPSO package is based on the particle swarm optimization (PSO) method, which is very efficient in prediction structure of various cluster systems,<sup>47-52</sup> including boron clusters<sup>48</sup> and nitrogen clusters.<sup>34,47</sup> After cluster structural searches, numerous of neutral and cationic  $\text{CrN}_n^{0/+}$  with were obtained. We then selected candidate isomers for re-optimization based on the following criteria: (a) the isomer with relative lower energy less than 3 eV compared to

the lowest-energy structure. (b) The isomer with high symmetry. (c) The isomers with variegated geometries. Subsequently, the selected structures were re-optimized at the high-accuracy level of M06-2X/6-311+G(d,p), which was verified to be reliable in various DFT calculations of metal doped nitrogen clusters. The calculated bond length of  $N_2$  molecular is 1.090 Å which is in agreement with the experimental value of 1.097 Å.<sup>53</sup> For each isomer, various spin multiplicities (doublet, quartet, sextet for neutrals and singlet, triplet, quintet for cations) were considered. During the geometric optimizations, the vibration frequencies were considered for all low-lying isomers to ensure that the structures are stable and without imaginary frequencies. Chemical bonding analyses were performed using the natural bond orbital (NBO) and adaptive natural density partitioning (AdNDP) methods<sup>54</sup> to gain deeper insights into bonding characteristics. All computations were carried out using the Gaussian 09 package.<sup>55</sup>

### 3 Results and discussions

As depicted in Fig. 1(a), the chromium–nitrogen clusters produced by laser bombardment of Cr/AlN samples are mainly  $CrN_6^+$ ,  $CrN_8^+$ ,  $CrN_9^+$ , and  $CrN_{11}^+$  clusters. Notably, the signal intensity of  $CrN_8^+$  cluster is significantly higher than that of other chromium–nitrogen clusters. This observation suggests that  $CrN_8^+$  cluster represents the most stable isomer among the synthesized chromium–nitrogen clusters. In addition, mass spectral peaks of aluminum–nitrogen clusters, specifically

$AlN_2^+$ ,  $AlN_4^+$  and  $AlN_6^+$  are observed due to the presence of aluminum impurities. Then, laser photolysis of  $CrN_8^+$  cluster is performed at 266 nm, as shown in Fig. 1(b). The cationic  $CrN_8^+$  cluster exhibits two dissociation channels: one involving the loss of six N atoms, resulting in the production of  $CrN_2^+$  fragment ions, and the other involving the loss of eight N atoms, leading to the generation of  $Cr^+$  fragment ions.

The geometries, symmetries, spin multiplicities and relative energy differences of neutral and cationic chromium–nitrogen clusters are presented in Fig. 2 and 3, respectively. Each isomers of the neutral chromium–nitrogen cluster are labeled as  $na$ ,  $nb$ , and  $nc$  ( $na^+$ ,  $nb^+$ , and  $nc^+$  for cations), where  $n$  represents the number of N atoms in isomers. The letters a, b, and c ( $a^+$ ,  $b^+$ ,  $c^+$ ) denote the energy order of the isomers, respectively. By considering vibration frequencies, all the shown structures are identified to be stable. The calculated total energies and minimum frequencies of ground state and metastable isomers of chromium–nitrogen clusters are listed in Tables S1 and S2 of the ESI.† In addition, the electronic states of the ground state isomers are listed in Table 1.

The geometries of neutral  $CrN_n$  ( $n = 2$ –11) clusters are illustrated in Fig. 2. As for  $CrN_2$  cluster, the 2a ground state is a stable linear Cr–N–N configuration with electronic state of  $^5\Sigma$  and  $C_{\infty v}$  symmetry. Two metastable 2b and 2c isomers with  $C_{2v}$  symmetry are identified, representing a planar triangular geometry and an N–Cr–N nonlinear structure, respectively. The most stable structure of  $CrN_3$  cluster is 3a, wherein the Cr atom is nonlinearly attached to the  $N_3$  chain, exhibiting  $C_s$  symmetry.

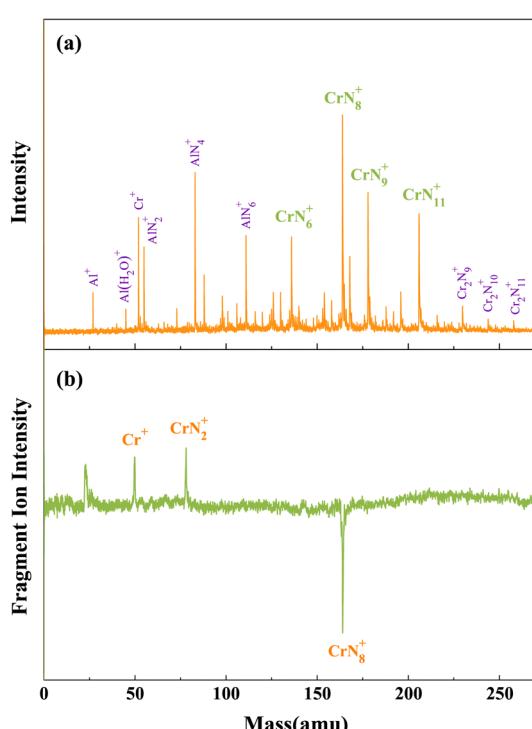


Fig. 1 (a) Mass spectra of  $CrN_n^{0/+}$  clusters produced by laser bombardment of Cr/AlN samples. (b) Photolysis mass spectra of  $CrN_8^+$  cluster at 266 nm.

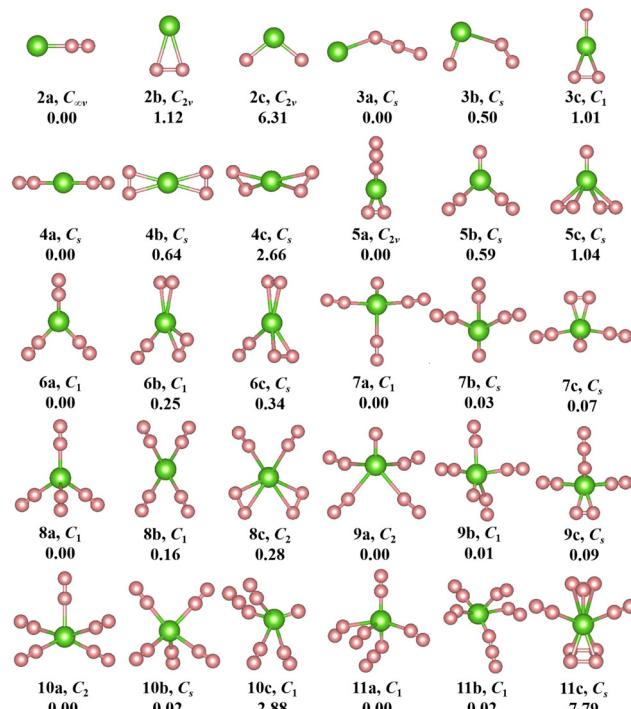


Fig. 2 The geometries, symmetries and relative energies (in eV) of optimized neutral  $CrN_n$  clusters ( $n = 2$ –11) at the M06-2X/6-311+G(d,p) level. The green and pink spheres represent Cr and N atoms, respectively.

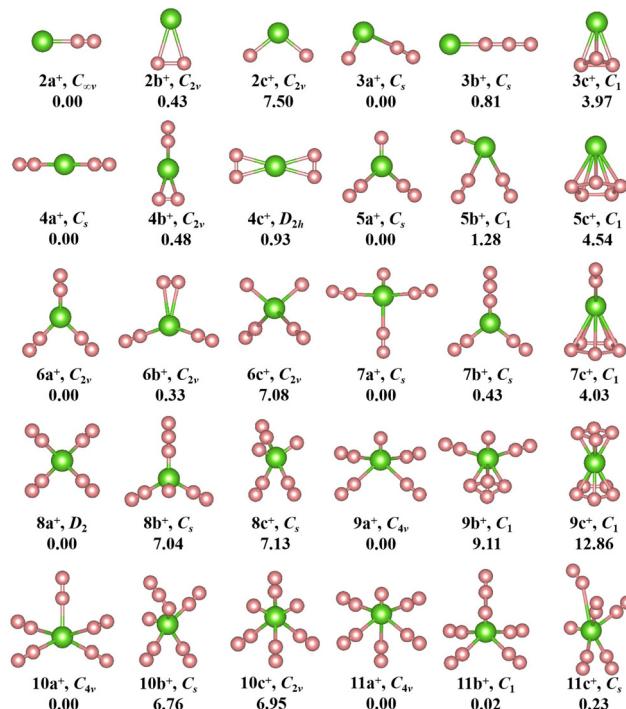


Fig. 3 The geometries, symmetries and relative energies (in eV) of optimized cationic  $\text{CrN}_n^+$  clusters ( $n = 2–11$ ) at the M06-2X/6-311G(d,p) level. The green and pink spheres represent Cr cation and N atoms, respectively.

Table 1 Electronic state,  $E_b$  (eV),  $\Delta^2E$  (eV) and charges  $Q(\text{Cr})$  (e) distributed on Cr atom for the low-lying  $\text{CrN}_n^{0/+}$  clusters

$\text{CrN}_n$				$\text{CrN}_n^+$				
$n$	State	$E_b$	$\Delta^2E$	$Q(\text{Cr})$	State	$E_b$	$\Delta^2E$	$Q(\text{Cr}^+)$
2	$^5\Sigma$	0.32		0.01	$^6\Sigma$	0.78		0.99
3	$^6A'$	-1.00	-3.57	0.75	$^3A''$	-1.37	-6.57	1.06
4	$^5A'$	0.13	3.01	-0.08	$^6A'$	0.84	6.55	0.89
5	$^6A_1$	-0.40	-2.65	0.80	$^3A''$	-0.46	-6.19	0.85
6	$^5A$	0.14	3.13	0.38	$^6A_1$	0.75	6.00	0.81
7	$^4A$	-0.38	-3.72	0.28	$^3A''$	-0.11	-5.80	0.61
8	$^5A'$	0.17	3.86	0.35	$^6A$	0.70	6.00	0.67
9	$^4A$	-0.27	-3.74	0.26	$^3A_2$	-0.01	-5.91	0.52
10	$^5B$	0.14	2.59	0.27	$^6A_2$	0.61	5.82	0.57
11	$^6A$	-0.01		0.58	$^3A_2$	0.06		0.41

The corresponding electronic state is  $^6A'$ . For  $n = 4$ , the ground state  $4a$  ( $^5A'$  electronic state) also possesses  $C_s$  symmetry and constitutes a linear  $\text{N}_2\text{-Cr-N}_2$  geometry derived by adding the  $\text{N}_2$  unit to  $2a$ . The replacement of the single N atom at the topmost part of  $3c$  by the  $\text{N}_3$  chain leads to the formation of  $5a$ . It is  $C_{2v}$  symmetry with  $^6A_1$  electronic state. In the  $\text{CrN}_6$  cluster, the  $^5A\text{-}6a$  ground state exhibits low symmetry of  $C_1$ , resembling a herringbone geometry similar to  $5b$ , with the central Cr atom attached to three  $\text{N}_2$  units. The geometry of  $7a$  (electronic state  $^3A$ ) in the  $\text{CrN}_7$  cluster is characterized by  $C_1$  symmetry, where the central Cr atom is linked by three  $\text{N}_2$  units and an isolated N atom. For  $\text{CrN}_8$  cluster, the  $^5A'\text{-}8a$  ground state is  $C_s$  symmetry and adopts an orthotetrahedral geometry containing

four  $\text{N}_2$  ligands. In the case of  $n = 9$ , the lowest energy isomer  $9a$  assumes the configuration of  $\text{CrN}(\text{N}_2)_4$  with  $^4A$  electronic state and  $C_1$  symmetry. The ground state isomer of  $\text{CrN}_{10}$  cluster is  $10a$ . It is  $C_2$  symmetry formed by the addition of the  $\text{N}_2$  unit to the  $8b$  isomer, which exhibits a spread-eagled shape, representing the configuration of  $\text{Cr}(\text{N}_2)_5$ . As for  $\text{CrN}_{11}$  cluster, the most stable isomer is  $11a$  ( $^6A$ ,  $C_1$ ) with the configuration of  $\text{CrN}_3(\text{N}_2)_4$ , which contains a  $\text{N}_3$  chain similar to  $3a$  and  $5a$ .

The geometries of cationic  $\text{CrN}_n^+$  ( $n = 2–11$ ) clusters are depicted in Fig. 3. The ground state structure of cationic  $\text{CrN}_2^+$  clusters, like neutral  $\text{CrN}_2$  cluster, is  $2a^+$  isomer. It is stable linear Cr–N–N geometry with  $C_{\infty v}$  symmetry. Two additional low-lying isomers are also observed: the planar triangular structure  $2b^+$  and the nonlinear N–Cr–N structure  $2c^+$ . Both exhibit  $C_{2v}$  symmetry. In  $\text{CrN}_3^+$  cluster, the ground-state  $3a^+$  is similar to neutral  $3b$  isomer, containing an isolated N atom and an  $\text{N}_2$  unit. It is  $C_s$  symmetry and the corresponding electronic state is  $^3A''$ . The  $3a$  ground state of neutral  $\text{CrN}_3$  undergoes a structural transition from a nonlinear geometry to a linear structure  $3b^+$  ( $\text{Cr}^+\text{-N}_3$ ) after the loss of one electron. For  $\text{CrN}_4^+$  clusters, like neutral isomer  $4a$ , the ground state is  $4a^+$  ( $^6A'$ ) with  $C_s$  symmetry, which is also a linear  $\text{N}_2\text{-Cr-N}_2$  structure. Similar to the neutral  $5b$  isomer, the most stable structure of the  $\text{CrN}_5^+$  cluster is  $5a^+$ . Its electronic state is  $^3A''$ . It is characterized by a herringbone shape with  $C_s$  symmetry. In the case of  $n = 6$ , the  $^6A_1\text{-}6a^+$  ground state contains three  $\text{N}_2$  units, similar to the neutral  $6a$ , but exhibits a herringbone geometry with  $C_{2v}$  symmetry. For  $\text{CrN}_7^+$  cluster, the geometry of the  $^3A''\text{-}7a^+$  ground state assumes an X-like shape of  $\text{Cr}^+\text{N}(\text{N}_2)_3$ , characterized by higher  $C_s$  symmetry compared to the neutral  $7a$ . Similar to  $7a$ ,  $8b$ , and  $7a^+$ , the ground state isomer  $8a^+$  (electronic state  $^6A$ ) with  $D_2$  high symmetry features the standard X-shape, where four  $\text{N}_2$  molecules interact equitably with the central Cr atom through their terminal nitrogen atoms. The ground state of  $\text{CrN}_n^+$  ( $n = 9–11$ ) clusters,  $^3A_2\text{-}9a^+$ ,  $^6A_2\text{-}10a^+$  and  $^3A_2\text{-}11a^+$ , exhibit a similar spread-eagled shape with the same  $C_{4v}$  symmetry, which are characterized by  $\text{Cr}^+\text{N}(\text{N}_2)_4$ ,  $\text{Cr}^+\text{N}(\text{N}_2)_5$ , and  $\text{Cr}^+\text{N}(\text{N}_2)_6$ , respectively.

Interestingly, the most stable structures of  $\text{CrN}_n^{0/+}$  ( $n = 2–11$ ) clusters, where  $n$  is even, the distinctive conformations,  $\text{Cr}(\text{N}_2)_{n/2}$  (or  $\text{Cr}^+\text{N}(\text{N}_2)_{n/2}$ ), are observed, which are characterized by N atoms interacting with the central Cr ion through the  $\text{N}_2$  ligands. Meanwhile, it is noted that the most stable isomers of neutral  $\text{CrN}_n$  ( $n = 2–11$ ) clusters transition from one-dimensional linear ( $C_{\infty v}\text{-}2a$ ,  $C_s\text{-}4a$ ) to two-dimensional branching ( $C_1\text{-}6a$ ) and further to three-dimensional tetrahedral ( $C_s\text{-}8a$ ) and square pyramid ( $C_2\text{-}10a$ ) configurations with the increase of number of  $\text{N}_2$  units, whereas the most stable isomers of cationic  $\text{CrN}_n^+$  ( $n = 2–11$ ) clusters transform from one-dimensional linear ( $C_{\infty v}\text{-}2a^+$ ,  $C_s\text{-}4a^+$ ) to two-dimensional branching ( $C_{2v}\text{-}6a^+$ ,  $D_2\text{-}8a^+$ ) and finally to three-dimensional square pyramid ( $C_{4v}\text{-}10a^+$ ) configurations. When the number of N atoms is odd (except for  $\text{CrN}_3$ ,  $\text{CrN}_5$  and  $\text{CrN}_{11}$ ), the N atoms are connected to the Cr atom to form the configurations of  $\text{CrN}(\text{N}_2)_{(n-1)/2}$  (or  $\text{Cr}^+\text{N}(\text{N}_2)_{(n-1)/2}$ ). These findings indicate that the chromium–nitrogen clusters are composed of Cr atom

(or  $\text{Cr}^+$  ion) and  $\text{N}_2$  molecules. The isomer with more number of  $\text{N}_2$  units usually exhibit relatively lower energies than the isomer with all-nitrogen units, such as the cationic  $\text{CrN}_9^+$  cluster. Similar results were reported by Ding *et al.*<sup>28,33,34</sup> for other metal doped nitrogen clusters. Notably, on the one hand, although the loss of an electron changes the spin multiplicity of chromium–nitrogen cluster, the geometrical symmetries and electronic states of  $2a^+$  and  $4a^+$  cations remain unchanged compared to their corresponding neutral ground states. On the other hand, in 3a, 5a and 11a, nitrogen units interact with Cr atoms in forms of  $\text{N}_3$  chains and  $\text{N}_2$  ligands. In addition, the spin multiplicities of ground states are mostly 4, 5 and 6 (6 for the  $\text{CrN}_n$  clusters ( $\text{CrN}_3$ ,  $\text{CrN}_5$  and  $\text{CrN}_{11}$ ) possessing  $\text{N}_3$  ligand) for neutral  $\text{CrN}_n$  clusters, and the symmetries of ground states in the large-sized  $\text{CrN}_n$  clusters decreases to  $C_1$  symmetry, except for  $\text{CrN}_{10}$  cluster. However, unlike the neutral clusters, the geometries of ground state cationic isomers exhibit relatively high symmetries with spin multiplicities of 3 or 6, which suggest that the loss of one electron in large-sized chromium–nitrogen clusters can result in enhanced symmetry.

To estimate the strengths of the interactions between Cr atom and N ligands as well as the relative stabilities among the  $\text{CrN}_n^{0/+}$  clusters, we have calculated the average binding energy and the second-order difference. The average binding energy  $E_b$  serves as an effective criterion for assessing the thermodynamic stability of cluster, while the second-order difference  $\Delta^2E$  is a crucial parameter reflecting the relative stability between adjacent clusters. The average binding energy and second-order difference values are calculated as below:

$$E_b(\text{CrN}_n^{0/+}) = 2[E(\text{Cr}^{0/+}) + n/2E(\text{N}_2) - E(\text{CrN}_n^{0/+})]/n \quad (1)$$

$$\Delta^2E(\text{CrN}_n^{0/+}) = E(\text{CrN}_{n+1}^{0/+}) + E(\text{CrN}_{n-1}^{0/+}) - 2E(\text{CrN}_n^{0/+}) \quad (2)$$

where  $E(\text{Cr}^{0/+})$  and  $E(\text{N}_2)$  denote the energies of Cr atom (or Cr cation) and  $\text{N}_2$  ligands, respectively, and  $E(\text{CrN}_n^{0/+})$  represents the total energy of  $\text{CrN}_n^{0/+}$  clusters. According to eqn (1), the calculated  $E_b$  values are presented in Table 1 and Fig. 4(a). The binding energy of the ground state of  $\text{CrN}_8^+$  cluster is 0.70 eV. It is noteworthy that the energy of photon in 266 nm laser is about 4.67 eV, which exceeds the energy required for the dissociation of  $\text{CrN}_8^+$  cluster into  $\text{Cr}^+$  cation and four  $\text{N}_2$  molecules (2.79 eV). It is in good agreement with the observation of  $\text{Cr}^+$  cation mass spectra peaks in the photolysis experiments. However, a small amount of  $\text{CrN}_2^+$  is still present in the photolysis products, which suggests potential factors influencing the experiments, such as the photon absorption cross section of the clusters. The calculated average binding energies are consistent with the photolytic experiments, thereby confirming that the current cluster structure searches of chromium–nitrogen clusters are reliable and the ground state structures are indeed the true local minima for respective cluster sizes.

The  $E_b$  curves show odd–even oscillations for both neutral and cationic chromium–nitrogen clusters with the increase of cluster sizes.  $E_b$  is positive when  $n$  is even, otherwise it is

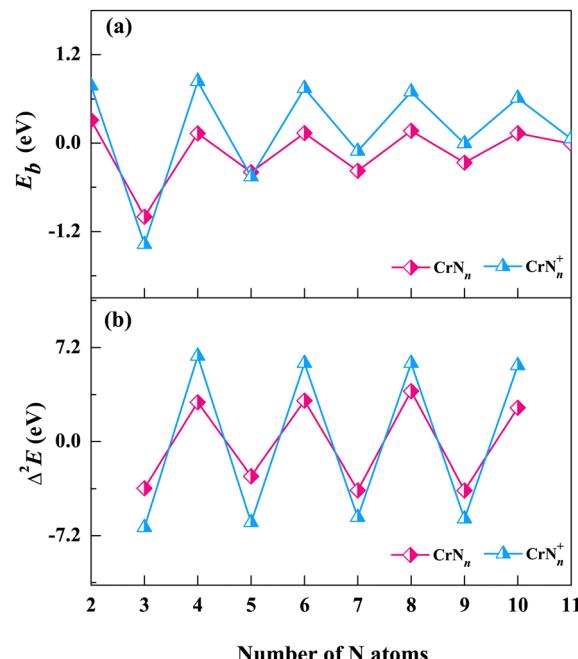


Fig. 4 The average binding energy  $E_b$  and the second order difference  $\Delta^2E$  of the low-lying isomers of  $\text{CrN}_n^{0/+}$  clusters. (a) average binding energy and (b) second order difference.

negative. The negative values indicate the absorption of the energies. Notably, the prominent peaks appear at  $n = \text{even}$ , and the peaks for cationic clusters are higher than those of neutral clusters. The odd–even oscillations observed in the  $E_b$  curves of  $\text{CrN}_n^{0/+}$  clusters are attributed to the interplay of quantum mechanical effects, particularly the shell structures of clusters. This phenomenon arises due to the quantization of energy levels associated with the discrete arrangement of Cr atom/cation within the  $\text{CrN}_n^{0/+}$  clusters. In  $\text{CrN}_n^{0/+}$  clusters with an even number of N atoms, such as  $n = 4, 6, 8, 10$ , the presence of the unpaired Cr atom/cation leads to enhanced stability, as the unpaired Cr atom/cation occupies a lower energy level, resulting in a higher average binding energy. Meanwhile, geometric analyses reveal that the low-lying isomers of  $\text{CrN}_n^{0/+}$  clusters predominantly adopt conformations of  $\text{Cr}(\text{N}_2)_{n/2}$  (or  $\text{Cr}^+(\text{N}_2)_{n/2}$ ) when  $n$  is even, which suggests the propensities of Cr atom/cation in both neutral and cationic chromium–nitrogen clusters readily interact with  $\text{N}_2$  ligands, resulting in the formation of stable structures. It is worth noting that, except for  $n = 3$  and 5, the  $E_b$  of cationic clusters are higher than those of the corresponding neutral clusters, especially pronounced when  $n = \text{even}$ . This observation implies that the removal of one electron enhances the stability of the most chromium nitrogen clusters.

The second-order difference values, calculated according to eqn (2), are presented in Table 1 and Fig. 4(b). The second-order difference curve also exhibits the obvious trend of odd–even oscillations, which is consistent with the average binding energy curves. Similarly, the significant peaks on the second-order difference curves are located at the points where  $n$  is even, with cationic clusters displaying greater amplitude of

oscillations. In cationic chromium–nitrogen clusters, the maximum value of  $\Delta^2E$  is 6.55 eV ( $\text{CrN}_4^+$ ), followed by 6.00 eV ( $\text{CrN}_8^+$ ). In neutral clusters, the maximum value is 3.87 eV ( $\text{CrN}_8$ ). The calculated results of both cationic and neutral clusters show that the chromium–nitrogen clusters with even number of N atoms are more stable in comparison to their adjacent clusters, reconfirming the stabilities of clusters containing the  $\text{N}_2$  units are more stable than those containing the single N atom. However, mass spectral results reveal that  $\text{CrN}_9^+$  and  $\text{CrN}_{11}^+$  with an odd number of N atoms also exhibit relatively high intensities in their mass spectral peaks, which is possibly attributed to their “kinetically easier formation” under the present reaction conditions. In addition, the HOMO–LUMO gap (HLG) is another important parameter to describe the thermodynamic stability of cluster, which reflects the energy required for the electron to transition from the HOMO to the LUMO, *i.e.*, the energy needed for an excited state transition. The HLGs of  $\text{CrN}_n^{0/+}$  clusters are listed in Table S3 of the ESI.† It can be seen that the HLGs of  $\text{CrN}_8^+$  clusters are 8.23 eV and 13.33 eV for  $\alpha$  and  $\beta$  orbitals, respectively, indicating their remarkable stabilities.

We next explore the electronic structures of  $\text{CrN}_n^{0/+}$  ( $n = 2–11$ ) clusters by assessing the charge transfer of Cr atoms (or  $\text{Cr}^+$  cations) using natural population analysis (NPA). The natural charges on Cr atoms (or  $\text{Cr}^+$  cations) are determined for structures corresponding to the lowest energy isomers. As shown in Fig. 5, the charge curve of Cr atom is positive (between 0 and 1) for neutral  $\text{CrN}_n$  clusters, except for  $\text{CrN}_4$ . The most notable peaks occur at  $n = 3, 5$  and  $11$ , and the Cr atoms in these clusters are observed to interact with the  $\text{N}_3$  ligand. The  $\text{Cr}^+$  cation charge distributions of cationic  $\text{CrN}_n^+$  clusters are also positive in the range of 0 to 1, except for  $n = 3$ , which show gradual decrease with  $n$  increasing. These results indicate that Cr atoms easily lose electrons in neutral  $\text{CrN}_n$  clusters, on the contrary, the  $\text{Cr}^+$  cations in  $\text{CrN}_n^+$  clusters are more likely to gain electrons. Notably, for  $n = 2$ ,  $\text{CrN}_2$  and  $\text{CrN}_2^+$  clusters share the same geometrical configuration of linear Cr–N–N. However, the charge of Cr atom in  $\text{CrN}_2$  cluster is 0, while the charge of  $\text{Cr}^+$  cation in  $\text{CrN}_2^+$  cluster is approximately 1, which suggests the more charge exchanges between the  $\text{N}_3$  ligand and the Cr atom compared to

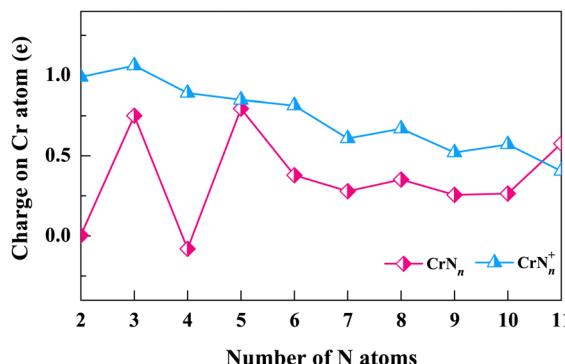


Fig. 5 Charges on the Cr atoms (or  $\text{Cr}^+$  cations) in the ground state structures of  $\text{CrN}_n^{0/+}$  clusters.

the  $\text{N}_2$  ligand. The NPA results suggest that the factors such as the cluster size, the N ligand configurations, and the oxidation states of Cr (neutral or cationic) in  $\text{CrN}_n^{0/+}$  ( $n = 2–11$ ) clusters are likely to influence the interactions and charge transfers between Cr atoms (or  $\text{Cr}^+$  cations) and N ligands.

Our experimental mass spectra of  $\text{CrN}_n^+$  ( $n = 2–11$ ) clusters reveal the predominant presence of the  $\text{CrN}_8^+$  cluster. Additionally, the comprehensive theoretical analyses of the relative stabilities of  $\text{CrN}_n^{0/+}$  ( $n = 2–11$ ) clusters demonstrate that the  $\text{CrN}_8^+$  cluster exhibits high  $D_2$  symmetry and excellent stability. Thus, we selected  $\text{CrN}_8^+$  cluster as an example to explore the molecular orbitals and the chemical bonding patterns of chromium doped nitrogen clusters. Clearly, the  $\text{CrN}_8^+$  cluster is open-shell structure. The diagrams of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as well as their eigenvalues with nearest-neighbor molecular orbitals (MOs) of  $\text{CrN}_8^+$  cluster are displayed in Fig. 6. The representations are segregated into  $\alpha$ - (spin-up) and  $\beta$ -orbitals (spin-down). The HOMO–LUMO gap for  $\text{CrN}_8^+$  cluster is 8.23 and 13.33 eV for  $\alpha$ - and  $\beta$ -orbitals, respectively. In  $\alpha$ -MOs, both LUMOs and HOMOs of  $\text{CrN}_8^+$  cluster are triple degeneration. The LUMOs are mainly contributed by N-2p atomic orbitals (AOs), especially  $2p_x$ , while Cr AOs contribute only 19.07–19.25%. The HOMOs are contributed by Cr-3d orbitals (88.93–88.98%), particularly  $3d_{xy}$ . Similarly, in  $\beta$ -MOs, triple degenerate LUMOs and HOMOs are also observed. The  $\beta$ -LUMOs are mainly contributed by Cr-AOs with 4p orbitals accounting for 35.71–36.06% and 3d orbitals for 14.59–14.75%. The largest contribution to  $\beta$ -HOMOs is the N-2p orbitals, with Cr-AOs accounting for only 2.67–2.68%. As mentioned above, the triple degeneracy of LUMOs and HOMOs at the  $\alpha$  and  $\beta$  orbitals of cationic  $\text{CrN}_8^+$  cluster is attributed to the fourfold collocation of  $\text{Cr}^+$  ion with the  $D_2$  symmetry, which leads to the splitting of the  $\text{Cr}^+$ -4p orbitals into the triple degenerate  $p_x$ ,  $p_y$ , and  $p_z$  orbitals and the  $\text{Cr}^+$ -3d orbitals into

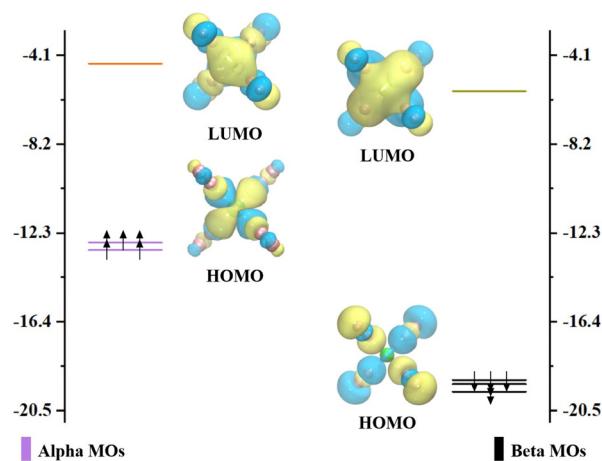


Fig. 6 The molecular orbitals of the ground state structure of  $\text{CrN}_8^+$  cluster. The purple and black lines indicate positions of the occupied  $\alpha$  and  $\beta$  orbitals, while the orange and green lines indicate the unoccupied  $\alpha$  and  $\beta$  orbitals, respectively.

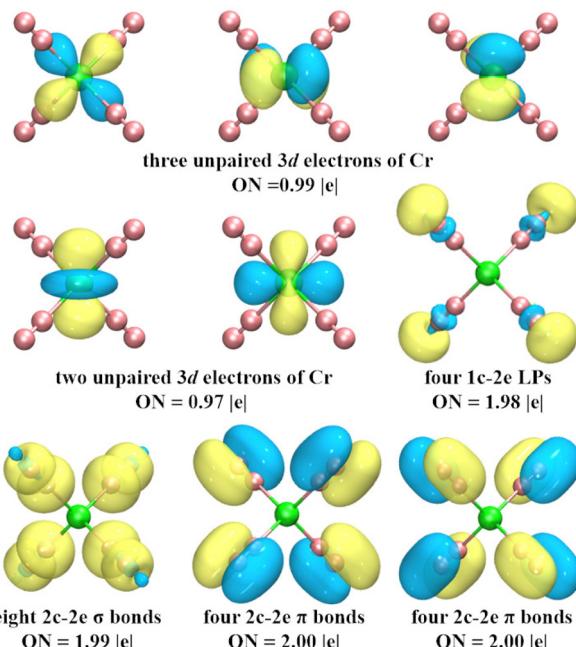


Fig. 7 AdNDP analysis of the ground state structure of  $\text{CrN}_8^+$  cluster. ON indicates the number of occupied electrons.

the triple degenerate  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals, as well as the double degenerate  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. However, as shown in Fig. S4 (ESI†), no degeneracy orbitals appear in the MOs of neutral  $\text{CrN}_8$  cluster. It is found that the neutral  $\text{CrN}_8$  cluster possesses an additional electron in comparison to  $\text{CrN}_8^+$  cluster, which induces the Jahn-Teller effect. The loss of an electron from the neutral  $\text{CrN}_8$  cluster leads to the degeneracy of AOs and the increase of the HLG values in  $\text{CrN}_8^+$  cluster. Meanwhile, the symmetry changes from  $D_2$  to  $C_s$ . The stability of  $\text{CrN}_8^+$  cluster is attributed to the strong interactions between the Cr-3d AOs and the N-2p AOs.

To explore the chemical bonding of  $\text{CrN}_8^+$  cluster, the multicenter chemical bonds between  $\text{Cr}^+$  cation and N atoms are analyzed by AdNDP method. The multicenter bonding is denoted as the  $xc$ -2e, where  $x$  denotes the number of centers involved ( $x$  can range from one center (*i.e.*, lone electrons on single atom) to the maximum number of atoms in the cluster (*i.e.*, fully delocalization bonding)), and ON denotes the number of electrons occupying the cluster, with an ideal value of 2.00 |e|. The AdNDP results (Fig. 7) show that the chemical bonding patterns of  $\text{CrN}_8^+$  clusters can be categorized into: five localized spin orbitals (LSOs) occupied by a single electron, four lone pairs (LPs), and 16 two center–two electron bonds (2c-2e). The five 3d subshell layers are occupied by Cr-3d electrons. These LSOs exhibit inert characteristics, devoid of participating in the chemical bonding. The four LPs with ON = 1.98 |e| mainly comprise 2s electrons of N atoms. The sixteen 2c-2e bonds, with ON values approximating the ideal value of 2.00 |e|, contain three types of bonds: the N–N  $\sigma$  bond, the N–N  $\pi$  bond, and the Cr–N  $\sigma$  bond. Among them, eight N–N  $\pi$ -bonds and four N–N  $\sigma$ -bonds contribute to the chemical bonding between the  $\text{N}_2$  units, while the remaining four  $\sigma$ -bonds

between Cr and N describe the strong chemical bonds between the central Cr cation and the  $\text{N}_2$  units. These bonds are collectively responsible for the stability of cationic  $\text{CrN}_8^+$  cluster. In addition, the chemical bonding patterns of neutral  $\text{CrN}_8$  cluster are shown in Fig. S5 (ESI†). Similarly, the fifteen 2c-2e bonds of  $\text{CrN}_8$  cluster are divided into three bonding modes, *i.e.* N–N  $\sigma$  bonds, N–N  $\pi$  bonds, and Cr–N  $\sigma$  bonds. Thus, it can be inferred that the presence of strong chemical bonds between Cr cation and  $\text{N}_2$  ligands enhances the stability of cationic  $\text{CrN}_8^+$  cluster.

## 4 Conclusions

In summary, we have produced chromium heteroazide clusters, namely  $\text{CrN}_6^+$ ,  $\text{CrN}_8^+$ ,  $\text{CrN}_9^+$ , and  $\text{CrN}_{11}^+$ , using laser sputtering techniques. The photodissociation results indicate the remarkable abundance of  $\text{CrN}_8^+$  cluster compared to other chromium–nitrogen clusters. Subsequently, we have systematically studied the geometries, stabilities and electronic properties of  $\text{CrN}_n^{0/+}$  clusters ( $n = 2$ –11) by CALYPSO cluster structural search method and DFT calculations at the M06-2X/6-311+G(d,p) level. The obtained ground state structures of cationic chromium–nitrogen clusters are in good agreement with the mass spectra experiments. The calculated results reveal that the isomer with multiple  $\text{N}_2$  units tend to possess relatively lower energy than those with all-nitrogen units in chromium–nitrogen clusters. Cationic  $\text{CrN}_n^+$  ( $n = 2$ –11) clusters, upon electron loss, exhibit enhanced symmetry and stability, especially for  $\text{CrN}_8^+$  ( ${}^6\text{A}$ ,  $D_2$ ) cluster. Most ground state structures conform to configurations of  $\text{Cr}^{0/+}(\text{N}_2)_{n/2}$  and  $\text{Cr}^{0/+}\text{N}(\text{N}_2)_{(n-1)/2}$ . Molecular orbital analyses of  $\text{CrN}_8^{0/+}$  clusters elucidate the emergence of the Jahn–Teller effect, primarily influenced by the interactions of the Cr-3d and N-2p orbitals. This effect is accompanied by a notable elevation in the HOMO–LUMO gap of cationic  $\text{CrN}_8^+$  cluster. These results provide valuable insights for understanding the structural evolutions, chemical bonding and growth mechanisms of Cr doped nitrogen clusters, which provide an important avenue for the design and synthesis of novel transition metal nitrides.

## Conflicts of interest

There are no conflicts to declare.

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