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Mass Spectrometry and Theoretical Investigation of VN_n^+ (n = 8, 9, and 10) Clusters

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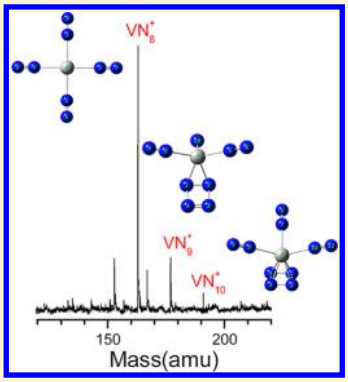
ABSTRACT: VN_n^+ clusters were generated by laser ablation and analyzed by mass spectrometry. The results showed that VN_8^+, VN_9^+, and VN_{10}^+ clusters were formed, and the mass peak of VN_8^+ is dominant in the spectrum. The VN_8^+ cluster was further investigated by a photodissociation experiment with 266 nm photons. Density functional theory calculations were conducted at the M06-2X/6-311+G(d,p) level to search for stable structures of VN_n^+ (n = 8, 9, and 10) and their neutral counterparts. The theoretical calculations revealed that the most stable structure of VN_8^+ is in the form of $V(N_2)_4^+$ with D_{4h} symmetry. The binding energy from the calculation is in good agreement with that obtained from the photodissociation experiments. The global minimum structures of VN_8, $VN_9^{+/0}$, and $VN_{10}^{+/0}$ contain a similar substructure of the N_4 ring and exhibit energy properties. The most stable structure of VN_9^+ is in the form of $(\eta^2\text{-}N_4)V^+N(N_2)_2$ with C_1 symmetry, while that of VN_{10}^+ is in the form of $(\eta^4\text{-}N_4)V^+(N_2)_3$ with C_s symmetry. For neutral VN_8, VN_9, and VN_{10}, $(\eta^4\text{-}N_4)V(N_2)_2$, $(\eta^4\text{-}N_4)V(N_3)(N_2)$, and $(\eta^4\text{-}N_4)V(N_2)_3$ are their ground-state structures, with decomposition into one V atom, and corresponding quantities of N_2 can release energies of about 50.20, 96.28, and 57.76 kcal/mol, respectively.



1. INTRODUCTION

The polynitrogen compounds are of significant interest as potential candidates for high-energy-density materials (HEDM).[1,2] Their high energy content stems from the N−N single and double bonds as well as the tension rings they possess.[3] Numerous theoretical[4,5] and experimental studies have been carried out to find new polynitrogen species, but only a few efforts have been successful. Christe and co-workers synthesized the N_5^+ ion in the form of an AsF_6^- salt in 1999.[6] Cacace and co-workers[7] detected a N_4 isomer with open-chain structure in 2002. At about the same time, Ashwani Vij and co-workers produced N_5^- following the collision-induced dissociation of the *para*-pentazolylphenolate anion.[8] One year later, Hansen and Wodtke[9] reported the first evidence for the production of a ring isomer of N_3, which is confirmed by later experimental[10−12] and theoretical[13,14] work. The synthesis of the N_4 ring was attempted as early as 1982 through a (2 + 2) cycloaddition reaction,[15−20] but it was not until 2012 that Camp and co-workers detected a tetraalkyl tetrazetidinetetracarboxylate radical cation,[21] which was the first discovery of a substituted N_4 ring in experiment as far as we know.

At same time, some scientists turned their eyes to metal-doped nitrogen clusters and predicted that novel all-nitrogen units comprising cyclic N_4,[22−25] N_5,[26] N_6,[27] and N_7[28] could exist in M−N clusters. This might be because the polynitrogen rings can be stabilized by the metal−ligand interaction. Cheng and Li predicted that an alkali metal cation (Li^+, Na^+, K^+, Rb^+, or Cs^+) and N_4^{2-} ring could form bipyramidal M_2N_4 structures,[23] which are likely to be stable and to be observed experimentally due to their significant isomerization or dissociation barriers. They also calculated MN_4 pyramidal structures formed by an alkaline earth cation (Ca^{2+}, Sr^{2+}, or Ba^{2+}) and the N_4 ring.[24] Mercero has studied the sandwich-like complexes $(N_4MN_4)^q$ ((M, q) = (Cr, Ni, 0), (V, Co, −1), (Ti, Fe, −2)) with a N_4^{2-} aromatic ring.[25] Jin and Ding calculated a type of heterodecked sandwichlike structure $(N_3MN_5)^q$ ((M, q) = (Ni, 0), (Co, −1), (Fe, −2)) containing two odd-membered all-nitrogen rings (N_3 and N_5).[26] Tsipis and Lein calculated first-row transition-metal pentazolato complexes.[27,28] Choi and co-workers predicted that $Ti(N_5)_4$ is a potential nitrogen-rich, stable, high-energy-density material.[29] Straka and Pyykkö proposed the possible high-energy nitrogen-rich pentazolides with a very large nitrogen-to-element ratio, such as $(M(N_5)_8)^{2-}$ (M = Cr, Mo, W).[30] Duan and Li investigated MN_6 (M = Ti, Zr, Hf, Th, Sc, and V) with polynitrogen rings using density functional theory calculations.[31] Gagliardi and Pyykkö found that ScN_7 has a local minimum with C_{7v} symmetry[32] and the

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sandwich structures of N_5MN_7 (M = Ti, Zr, Hf, and Th) are locally stable.[33]

Because of the additional advantages of M−N binary clusters in designing new structural groups, extensive work with a variety of experimental techniques has been undertaken to investigate novel metal nitrides. The binary azides, $M(N_3)_n$, of groups 4,[34] 5,[35−37] 6,[38] 14,[39−41] 15,[42,43] and 16[44,45] elements (M = Ti, Nb, Ta, Mo, and W) were synthesized and isolated in the experiments. $Nb^+(N_2)_n$ and $V^+(N_2)_n$ complexes were investigated by Duncan and co-workers using photodissociation spectroscopy.[46,47] The $Rh(N_2)_4^+$ complex was studied via infrared laser photodissociation spectroscopy and theoretical calculations.[48] The structure, bonding, and vibrations of $Fe(N_2)_n$ (n = 1−5) were investigated by density functional theory.[49] Jin and co-workers reported the spectroscopic identification of the $[B_3(N_2)_3]^+$ complex which features the smallest π-aromatic system, B_3^+.[50] Zhou studied the $[Gd_2N_2]$ complex and found remarkable N_2 activation and cleavage by the Gd dimer.[51] In our previous work, the TiN_{12}^+ clusters were generated by laser ablation, the most stable structure of which was found to be $Ti(N_2)_6^+$ with O_h symmetry.[52] Nevertheless, the N_3 and N_2 units studied in the above works are well known. It is still a great challenge to add new members to the polynitrogen compound family.

Vanadium, one of the early transition metals, can easily form multiple-decker sandwich structures with benzene (V_nBz_{n+1})[53−55] and could also be encapsulated by silicon to form VSi_n clusters.[56,57] In this study, we investigated the vanadium−nitrogen binary clusters by laser ablation and photodissociation experiments coupled with theoretical calculations in order to gain insight into the geometric structure of generated clusters and their neutral counterparts.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

2.1. Experimental Method. The experiments were conducted on a home-built apparatus equipped with a laser vaporization supersonic cluster source and a reflectron time-of-flight mass spectrometer (RTOF-MS), which has been described elsewhere.[58] Briefly, the VN_n^+ (n = 8, 9, and 10) cluster cations were generated in the laser vaporization source via laser ablation of a rotating and translating disk target of a V and BN mixture (13 mm diameter, V/BN mole ratio of 2:1) with the second harmonic of a nanosecond Nd:YAG laser (Continuum Surelite II-10). The typical laser power used in this work is about 10 mJ/pulse. Nitrogen gas with ∼4 atm backing pressure was allowed to expand through a pulsed valve (General Valve Series 9) into the source and to cool the formed clusters. The generated cluster cations were mass analyzed with the RTOF-MS. To further study the structure of the VN_n^+ (n = 8, 9, and 10) cluster, photodissociation experiments were employed. During the photodissociation experiments, the VN_8^+ 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 nm photons from another nanosecond Nd:YAG laser (Continuum Surelite II-10). The fragment ions and parent ions were then reaccelerated 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 digital data were collected on a laboratory computer with homemade software. In photodissociation experiments on the VN_9^+ and VN_{10}^+ cluster ions, no fragment ion was observed due to the weak mass signals of the parent ions.

2.2. Computational Method. A quantum chemistry study was performed with Gaussian 09 at the M06-2X/6-311+G(d,p) level of density functional theory (DFT) for geometry optimization and frequency calculations.[59−61] Every stationary point on the potential energy surface (PES) was confirmed to be local minimum-energy structure by all positive harmonic frequencies. The bond length of the N_2 molecule was calculated to verify the accuracy of our method. The calculated N−N bond length is about 1.090 Å, which is consistent with an experimental value of 1.097 Å.[62] The binding energy is defined as

$$E_{b1} = -2[E(VN_n) - E(V) - n/2E(N_2)]/n \text{ (for the neutral clusters)} \quad \text{(I)}$$

$$E_{b2} = -2[E(VN_n^+) - E(V^+) - n/2E(N_2)]/n \text{ (for the positive clusters)}$$

The formation energy is calculated with

$$\Delta_f E_1 = E(VN_n) - E(V) - n/2E(N_2) \text{ (for the neutral clusters)} \quad \text{(II)}$$

$$\Delta_f E_2 = E(VN_n^+) - E(V^+) - n/2E(N_2) \text{ (for the positive clusters)}$$

Throughout this article, bond lengths are given in angstroms, bond angles are given in degrees, and relative energies are given in kcal/mol.

3. RESULTS

3.1. Experimental Results. Figure 1 shows a typical mass spectrum of clusters generated in our experiment. It can be seen that the main mass peaks are V^+, VN_8^+, VN_9^+, VN_{10}^+, $V(H_2O)N_6^+$, and $V(H_2O)N_7^+$. The signal intensity of VN_8^+ is predominant compared to that of other vanadium−nitrogen clusters, which indicates that VN_8^+ may have the most stable or most symmetric structure in comparison to other clusters.

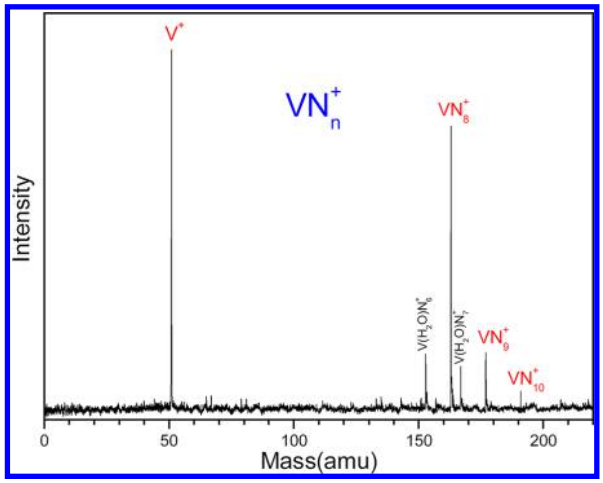

Figure 1. Typical mass spectrum of V−N clusters generated by laser ablation of a V/BN mixture target.

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The photodissociation of VN_8^+ was conducted with 266 nm photons. The products were VN_2^+ and V^+ fragment ions as shown by the mass spectrum in Figure 2, among which the abundance of V^+ is much higher. The result shows that the main dissociation channel is the loss of eight nitrogen atoms and the secondary channel is the loss of six nitrogen atoms. We also tried to conduct the photodissociation of VN_9^+ and VN_{10}^+, but no fragment ions were observed because of their weak mass signal.

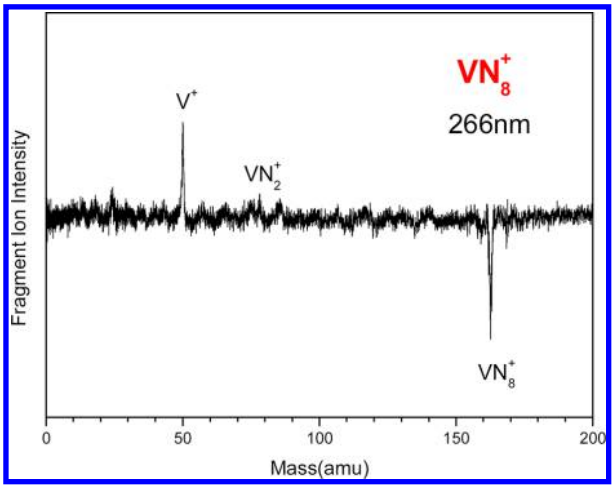

Figure 2. Photodissociation mass spectrum of the VN_8^+ cluster at 266 nm.

3.2. Theoretical Results. To search for the stable states of VN_n^+ and VN_n (n = 8, 9, and 10), we have conducted calculations for nine different systems, from VN_2 to VN_{10}. From the simplest system with two nitrogen atoms and vanadium, we designed the initial structures and found the geometrical structures of the lowest total energy states of each of them (data not shown). Then, by adding one nitrogen each time to the system, we got more and more geometrical configurations as the system became larger. By putting the nitrogen in different locations, we designed initial geometrical configurations of N_2 molecules, the N_3 chain and ring, and the N_4, N_5, N_6, and N_7 rings and so on with vanadium atoms. To ensure that we obtained a true minimum at the PES as a result of the geometry optimization, we performed frequency calculations on the optimized geometries for all of them. This strategy of defining the initial geometries can avoid overlooking any possible initial structures. For each initial geometrical configuration, we also considered many spin multiplicities (2, 4, and 6 for neutral clusters and 1, 3, and 5 for positive clusters).

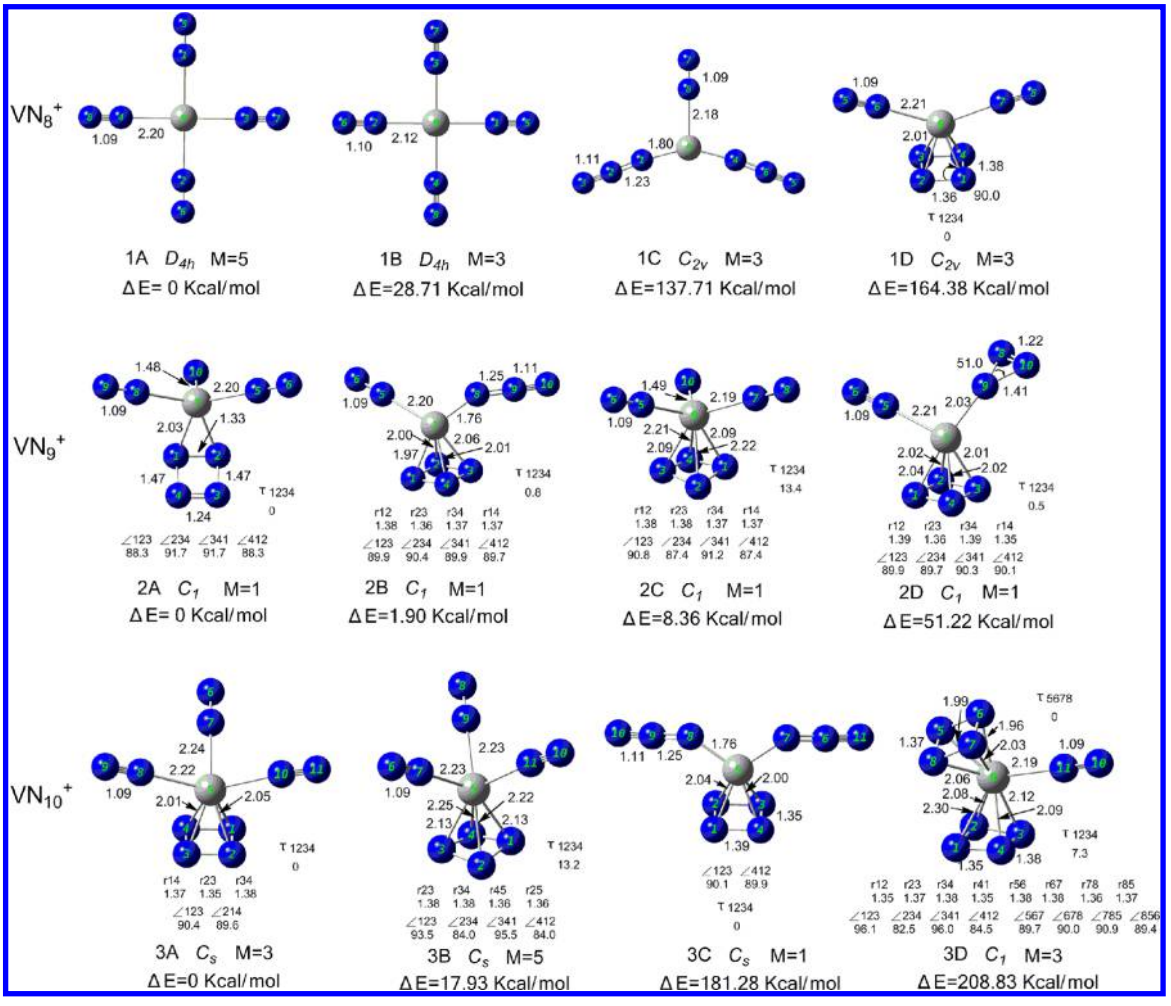

Figure 3. Structures and relative energies of the low-lying isomers of VN_n^+ (n = 8, 9, and 10) clusters. Bond lengths, angles, torsion angles of the planar ring (τ), symmetry, spin multiplicity (M), and ΔE are shown.

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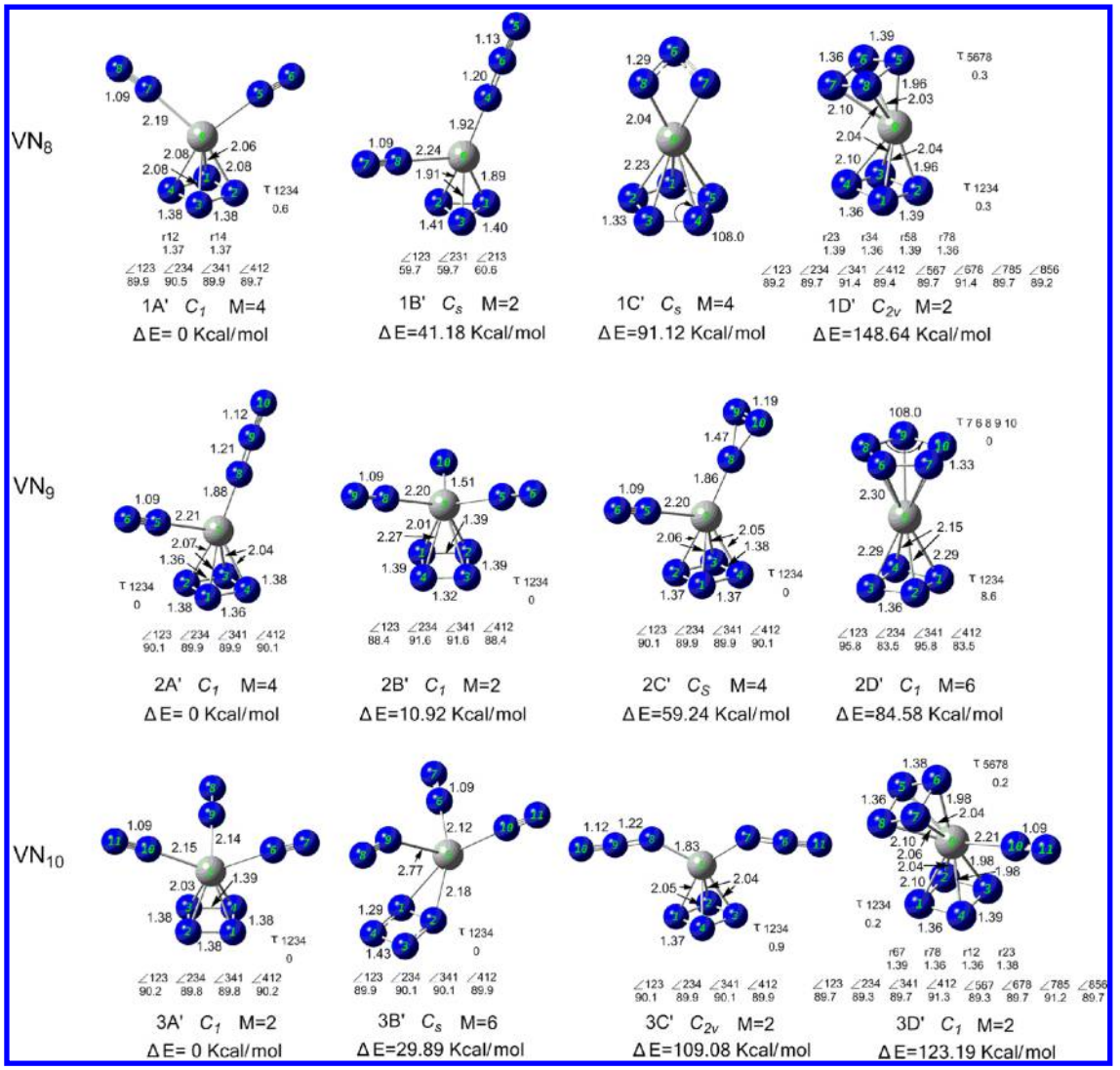

Figure 4. Structures and relative energies of the low-lying isomers of VN_n (n = 8, 9, and 10) clusters. Bond lengths, angles, torsion angles of the planar ring (τ), symmetry, spin multiplicity (M), and ΔE are shown.

After full relaxation, a rather large number of low-lying isomers of VN_n^+ and VN_n (n = 8, 9, and 10) were found. Here, we show the typical isomers of VN_n^+ (n = 8, 9, and 10) in Figure 3 with the most stable structures on the left and those of VN_n (n = 8, 9, and 10) in Figure 4. The calculated relative energies, binding energies, and formation energies of these low-lying isomers are summarized in Table 1.

3.2.1. Structures of VN_8^+ and VN_8. The calculated ground state of VN_8^+ (1A) has planar structure with D_{4h} symmetry in which four N_2 molecules interact equally with the central vanadium atom via their terminal nitrogen atoms. The N−N bond lengths in the N_2 units are 1.09 Å, equal to that of nitrogen molecules calculated in this work. Each V−N_2 distance is 2.20 Å. The second most stable isomer (1B) has a structure similar to that of 1A except that the V−N_2 distance is shortened to 2.12 Å. Accordingly, the energy of isomer 1B increases 28.71 kcal/mol compared to that of isomer 1A. The differences in the structures of 1A and 1B mainly originate from their spin multiplicity, which are 5 and 3, respectively.

Except for N_2 units, we also found other all-nitrogen ligands in low-lying isomers of VN_8^+. For example, the third most stable structure, 1C, is formed by attaching two N_3 ligands and one N_2 ligand to a vanadium atom. The N−N bond length in the N_2 molecule is also 1.09 Å. The N−N bond lengths in N_3 moieties are 1.23 and 1.11 Å, which are the same as those in a typical azide. Isomer 1C is much higher in energy than isomer 1A by 137.71 kcal/mol. 1D is the most stable isomer with an all-nitrogen ring in VN_8^+, which has two end-on bound N_2 molecules and one η^4-N_4 ring and exhibits C_{2v} symmetry. The N_4 ring in 1D has rectangular−planar structure with the bond lengths of N1−N2 and N2−N3 being 1.36 and 1.38 Å, respectively. The energy of isomer 1D is much higher than that of 1A by 164.38 kcal/mol.

For neutral VN_8, the low-lying states are considerably different from their positive counterparts. The isomer with only N_2 units has not been obtained after full optimization. Isomer 1A′ with two end-on bound N_2 molecules and one η^4-N_4 ring is the ground state of VN_8. Compared to the similar structure of 1D, the N_4 ring in 1A′ is distorted slightly from quadrate−planar structure and the symmetry of 1A′ degenerated to C_1. The bond lengths of N3−N2(N4) and N1−N2(N4) in the N_4 ring are 1.38 and 1.37 Å, which are shorter than the N−N single bond (1.45 Å) but much longer than the

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Table 1. Relative Energies, Binding Energies, and Formation Energies of the Low-Lying Isomers of V−N Clusters

cluster		symmetry	multiplicity	ΔE (kcal/mol)	E_b (kcal/mol)	$\Delta_f E$ (kcal/mol)
VN_8^+	1A	D_{4h}	5	0	24.84	−99.36
	1B	D_{4h}	3	28.71	17.66	−70.65
	1C	C_{2v}	3	137.71	−9.59	38.34
	1D	C_{2v}	3	164.38	−16.25	65.01
VN_8	1A′	C_1	4	0	−12.55	50.20
	1B′	C_s	2	41.18	−22.84	91.38
	1C′	C_s	4	91.12	−35.33	141.32
	1D′	C_{2v}	2	148.64	−49.71	198.83
VN_9^+	2A	C_1	1	0	−30.83	138.74
	2B	C_1	1	1.90	−31.25	140.64
	2C	C_1	1	8.36	−32.69	147.10
	2D	C_1	1	51.22	−42.21	189.96
VN_9	2A′	C_1	4	0	−21.39	96.28
	2B′	C_1	2	10.92	−23.82	107.20
	2C′	C_s	4	59.24	−34.56	155.51
	2D′	C_1	6	84.58	−40.19	180.85
VN_{10}^+	3A	C_s	3	0	−8.84	44.20
	3B	C_s	5	17.93	−12.43	62.13
	3C	C_s	1	181.28	−45.10	225.48
	3D	C_1	3	208.83	−50.61	253.03
VN_{10}	3A′	C_1	2	0	−11.55	57.76
	3B′	C_s	6	29.89	−17.53	87.65
	3C′	C_{2v}	2	109.08	−33.37	166.84
	3D′	C_1	2	123.19	−36.19	180.95

N═N double bond (1.25 Å). The ∠NNN angles in the N_4 ring are about 90°.

Some other all-nitrogen rings were also found in low-lying isomers of VN_8. Isomer 1B′ is the next most stable structure of VN_8 with one end-on bound N_2, one linear N_3, and an η^3-N_3 ring. It is 41.18 kcal/mol higher in energy than 1A′. The most stable isomer with a N_5 ring in VN_8 is 1C′. It contains an η^5-N_5 ring and an η^2-N_3 ring and exhibits C_s symmetry. The η^5-N_5 ring in 1C′ is aromatic with a N−N distance of 1.33 Å, which is similar to that in $V(\eta^5\text{-}N_5)_2$ as reported by Tsipis et al. (1.346 Å).[27] The 1D′ isomer has two N_4 rings coordinated to the V atom and displays a bent sandwichlike structure with eclipsed C_{2v} symmetry. It is worth mentioning that the structure of 1D′ calculated in this work is in agreement with that obtained from previous theoretical calculations by Mercero et al.[25] Isomers 1C′ and 1D′ lie 91.12 and 148.64 kcal/mol higher in energy than isomer 1A′, respectively.

3.2.2. Structures of VN_9^+ and VN_9. As shown in Figure 3, the most stable isomer of VN_9^+ (2A) consists of one nitrogen atom, two N_2 molecules, and one N_4 ring around the vanadium atom. The N_4 ring connects to the V atom through only two nitrogen atoms on one side (N1 and N2) and exhibits an isosceles trapezoidal structure with bond lengths of N1−N2, N3−N4, and N2−N3 (N1−N4) that are 1.33, 1.24, and 1.47 Å, respectively. The bond length of N3−N4 is very close to that of N═N (1.25 Å), whereas the bond length of N2−N3 (N1−N4) is close to that of N−N (1.45 Å). The N10 atom connects to the vanadium atom tightly with a short V−N10 distance of 1.48 Å. 2B is the second most stable structure with one N_2 molecule, one N_3 moiety, and one η^4-N_4 ring. It lies 1.90 kcal/mol higher in energy than 2A. The η^4-N_4 ring in 2B has a trapeziform structure with N−N bond lengths of about 1.37 Å. The next most stable isomer of VN_9^+ is 2C, which has a composition similar to that of 2A. However, the N_4 ring in 2C interacts with the vanadium atom by all four nitrogen atoms. Moreover, it is distinctly distorted from planar structure with a torsion angle of 13.4. The energy of isomer 2C lies 8.36 kcal/mol above that of isomer 2A.

We also found the N_3 ring in the obtained low-lying isomers of VN_9^+, but we have not found any isomers containing the N_5 ring. The most stable isomer with multirings in VN_9^+ is 2D, which is formed by adding one N_3 ring, one η^4-N_4 ring, and one end-on bound N_2 molecule to the V atom. The N_3 ring connects to the V atom via only one nitrogen atom (N9) with a V−N_3 distance of 2.03 Å. The η^4-N_4 ring in 2D has an irregular trapeziform structure with N−N bond lengths ranging from 1.35 to 1.39 Å. 2D exhibits C_1 symmetry and lies 51.22 kcal/mol in energy above isomer 2A.

For neutral VN_9, the low-lying isomers are similar to their positive counterparts. As shown in Figure 4, 2A′ is the most stable structure with one N_2 molecule, one N_3 moiety, and one η^4-N_4 ring. 2B′ is the second most stable structure with one nitrogen atom, two N_2 molecules, and one η^4-N_4 ring, lying 10.92 kcal/mol higher in energy than 2A′. In general, the structures of 2A′ and 2B′ are analogous to those of 2B and 2C, respectively. However, their η^4-N_4 rings are coplanar, and the V−N_4 parts have leaning pyramidal structure. For 2A′, the N−N bond lengths in η^4-N_4 rings are concentrated in the small range of 1.36−1.38 Å. The V−N1(N2) and V−N3(N4) distances are 2.07 and 2.04 Å, respectively. As for isomer 2B′, the vanadium atom is connected tightly to N1 and N2 with a short V−N1(N2) distance of 2.01 Å, whereas the V−N3(N4) connection is looser with a long distance of 2.27 Å.

Among the obtained low-lying states of VN_9, the N_3 and N_5 rings were also found and they tend to form multirings isomers. The most stable isomer with N_3 rings in VN_9 is 2C′, which is very similar to 2D. The most stable isomer with the N_5 ring is 2D′, in which a N_5 ring and another N_4 ring are coordinated to the V atom face to face. The sandwichlike structure of 2D′ is reported for the first time as far as we know. η^5-N_5 in 2D′ is an

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aromatic ring with a uniform N−N distance of 1.33 Å and a ∠NNN angle of 108.0°. η^4-N_4 in 2D′ also has a uniform N−N bond length of 1.36 Å, but it is distorted from planar structure with a torsion angle of 8.6°. The energy of isomers 2C′ and 2D′ lies 59.24 and 84.58 kcal/mol above that of isomer 2A′, respectively.

3.2.3. Structures of VN_{10}^+ and VN_{10}. The two most stable isomers of VN_{10}^+ were shown to be 3A and 3B, in which 3B lies 17.93 kcal/mol above isomer 3A. They were all formed by adding three end-on bound N_2 units and one η^4-N_4 ring to the V atom in different manners, and they all exhibit C_s symmetry. The structure of V−N_4 in 3A is slightly leaning pyramidal with V−N_4 distances of about 2.01−2.05 Å. The N_4 ring in 3A has isosceles trapezoid structure with N−N bond lengths of about 1.37 Å. In contrast, the N_4 ring in 3B is distorted from planar structure with a torsion angle of 13.2, and V−N_4 distances extend to 2.13−2.25 Å.

The most stable isomer with the N_3 unit in VN_{10}^+ is 3C, which has two end-on bound N_3 units and one N_4 ring around the vanadium atom and exhibits C_s symmetry. The N−N bond lengths in N_3 moieties are 1.25 and 1.11 Å, which are similar to those in a typical azide. The N_4 ring and V−N_4 in 3C also have isosceles trapezoid and slightly leaning pyramidal structure, respectively. The energy of 3C is much higher than that of 3A by 181.28 kcal/mol. Among the low-lying isomers of VN_{10}^+, we also found 3D with two η^4-N_4 rings and one end-on bound N_2 molecule. It has C_1 symmetry and displays an eclipsed sandwichlike structure in which one N_4 ring is coplanar and the other one is obviously distorted with a torsion angle of 7.3. The energy of isomer 3D lies 208.83 kcal/mol above that of isomer 3A.

As shown in Figure 4, the constitution of neutral VN_{10} isomers is analogous to that of their positive counterparts. The most stable isomer of VN_{10} is 3A′ with three end-on bound N_2 units and one η^4-N_4 ring. The N−N bond lengths in the N_4 ring are almost the same (1.38−1.39 Å). The vanadium atom is located right above the coplanar N_4 ring with an equal V−N_4 distance of 2.03 Å. The second most stable isomer (3B′) lies 29.89 kcal/mol above 3A′, respectively. It exhibits C_s symmetry in which the position between the vanadium atom and N_4 ring is slipped and only two nitrogen atoms on one side of the N_4 ring interact directly with the vanadium atom. Consequently, the N−N bond in the N_4 ring connected to the vanadium atom has a length of 1.43 Å, which is very close to the N−N single bond (1.45 Å), whereas the neighboring bonds have lengths of about 1.29 Å, which are close to the N=N double bond (1.25 Å).

Among the obtained low-lying states of VN_{10}, the most stable isomer with a N_3 unit is 3C′ with two end-on bound N_3 units and one η^4-N_4 ring. The most stable isomer with multirings is 3D′ with one end-on bound N_2 unit and two η^4-N_4 rings. The structures of 3C′ and 3D′ are very similar to those of 3C and 3D, respectively. However, their η^4-N_4 rings are nearly coplanar, and the N−N bond lengths in each N_4 ring are concentrated in a small range. Isomers 3C′ and 3D′ lie 109.08 and 123.19 kcal/mol in energy above isomer 3A′, respectively.

4. DISCUSSION

4.1. Binding Energies of V−N Clusters. To estimate the strength of the interactions between the V atom and nitrogen ligands, we performed calculations on the binding energies of various VN_n^+ and VN_n (n = 8, 9, and 10) complexes. The calculation results are listed in Table 1. For the low-lying isomers of the VN_8^+ cluster with four end-on bound N_2 units, the average binding energy (E_b) calculated with formula I refers to the bond energy between the vanadium cation and N_2 units. Therefore, on the basis of the calculated binding energy of the most stable structure of the VN_8^+ cluster (24.84 kcal/mol, that is 1.08 eV), the energy of a 266 nm photon (4.66 eV) is able to dissociate four N_2's from isomer 1A of the VN_8^+ cluster. That is in good agreement with our photodissociation experiment, as the experiment showed that the photodissociation of VN_8^+ at 266 nm can mainly remove eight nitrogen atoms (four N_2 molecules). The good agreement between the experiment and theoretical calculations validates the selection of the theoretical method in this work and confirms that the VN_8^+ cluster detected in our experiment is in the form of $V(N_2)_4^+$ with D_{4h} symmetry.

As seen from Table 1, the binding energies of the low-lying isomers of VN_8^+ (1A, 1B) are positive, suggesting substantial energy stabilization of the VN_8^+ species as compared to that of the bare vanadium cation and N_2 molecules. Furthermore, the binding energy of the ground state of VN_8^+ (1A) is much higher than those of VN_9^+ (2A) and VN_{10}^+ (3A), indicating that the VN_8^+ cluster would be more stable than the VN_9^+ and VN_{10}^+ clusters. These results are in good agreement with the mass spectrum obtained from the laser ablation experiment.

4.2. Structures of V−N Clusters. Several of the most stable structures of VN_n^+ and VN_n (n = 8, 9, and 10) as well as some typical low-lying isomers with various all-nitrogen units have been shown in Figures 3 and 4. The end-on bound N_2 units are most common in them with a N−N bond length of about 1.09 Å, which is the same as that in nitrogen molecules calculated in this work. The N−N bonds in side-on bound N_2 units are obviously weakened by coordination with N−N bond lengths of about 1.13 Å. The N_4 rings are the second most common ligands in VN_n^+ and VN_n (n = 8, 9, and 10) isomers. They can connect to vanadium only by one side (2A, 3B′) or by a whole face with V located directly above them (1D, 3A′). In most cases, the relative positions of vanadium atoms and N_4 rings lie between the above two states, giving rise to leaning pyramidal V−N_4 structures. In addition, N_4 together with other all-nitrogen rings could interact with V to form sandwich-like structures, such as N_4VN_4 (1D′) and N_4VN_5 (2D′).

Regarding the N−N bond distances in N_4 rings of low-lying isomers, for nonpyramidal V-η^2-N_4 structures (2A, 3B′), the presence of vanadium on the side of the ring induces alternating N−N distances, and these N_4 ligands can be regarded as a complex composed of two N_2 units. Specifically, the N_4 ring in 2A is formed by a side-on bound N_2 ligand with a N−N distance of 1.33 Å and an unbound N_2 unit with a N−N distance of 1.24 Å, while N_4 ring in 3B′ is formed by two end-on bound N_2 ligands with a N−N distance of about 1.29 Å. The interaction between N_2 units in the above N_4 rings is relatively weak as the N−N distances are up to 1.43−1.47 Å, very close to the bond length of the N−N single bond (1.45 Å). For pyramidal V-η^4-N_4 structures, all N−N bond distances are concentrated in a small range of 1.35−1.39 Å, especially around 1.37 Å, within the bond length of N−N single (1.25 Å) and double bonds (1.45 Å) and close to those in the bare N_4^{2-} ring (1.38 Å) calculated by Cheng et al.[24]

4.3. Energy Properties of V−N Clusters. The N−N bond lengths of N_4 rings found in this work lie between those of the N−N single and double bonds. The ∠NNN angles in them are close to 90°. Therefore, as predicted by Cheng et al.,[24] the N_4 rings found in this work are energetic. To understand the high-

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energy nature of the V−N clusters, we have calculated their formation energies with formula II. As shown in Table 1, the formation reactions of all isomers except 1A and 1B are endothermic, indicating that those clusters found in this work are all energetic species. More specifically, the ground state of VN_9^+ (2A) lies 138.74 kcal/mol higher in energy above a V cation and 9/2 N_2 molecules. Previously suggested ThN_6,[31] ScN_7,[32] and N_5ThN_7[33] lie approximately 72, 125, and 132 kcal/mol higher in energy than the corresponding atom and N_2 molecules, respectively. Therefore, isomer 2A observed in our experiment is energetically higher than the predicted metal nitrides. The most stable isomer of VN_{10}^+ (3A) gives an energy of 44.20 kcal/mol above a V cation and five N_2 molecules. As for the ground state of neutral clusters, VN_8, VN_9, and VN_{10} can release energies of about 50.20, 96.28, and 57.76 kcal/mol when they decompose into a V atom and a corresponding number of N_2 molecules, respectively.

Except for the N_4 rings, end-on bound N_2 molecules do not make any contributions to the energy of the above clusters, so converting the remaining N_2 ligands in V-doped nitrogen clusters could make them effective HEDMs. For example, the formation energies of isomer 1D′ with a structure of $(\eta^4\text{-}N_4)V(\eta^4\text{-}N_4)$, isomer 2D′ with a structure of $(\eta^4\text{-}N_4)V(\eta^5\text{-}N_5)$, and isomer 3C with a structure of $(\eta^4\text{-}N_4)V^+(N_3)_2$ are up to 198.83, 180.85, and 225.48 kcal/mol, respectively.

5. CONCLUSIONS

VN_8^+, VN_9^+, and VN_{10}^+ clusters were generated by a laser ablation experiment. The mass spectrometry showed that the abundance of VN_8^+ is much higher than those of VN_9^+ and VN_{10}^+. The VN_8^+ cluster was further investigated by a photodissociation experiment with 266 nm photons. Density functional calculations were made to search for the stable structures of V−N clusters. The theoretical calculations found that the most stable structure of VN_8^+ is in the form of $V^+(N_2)_4$ with D_{4h} symmetry. The calculated binding energy is in good agreement with that obtained from the photodissociation experiments. The ground states of VN_8, $VN_9^{+/0}$, and $VN_{10}^{+/0}$ all consist of a N_4 ring and exhibit an energetic nature. The most stable isomer of VN_9^+ is in the form of $(\eta^2\text{-}N_4)V^+N(N_2)_2$ with C_1 symmetry, while that of VN_{10}^+ is $(\eta^4\text{-}N_4)V^+(N_2)_3$ with C_s symmetry. They lie 138.74 and 44.20 kcal/mol higher in total energy above a V cation and a corresponding number of N_2 molecules, respectively. For neutral VN_8, VN_9, and VN_{10}, $(\eta^4\text{-}N_4)V(N_2)_2$, $(\eta^4\text{-}N_4)V(N_3)(N_2)$, and $(\eta^4\text{-}N_4)V(N_2)_3$ are their ground states. The N_4 ring was found not only in the ground states of VN_9^+ and VN_{10}^+, which have been detected in this work, but also in many low-lying isomers of VN_n^+ and VN_n (n = 8, 9, and 10). As a new all-nitrogen ligand, the N_4 ring would be an energetic building block for constructing nitrogen-rich compounds.

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