Supplementary Material

First-Principles Study of Structural, Electronic and Magnetic Properties of Metal-Centered Tetrahexahedral V_{15}^{+} Cluster

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Contents:

- Up-spin DOS and MOs of the low-lying **A** structure for V_{15}^{+}, Fig. S1
- Six totally delocalized bonding patterns for V_{15}^{+} revealed by AdNDP analysis, Fig. S2
- Magnetic moments of two low-lying isomers (**A bha** and **B bcc**) for V_{15}^{+}, Table S1
- Optimized atomic coordinates of the lowest-energy A isomer for V_{15}^{+}, Table S2

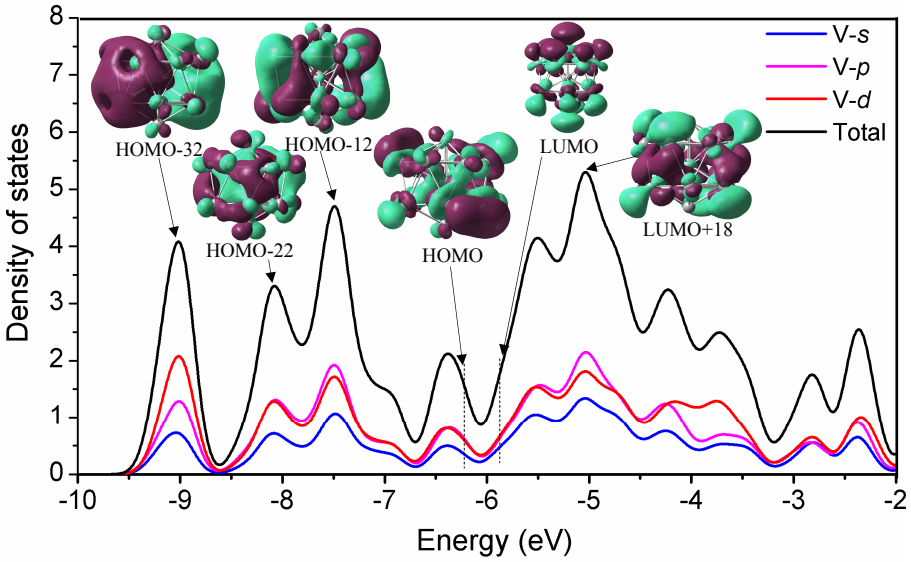
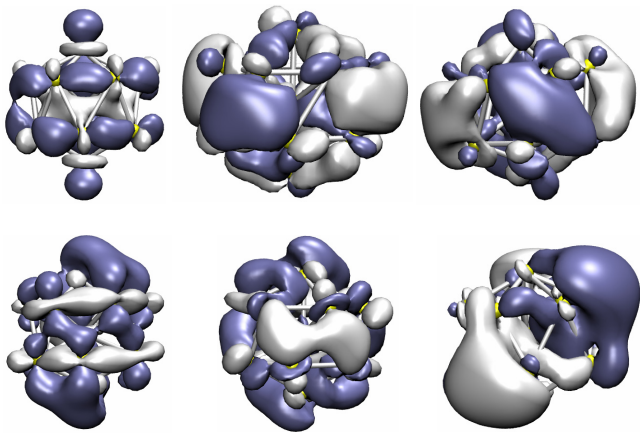


Fig. S1 Up-spin density of states (DOS) of the low-lying **A** structure for V_{15}^{+}, obtained at the PBE/def-SVP level of theory. The molecular orbitals are related to the mainly up-spin DOS bands.



six totally delocalized MOs
ON = 2.00 |e|

Fig. S2 Six totally delocalized bonding patterns (molecular orbitals) for the V_{15}^{+} cluster, revealed by AdNDP method[1] at the PBE/def-SVP level of theory, ON denotes the electron occupation number. All of the molecular isovalue graphs were visualized using the VMD program.[2]

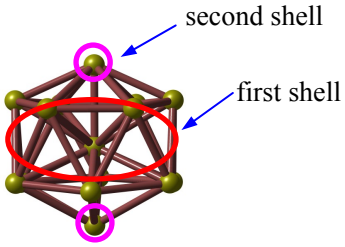
1. D. Y. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5207–5217.
2. W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graphics* 1996, **14**, 33–38.

Table S1 Magnetic moments (in μ_B) of two isomers A (bicapped hexagonal antiprism, **bha**) and B (body-centered cube, **bcc**) for the V_{15}^+ cluster: μ is the average magnetic moment per atom; μ_1, μ_2, and μ_3 are the average local magnetic moments for center, first shell, and second shell atoms, respectively.

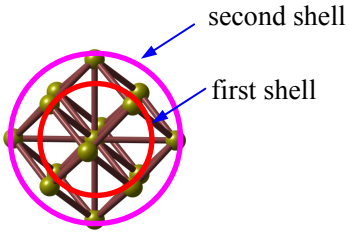
Isomers	Spin states	Magnetic moments[a]			
		μ	μ_1	μ_2	μ_3
A bha	S=1	0.13	+0.27	+0.18	−0.20
B bcc	S=1	0.13	+0.22	+0.16	+0.09

[a]The magnetic moments were calculated by using the PBE/def-SVP level of theory.

Shell defination:



A hp



B bcc

Table S2 Optimized atomic coordinates of the lowest-energy isomer (A) in different spin states, for the cationic V_{15}^{+} cluster.

isomers	Atom	X(Å)	Y(Å)	Z(Å)	isomers	Atom	X(Å)	Y(Å)	Z(Å)
A	V	3.3691151	-0.624274	0.3435209	A	V	3.3050438	-0.745791	0.3772514
S=0	V	0.8033133	-0.571607	0.3228301	*S*=1	V	0.7648149	-0.514081	0.2876804
	V	-1.398184	0.7329318	0.8625263		V	-1.423715	0.7852288	0.8638335
	V	2.1499128	1.3849843	-0.738424		V	2.3249223	1.339609	-0.677379
	V	0.4927554	0.2382071	2.6761637		V	0.2880789	0.2887488	2.6640119
	V	0.1930817	-1.915413	-1.844635		V	0.1026531	-1.897812	-1.823589
	V	2.0179956	-0.794024	-1.988596		V	1.8887534	-0.707167	-1.997021
	V	-0.289177	-2.874372	0.6320758		V	0.0676414	-2.964207	0.4785844
	V	1.975505	-2.587636	-0.472949		V	2.0037323	-2.695484	-0.424587
	V	1.6142764	-1.66006	2.100838		V	1.6550588	-1.736648	2.0173355
	V	0.6776367	2.0110845	0.6996041		V	0.6946023	2.0247012	0.5541353
	V	2.6504676	0.7680785	1.6595005		V	2.5365507	0.7406361	1.7338646
	V	-1.056835	-1.510841	1.9493188		V	-0.963837	-1.356174	2.0496897
	V	-0.091035	0.6532018	-1.455887		V	-0.128742	0.7092895	-1.441838
	V	-1.656214	-0.95719	-0.441095		V	-1.662943	-0.977777	-0.357177