

Research paper

A Frank-Kasper polyhedral structure of 17-atom vanadium clusters

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HIGHLIGHTS

- The cationic V_{17}^+ cluster reproduces well the experimental IR-MPD spectroscopy.
- Frank-Kasper polyhedral structure of V_{17} can be identified as global minimum.
- The calculated ionization potentials and electron affinities are close to experiments.
- Shell-closed V_{17}^+ structure is stabilized by the chemical bonds on outer and inner shells.

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ABSTRACT

A distorted Frank-Kasper polyhedral structure (A) as the putative global minimum was identified for the neutral and charged V_{17} clusters by using the Monte Carlo basin-hopping algorithm based on semi-empirical Gupta potential and density functional theory calculations. The cationic V_{17}^+ cluster reproduces well the experimental infrared multiple photon dissociation spectroscopy, and the calculated adiabatic ionization potentials and electron affinities of the A structure are close to its experimental values. It is also found that the shell-closed V_{17}^+ structure can be stabilized by 20 delocalized 3c-2e and 4 delocalized 6c-2e σ bonds on the outer shell and 12 delocalized 4c-2e σ bonds on the inner shell. Our results will inevitably stimulate future theoretical and experimental studies for the design and exploration of largely nanoscale materials.

1. Introduction

In recent years, clusters have attracted a lot of attention due to the increasing surface to volume ratio, resulting in novel physicochemical properties, which are distinct from those of individual atoms and molecules or bulk matter [1–3]. In particular, transition metal (TM) clusters are of interest as the basic building blocks for nanoscience and intermediates linked to the isolated atoms and bulk phases, and possess strongly dependence on their fascinating physical and chemical properties, e.g., optical [4–6], magnetic [7,8] and catalytic [9–11] features, which play an important role in various scientific and industrial applications of nanomaterials [12]. It is well-known that the knowledge of the structural properties of isolated clusters is very significant for the further understanding of these fascinating properties, but it is not straightforward to obtain the accurately structural information of clusters, which can be solved well to determine the cluster structure by using the combination of experimental techniques and density functional theory calculations, but only for small cluster size.

Up to now, a great number of studies both experimentally and

theoretically have been carried out to explore the metal cluster structures [13–15]. The infrared multiple photon dissociation (IR-MPD) spectroscopy of Tb_n^+ ($n = 5–16$) has been also performed to identify the lowest-energy structures in the molecular beam by comparing with the density functional theory (DFT) calculations [16,17], as well as for Ru_n^+ ($n = 7, 8$ and 9) [18] that all three cluster sizes are predicted to possess the cubic motif. Shayeghi and co-workers [19] have reported the structures and optical properties of the mixed Ag-Au tetramer cations by using the photodissociation spectroscopy and time-dependent DFT (TD-DFT) scheme, and the experimental absorption spectra of the clusters are clearly assigned. Harbich et al. [20] have presented the geometric structures of neutral Au_n ($n = 1–5$ and $7–9$) clusters by using a combination of experimental techniques and theoretical calculations. Additionally, previously there are many solely DFT studies for small metal cluster size, e.g., $(PbSe)_n$ ($n = 1–10$) [21], $Sn_{12}Cd$ [22], Au_n ($n = 4–20$) [23] etc., which are notably less complicated than the cluster systems with a larger number of atoms. For large clusters, in fact, an accurate and extensive DFT calculations are nearly impossible to perform the global optimization on the potential energy surface

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(PES), owing to the increase of the number of local minima with increasing cluster sizes [24]. Therefore, accurate theoretical prediction with less computational costs to locate cluster geometry is greatly desired for large cluster size, and offers the possibility to find unusual geometrical structures.

The usual scheme is to use a combination of empirical or semi-empirical methods [2,25–27] and global optimization techniques, e.g., Monte Carlo basin-hopping algorithm [28,29], genetic algorithm [30,31], and simulated annealing [32], to determine the large cluster structure (e.g., $N = 100$), but an unbiased global minimum (GM) search method and reliability of the scheme are rather crucial, especially validated by experiment techniques. With this motivation, we will study the bulklike V_{17} cluster [33] as benchmark system to test the reliability of the global search method, in which the more popular Monte Carlo basin-hopping algorithm based on semi-empirical Gupta potential [34] is considered.

Meanwhile, the vanadium clusters have attracted particular attention in novel catalytic activities and magnetic materials [8,35,36], and previous efforts are mainly focused on the experimental studies of the cluster systems, e.g., the electron affinities (EAs) [33] and ionization potentials (IPs) [37] of V_n ($n = 3–65$ for EAs; $n = 1–22$ for IPs), dissociation energies of V_n^+ ($n = 2–20$) [38], and Far-Infrared spectroscopy of V_n^+ ($n = 6–23$) [39]. Only few theoretical studies were successfully performed to determine the lowest-energy structures of small V_n^+ ($n = 3–15$) clusters [40], since it still remains a actual difficulty to locate the geometric structures for large vanadium clusters, which exist a great number of possible isomers on the PES and need expensive computational costs by the accurate DFT calculations, while various physical and chemical properties rely strongly on the precise geometric structures. In addition, the structure and dynamical behaviour of clusters are all manifestations of the underlying PES [41], and depend upon the relative potential energies of the local minima and how the various local minima are connected via energy barriers. Thus, the potential-energy disconnectivity graphs will provide further insight into the transition regions among these basins [42,43].

In this paper, we explore the global minimum on potential energy surface of neutral V_{17} cluster using the semi-empirical Gupta many-body potential and Monte Carlo basin-hopping algorithm [28,29], and by using the DFT computations determine the neutral and charged lowest-energy structures, compared with available experimental IR-MPD spectroscopy. Most impressively, we found that the global minima with distorted Frank-Kasper polyhedron were identified for neutral and charged clusters, the search strategy mentioned above is effective and reliable for predicting and designing the building block of largely novel nanoscale materials, making it promising guide for theoretical and experimental studies in bulk materials.

2. Computational details

The many-body potential consists of the many-body attractive and repulsive interaction terms based on the second-moment approximation of tight-binding Hamiltonian, and describes the intermetallic bonding of transition metal clusters reasonably well [44]. A set of potential parameters (e.g., A , ξ , p , and q) for the homonuclear vanadium bulk metals, fitted to experimental values of cohesive energy, lattice parameters, and independent elastic constants at $T = 0$ K, are taken from the previous literature by Cleri and Rosato [44].

The basin-hopping algorithm is a stochastic global search method with the Monte Carlo (MC) simulation [45] which is performed on a transformed potential energy surface followed a local minimization step, the transformation allows the studied system to move from one basin to another more easily. In other words, the basin-hopping approach converts the whole potential energy surface of a cluster into the set of basins of attraction corresponding to all the local minima, and it has been proved to be an effective strategy to widely gain insight into the energy landscape not only for transition-metal clusters [2,46,47],

but also for peptides [48–50] and polymers [51], and so on. At each configuration search, a basin-hopping run of 100,000 Monte Carlo steps was considered for the neutral V_{17} cluster studied here, and all the global optimization calculations mentioned above were carried out using the PELE package developed by Wales's group [52], in which the potential-energy disconnectivity graph [53] can be used to visualize the energy landscapes and understand the global dynamics, on the basis of the double-ended transition state technique.

Quantum chemical calculations were performed with the Gaussian 09 program [54]. The low-lying structures obtained from the semi-empirical potential search were further refined at the DFT level using the generalized gradient approximation (GGA) exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) [55], in conjunction with the moderate def-SVP basis set for energy evaluation. The methodology has been shown to be successful for the structural assignment of the pure transition-metal clusters by reproducing well experimentally IR spectra, e.g. Tb_n^+ ($n = 5–9$) [16] and V_n^+ ($n = 3–15$) [40,56]. In our structural optimization, the high spin states, e.g., $S = 1$ or $3/2$, were also considered for the energy evaluation of each candidate structure.

3. Results and discussion

3.1. Structures of the neutral vanadium clusters

The multi-funnel [41,57,58] disconnectivity graphs of neutral V_{17} cluster obtained from the semi-empirical potentials and basin-hopping algorithm are presented in Fig. 1. The disconnectivity graphs clearly illustrates the energy barriers profiles associated with these two pathways that lead to local minima, and highlights the special position of the global potential energy minimum. As can be seen in Fig. 1, a total of eleven selected low-lying structures of the V_{17} cluster are illustrated, of which the global minimum (GM) with the S_4 symmetry, being similar to the Frank-Kasper (FK) polyhedron, is generated from one V_3 trimer being capped on the hexagonal faces of the icositetrahedron V_{14} cluster (see the Fig. S1 of the Supplemental Material). Meanwhile, it is also found that the global minimum structure prefers energetically the high coordinated geometry, and does not follow the icosahedral growth scheme.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cplett.2018.08.024>.

To check the validity of our global minimum search methods, we performed the further DFT optimizations for firstly distinct low-lying structures (A, B, and C) of the V_{17} cluster. Obviously, there is not any previous DFT study for these structures at the cluster size. The low-lying structures and relative energies obtained from semi-empirical Gupta

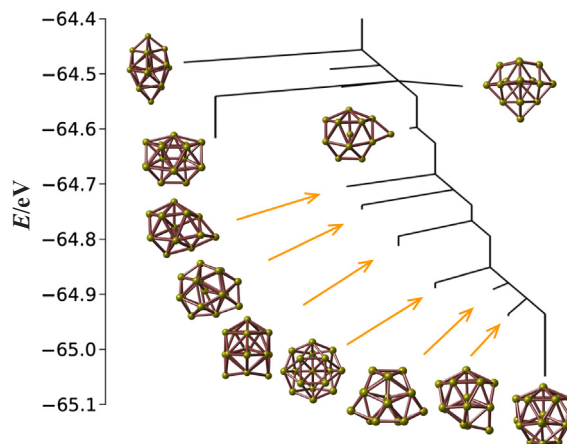


Fig. 1. Potential-energy disconnectivity graph for the neutral V_{17} cluster searched using the Gupta potentials and basin-hopping algorithm. The different structures corresponding to local minima are indicated.

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