Insights into the structural, electronic and magnetic properties of V-doped copper clusters: comparison with pure copper clusters

Dong Die\(^1\), Ben-Xia Zheng\(^1\), Lan-Qiong Zhao\(^1\), Qi-Wen Zhu\(^1\) & Zheng-Quan Zhao\(^1\)

The structural, electronic and magnetic properties of \(\text{Cun}^{+}1\) and \(\text{CunV}\) (\(n = 1–12\)) clusters have been investigated by using density functional theory. The growth behaviors reveal that V atom in low-energy \(\text{CunV}\) isomer favors the most highly coordinated position and changes the geometry of the three-dimensional host clusters. The vibrational spectra are predicted and can be used to identify the ground state. The relative stability and chemical activity of the ground states are analyzed through the binding energy per atom, energy second-order difference and energy gap. It is found that the stability of \(\text{CunV}\) (\(n \geq 8\)) is higher than that of \(\text{Cun}^{+}1\). The substitution of a V atom for a Cu atom in copper clusters alters the odd-even oscillations of stability and activity of the host clusters. The vertical ionization potential, electron affinity and photoelectron spectrum are calculated and simulated for all of the most stable clusters. Compare with the experimental data, we determine the ground states of pure copper clusters. The magnetism analyses show that the magnetic moments of \(\text{CunV}\) clusters are mainly localized on the V atom and decease with the increase of cluster size. The magnetic change is closely related to the charge transfer between V and Cu atoms.

During the last few decades, copper clusters have been demonstrated to have similar catalytic activities with those of gold clusters for the low temperature CO oxidation and partial oxidation of hydrocarbons\(^1\)–\(^6\). At the same time, theoretical and experimental work has also shown that the nature of small clusters can be considerably modified by the addition of impurity atom(s)\(^7\)–\(^36\). Copper clusters doped with different transition-metal atoms have been expected to tailor the desired catalytic, electronic, magnetic and optical properties for potential applications in solid state chemistry, microelectronics, nanotechnology and materials science\(^40\)–\(^50\). For instance, Yang \textit{et al.} reported that the adsorption property of copper cluster to CO\(_2\) can be modified by doping it with Ni atoms and icosahedral \(\text{Cu}_{14}\text{Ni}_{13}\) cluster, which is used as catalysts for methanol synthesis via CO\(_2\) hydrogenation, exhibits the strongest CO\(_2\) adsorption ability compared to \(\text{Cu}_{55}\) and \(\text{Cu}_{54}\text{Ni}\) clusters\(^39\). Wang \textit{et al.} found that the melting behavior of Cu-Co bimetallic clusters, which is different from that of pure copper clusters, is closely related to the component materials, stoichiometries and local structure. The Kondo temperature of a Co atom embedded in Cu clusters on Cu(111) exhibits a nonmonotonic variation with the cluster size\(^41\). Han \textit{et al.} noted that though most of the \(\text{CunNi}\) clusters possess similar geometries to those of pure copper clusters, Ni-doping introduces a dramatic modulation of the electronic structures, such as the density of states and d-band centers\(^42\). Recently, the Cu–V alloys have investigated due to their unique physical properties. It was shown that the addition of V in Cu alloys can improve mechanical properties and heat resistance of Cu alloys. This effect can be reinforced by increasing the solubility of V in Cu during the synthesis of the alloys\(^43\). The fcc crystalline structure of Cu–V alloys can be preserved in the solid solution model until the concentration of V reaches a critical value of 23 at.%. When the V concentration in a model is over 23 at.%, a crystal-to-crystal transition will take place\(^44\). To the best of our knowledge, however, there is a lack of work on small V-doped copper clusters. It has been proved that the
The optimized results for Cu₂ and CuV dimmers show that the former in singlet spin state is 1.56 eV lower than in triplet spin state and the latter in singlet, triplet and septet configurations. Owing to the spin polarization, every initial configuration was optimized at possible spin multiplicities. If an imaginary vibrational mode is found, a relaxation of the structure is performed until the true local minimum is actually obtained.

Table 1. The geometries and electronic properties of Cuₙ and V₂ dimers. Refs 62–65.

| Dimer | Functional/Basis set | r(Å) | Δr(Å) | D₁(eV) | f(cm⁻¹) | VIP(eV) | EA(eV) |
|-------|----------------------|------|-------|--------|---------|---------|--------|
|       |                      | Calc. | Expt. | Calc. | Expt. | Calc. | Expt. | Calc. | Expt. ||
| Cu₂   | B3LYP/LanL2DZ        | 2.26  | 2.22  | 2.02  | 2.01  | 256   | 264   | 7.99  | 7.90  | 0.63  | 0.83  |
|       | BLYP/LanL2DZ         | 2.25  | 2.28  | 2.64   | 8.06   | 0.62    |        |        |        |        |
|       | PW91/LanL2DZ         | 2.23  | j     | 2.35  | 273    | 8.09  | 0.72  |        |        |        |        |
| Cu₂   | B3LYP/6-311 + G(d)   | 2.28  | 1.80  | 239    | 8.07   | 0.81    |        |        |        |        |
| Cu₂   | BLYP/6-311 + G(d)    | 2.27  | 2.01  | 244    | 8.20   | 0.83    |        |        |        |        |
| Cu₂   | PW91/6-311 + G(d)    | 2.24  | 2.11  | 260    | 8.22   | 0.93    |        |        |        |        |
| V₂    | B3LYP/LanL2DZ        | 1.75  | 1.77  | 1.94  | 2.47 ± 0.22  | 6.39  | 6.35  |        |        |        |        |

Computational Methods
Geometry optimizations and vibrational frequency analyses of Cuₙ₋₁ and CuₙV clusters have been carried out in the framework of a DFT-based method using the GAUSSIAN09 package. The exchange-correlation functional B3LYP and an effective core potential basis set LanL2DZ were used for all of the calculations. The convergence thresholds are set to 4.5 × 10⁻⁶ a.u. for maximum force, 3.0 × 10⁻⁴ a.u. for root mean square (RMS) force, 1.8 × 10⁻³ a.u. for maximum displacement and 1.2 × 10⁻³ a.u. for RMS displacement. The accuracy of the theoretical level has been checked by calculations on copper dimer and vanadium dimer. The results have summarized in Table 1. To search the lowest energy structures of Cuₙ₋₁ and CuₙV clusters, lots of initial isomers, which include one-, two- and three-dimensional (3D) configurations, have been taken into account in our geometry optimizations. Owing to the spin polarization, every initial configuration was optimized at possible spin multiplicities. If an imaginary vibrational mode is found, a relaxation of the structure is performed until the true local minimum is actually obtained.

Results and Discussion

Geometrical structures and vibrational spectra. The optimized results for Cu₂ and CuV dimmers show that the former in singlet spin state is 1.86 eV lower than in triplet spin state and the latter in single, triplet and septet spin states is less stable than in quintet spin state by 2.54, 0.47 and 1.38 eV, respectively. Accordingly, the singlet Cu₂ and quintet CuV are the ground states. Their bond lengths are 2.26 Å for Cu₂ and 2.49 Å for CuV. The bond length of the Cu₂ is shorter than that of CuV. This may be attributed to the fact that the radius of Cu atom (1.28 Å) is smaller than that of V atom (1.34 Å). For each Cuₙ and CuₙV clusters, lots of initial isomers, which include one-, two- and three-dimensional (3D) configurations, have been taken into account in our geometry optimizations. Owing to the spin polarization, every initial configuration was optimized at possible spin multiplicities. If an imaginary vibrational mode is found, a relaxation of the structure is performed until the true local minimum is actually obtained.

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|       |                      | Calc. | Expt. | Calc. | Expt. | Calc. | Expt. | Calc. | Expt. ||
| Cu₂   | B3LYP/LanL2DZ        | 2.26  | 2.22  | 2.02  | 2.01  | 256   | 264   | 7.99  | 7.90  | 0.63  | 0.83  |
|       | BLYP/LanL2DZ         | 2.25  | 2.28  | 264   | 8.06   | 0.62    |        |        |        |        |
|       | PW91/LanL2DZ         | 2.23  | j     | 2.35  | 273    | 8.09  | 0.72  |        |        |        |        |
| Cu₂   | B3LYP/6-311 + G(d)   | 2.28  | 1.80  | 239    | 8.07   | 0.81    |        |        |        |        |
| Cu₂   | BLYP/6-311 + G(d)    | 2.27  | 2.01  | 244    | 8.20   | 0.83    |        |        |        |        |
| Cu₂   | PW91/6-311 + G(d)    | 2.24  | 2.11  | 260    | 8.22   | 0.93    |        |        |        |        |
| V₂    | B3LYP/LanL2DZ        | 1.75  | 1.77  | 1.94  | 2.47 ± 0.22  | 6.39  | 6.35  |        |        |        |        |
The ground state structure of Cu7 cluster is a pentagonal bipyramid (7A), lying just below the 7B. The 8A isomer with Td symmetry, which can be treated as a face-capped 7B, is found to be the lowest energy structure of Cu8 cluster. The 9A and 9B are nearly degenerate and ref. 57 suggests 9B as the most stable structure. Nevertheless, in view of vertical ionization potential (VIP) which will be discussed later, we deduce that the 9A is the ground state structure of Cu9 cluster. Simultaneously, the most stable structures of small Cu n (n = 2–9) clusters had studied by means of optical absorption spectra 58. Our results are consistent with the previous conclusion. From Cu10 to Cu13 clusters, the flat cage-like configurations are more stable than other structures, e.g. close-packing and globe-shaped structures. The 10A, 11A, 12A and 13A are the lowest energy structures of Cu 10, Cu11, Cu12 and Cu13 clusters, respectively. Several isomers reported in ref. 56 have also been optimized at B3LYP/LanL2DZ level and are higher in energy than our lowest energy structures. This is in agreement with Ramirez et al’s studies57.

With regard to Cu nV (n = 6–12) clusters, the ground state structures (6I, 7I, 8I, 9I, 10I, 11I and 12I) are entirely different from the most stable structure of the corresponding Cu n+1 clusters. The 6I, 7I and 8I structures are similar to the low-lying isomers (7D, 8D and 9C) of pure copper clusters. The 9I, 10I, 11I and 12I configurations are unstable or do not exist for Cu clusters in the lowest spin state. The 11I is obtained by distorting the geometry starting from C 5v to Cs symmetry. The 12I has a small deviation from I h symmetry. The Cu nV isomers, which resemble the lowest energy structures and low-lying isomers of Cu n+1 clusters, lay above each of the ground state.
structures (nI). The most stable structures of Cu\nV (n = 7–12) clusters all contain a pentagonal bipyramid. In addition, due to the Jahn-Teller effect, the 6IV and 7II isomers with \( \text{C}_3 \) symmetry have a slight deviation from \( \text{C}_3 \) symmetry. The 10I and 12I structures are more stable in doublet spin state than in quartet spin state. The V atom in Cu\nV clusters tends to occupy the site with the maximum coordination number. This may be ascribed to the principle of maximum overlap in molecular orbital theory. Because the orbital overlap between Cu and V atoms increases, the energy of Cu\nV cluster will decrease.

The combination of theoretical and experimental vibrational spectra is a good method for the structural determination of small isolated clusters and the method has been successfully applied in practice. Consequently, the vibrational spectra of the lowest energy Cu\nV, and Cu\nV (n = 1–12) clusters are shown in Fig. 3. The Cu\nV dimer merely has a stretching vibration without change of dipole moment, so there is no absorption peak. The absorbed peaks of planar or highly symmetrical clusters are less than those of other configuration clusters. The intense

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**Figure 2.** The ground-state structures and three low-lying isomers for Cu\nV (n = 2–12) clusters. The point group, spin multiplicity, and energy difference compared to each of the ground state structures are given below them. The grey and black balls represent Cu and V atoms, respectively.
| Clusters | $R_{\text{max}}$ (Å) | $R_{\text{min}}$ (Å) | C | $C_{\text{a}}$ (a.u.) | Clusters | $R_{\text{max}}$ (Å) | $R_{\text{min}}$ (Å) | C | N | $R_v$ (Å) | $C_{\text{a}}$ (a.u.) |
|----------|----------------|----------------|---|----------------|----------|----------------|----------------|---|---|----------|----------------|
| Cu$_2$   | 2.26           | 2.26           | 0.5| 0.5            | Cu$_V$   | 2.49           | 2.49           | 0.5| 1 | 2.49     | 0.04           |
| Cu$_3$   | 2.33           | 2.33           | 0.7| 8.60           | Cu$_2V$  | 2.47           | 2.47           | 0.7| 2 | 2.47     | 2.78           |
| Cu$_4$   | 2.45           | 2.31           | 1.3| 4.28           | Cu$_3V$  | 2.67           | 2.40           | 1.3| 3 | 2.63     | 12.25          |
| Cu$_5$   | 2.47           | 2.41           | 1.4| 2.68           | Cu$_4V$  | 2.59           | 2.40           | 1.4| 4 | 2.58     | 3.88           |
| Cu$_6$   | 2.5            | 2.41           | 1.5| 7.73           | Cu$_5V$  | 2.68           | 2.42           | 1.5| 4 | 2.64     | 7.56           |
| Cu$_7$   | 2.67           | 2.50           | 2.3| 1.31           | Cu$_6V$  | 2.65           | 2.40           | 2.1| 6 | 2.61     | 2.08           |
| Cu$_8$   | 2.56           | 2.49           | 2.3| 1.92           | Cu$_7V$  | 2.65           | 2.46           | 2.3| 6 | 2.64     | 2.50           |
| Cu$_9$   | 2.64           | 2.46           | 2.3| 1.43           | Cu$_8V$  | 2.74           | 2.54           | 2.6| 8 | 2.62     | 2.50           |
| Cu$_{10}$| 2.63           | 2.48           | 2.5| 3.98           | Cu$_9V$  | 2.64           | 2.47           | 2.7| 9 | 2.59     | 2.34           |
| Cu$_{11}$| 2.64           | 2.48           | 2.6| 3.44           | Cu$_{10V}$| 2.66          | 2.47           | 2.8| 10| 2.57     | 1.81           |
| Cu$_{12}$| 2.65           | 2.47           | 2.6| 4.12           | Cu$_{11V}$| 2.71          | 2.50           | 2.6| 11| 2.54     | 2.42           |
| Cu$_{13}$| 2.68           | 2.47           | 2.8| 2.72           | Cu$_{12V}$| 2.67          | 2.51           | 2.8| 12| 2.51     | 3.17           |

Table 2. The maximum and minimum bond lengths ($R_{\text{max}}$, $R_{\text{min}}$) and chemical bond per atom (C) for the most stable Cu$_{n+1}$ and Cu$_nV$ clusters. The averaged bond length between V and Cu atoms ($R_v$) and coordination number (N) of V atom in the ground state Cu$_nV$ clusters. The mean static polarizabilities ($C_{\text{a}}$).

Figure 3. Vibrational spectra of the ground state Cu$_{n+1}$ of Cu$_nV$ (n = 1–12) clusters.
peaks of 3D CuₙV (n = 6–12) clusters are more than those of corresponding pure Cuₙ₊¹ clusters. The vibrational fundamentals of all Cuₙ₊¹ and CuₙV clusters are found to be in the range of 5 to 330 cm⁻¹. The most intense peak of vibrational spectrum of each CuₙV clusters is related to the V-Cu stretching vibrations. The characteristic frequencies of the ground state structures and several low-lying isomers are given as Supplementary Material.

Relative stabilities and electronic properties. In this part, the relative stabilities and electronic properties of the ground state Cuₙ₊¹ and CuₙV (n = 1–12) clusters are discussed by means of the atomic averaged binding energies, second-order energy differences, energy gaps between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the VIP, the vertical electron affinity (VEA) and photoelectron spectroscopy (PES).

The atomic averaged binding energies (Eₐ) of the Cuₙ₊¹ and CuₙV clusters can be calculated as follows

$$Eₐ(Cuₙ₊¹) = [(n + 1)E(Cu) - E(Cu_{n+1})]/(n + 1),$$

Figure 4. Size dependence of the averaged binding energies for the ground state Cuₙ₊¹ and CuₙV (n = 1–12) clusters.

Figure 5. Size dependence of the second-order energy differences for the lowest energy Cuₙ₊¹ and CuₙV (n = 1–12) clusters.

Figure 6. Size dependence of the HOMO-LUMO energy gaps of the most stable Cuₙ₊¹ and CuₙV (n = 1–12) clusters.
For the ground state Cu clusters determined in mass spectroscopy experiment, is a particularly sensitive quantity that reflects the relative thermic stability. The Cu atom in Cu clusters possesses relatively higher thermic stability. The substitution of a V atom for a Cu atom in Cu clusters alters the stability of the host clusters. This phenomenon may be caused by structural changes. The configuration of CuV clusters, which is larger than that of Cu clusters for n≥8, is a monotonically increasing function of the number of atoms in clusters. This implies that the doped clusters can continue to gain energy during growth process. The agreement confirmed reliability of the available experimental data. The calculated VIPs of pure copper clusters are in good agreement with previous measurements obtained at discrete 2.5 nm intervals.

Table 3. VIP and EA of the most stable Cu_{n+1} and Cu_{n}V clusters. aRefs 60 and 66.

| Clusters | VIP(eV) Calc. | VIP(eV) Exp. | EA(eV) Calc. | Clusters | VIP(eV) Calc. | EA(eV) Calc. |
|----------|---------------|--------------|--------------|----------|---------------|--------------|
| Cu2      | 7.99          | 7.90         | 0.63         | CuV      | 6.43          | 0.77         |
| Cu3      | 5.94          | 5.80±0.05    | 1.05         | Cu2V     | 6.73          | 1.18         |
| Cu4      | 6.60          | 7.15±0.75    | 1.27         | Cu3V     | 5.93          | 1.21         |
| Cu5      | 6.24          | 6.30±0.05    | 1.70         | Cu4V     | 6.20          | 1.41         |
| Cu6      | 7.17          | 7.15±0.75    | 0.96         | Cu5V     | 6.04          | 1.05         |
| Cu7      | 6.04          | 6.07±0.05    | 1.68         | Cu6V     | 6.32          | 1.55         |
| Cu8      | 6.98          | 7.15±0.75    | 0.92         | Cu7V     | 5.66          | 1.15         |
| Cu9      | 5.27          | 5.36±0.05    | 1.43         | Cu8V     | 5.78          | 1.40         |
| Cu10     | 5.95          | 6.07±0.05    | 1.29         | Cu9V     | 5.85          | 1.56         |
| Cu11     | 5.84          | 5.91±0.05    | 2.11         | Cu10V    | 5.69          | 1.85         |
| Cu12     | 6.26          | 6.30±0.05    | 1.76         | Cu11V    | 5.79          | 1.86         |
| Cu13     | 5.57          | 5.66±0.05    | 2.07         | Cu12V    | 6.02          | 2.10         |

\[
E_g(Cu_n) = [nE(Cu) + E(V) - E(Cu_n^+)]/(n + 1),
\]

\[
\Delta E^2(Cu_{n+1}) = E(Cu_{n+1}) - E(Cu_n) - 2E(Cu_{n+1})
\]

\[
\Delta E^2(Cu_{n}V) = E(Cu_{n+1}V) + E(Cu_{n-1}V) - 2E(Cu_n V)
\]

The HOMO-LUMO energy gap \(E_g\), which relies on the eigenvalues of the HOMO and LUMO energy levels, is viewed as an important parameter that characterizes chemical stability of small clusters. A big energy gap usually relates to a high chemical inertness. For the ground state Cu_{n+1} and Cu_{n}V clusters, the energy gaps are plotted in Fig. 6. The pure copper clusters show an odd-even alternation in their energy gaps. This phenomenon can be interpreted by the electron pairing effect that the electron in a doubly occupied HOMO has stronger effective core potentials because the electron screening is weaker for electrons in the same orbital than for inner shell electrons. When a Cu atom ([Ar]3d^{10}4s^1) in Cu_{n+1} cluster is replaced by a V ([Ar]3d^{10}4s^2) atom, the closed electronic shell will become an opened electronic shell. So, the \(E_g\) of Cu_{n}V cluster for n = odd is smaller than that of Cu_{n+1} cluster. For n = 2, 4, 6 and 8, the unpaired electrons of Cu_{n}V cluster is more than those of the corresponding Cu_{n+1} cluster. The energy of the LUMO of Cu_{n}V cluster will rise because of the electrostatic interaction of unpaired electrons. The \(E_g\) of Cu_{n}V are larger than that of the Cu_{n+1} cluster. For n = 10 and 12, the Cu_{n}V cluster is equal to Cu_{n+1} cluster in unpaired electrons. However, the formers have a highly symmetrical geometry. Hereby, the \(E_g\) of Cu_{10}V and Cu_{12}V clusters is also larger than that of the Cu_{11} and Cu_{13} clusters, respectively.

The VIP and VEA are two basic quantities to get an insight into the electronic property and can be estimated as follows

\[
VIP = E(\text{cluster cation}) - E(\text{cluster})
\]

\[
EA = E(\text{cluster}) - E(\text{cluster anion})
\]
present theoretical method again. Meanwhile, we can distinguish the ground state structure of Cu₉ cluster by the aid of VIPs. The present and preceding calculations have shown that the 9A and 9B isomers are the candidate for the lowest energy structure of Cu₉ cluster. Our calculated VIPs are 5.27 eV for 9A and 5.99 eV for 9B. The measured value is 5.36 ± 0.05 eV. Thus, we deduced that the 9A structure is the most stable structure of Cu₉ cluster.

To offer reference material for PES experiment in future, the theoretical PES spectra of the global minimum structures of Cuₙ⁺₁ and Cuₙ₉ (n = 1–12) clusters were simulated by adding the occupied orbital energy relative to the HOMO to the VIP and fitting them with a broadening factor of 0.1 eV, as plotted in Fig. 7. The distribution of energy level for all clusters is in the range of 6 to 11 eV. The doped V atom made a change for the PES spectra of Cuₙ⁺₁ and Cuₙ₉. The total magnetic moment of the ground state Cuₙ⁺₁ and Cuₙ₉ (n = 1–12) clusters and local magnetic moment on the dopant atom V is shown in Fig. 8.

Figure 7. Simulated photoelectron spectra of the ground state Cuₙ⁺₁ (in red) and Cuₙ₉ (in black) (n = 1–12) clusters.

Figure 8. Total magnetic moment of the ground state Cuₙ⁺₁ and Cuₙ₉ (n = 1–12) clusters and local magnetic moment on the dopant atom V.
of copper cluster. This change is relatively pronounced for Cu_{n+1} and Cu_{n}V (n = 1–5) clusters. The pronounced change might be related with the planar configuration.

**Magnetic properties.** The magnetic properties of the clusters are not only widely used in the preparation of nano electronic devices and high density magnetic storage materials, but also have a very important theoretical significance in the basic research of physics. The total magnetic moments of cluster mainly include the orbital and spin magnetic moments of electrons. The orbital magnetic moment of an electron is far less than the spin magnetic moment and, consequently, the magnetic moment of cluster is dominated by the spin magnetic moment. For the ground-state Cu_{n+1} and Cu_{n}V (n = 1–12) clusters, the total magnetic moments are calculated and displayed in Fig. 8. The lowest energy copper clusters show an odd–even alternations with the increase of Cu atom in the total magnetic moment. The magnetic moment of Cu_{n+1} clusters with odd n is completely quenched.

**Figure 9.** SDOS of the lowest energy Cu_{n}V clusters. A broadening factor δ = 0.1 eV is used. Spin up (positive) and spin down (negative) densities are given in each case. The black part is the density difference (spin up minus spin down). The dashed line indicates the location of the HOMO level.

**Figure 10.** Free V atom as the reference point, the change of magnetic moments of V atom in Cu_{n}V clusters.
For the doped clusters, the magnetic moment of \( \text{Cu}_n\text{V} \) (\( n = 1–8 \)) cluster is far larger than that of \( \text{Cu}_n^+ \) clusters. The substitution of a V atom for a Cu atom can enhance the magnetism of the small host cluster. The \( \text{Cu}_2\text{V}, \text{Cu}_4\text{V}, \text{Cu}_6\text{V} \) and \( \text{Cu}_8\text{V} \) clusters have a magnetic moment of 3 \( \mu_B \), which is also the magnetic moment of a V atom.

The magnetic moment (4 \( \mu_B \)) of each \( \text{Cu}_n\text{V} \) (\( n = 1, 3, 5 \) and 7) clusters is just equal to the sum of the magnetic moments of the \( \text{Cu}_n \) cluster (1 \( \mu_B \)) and an isolated V atom (3 \( \mu_B \)). These imply that the interaction of Cu and V atoms may have similarities among \( \text{Cu}_n\text{V} \) (\( n = 1–8 \)) clusters. In case of big \( \text{Cu}_n\text{V} \) (\( n = 9–12 \)) cluster, the \( \text{Cu}_{10}\text{V} \) and \( \text{Cu}_{12}\text{V} \) clusters have the same magnetic moments as \( \text{Cu}_{11} \) and \( \text{Cu}_{13} \) clusters. The magnetic moment (2 \( \mu_B \)) of \( \text{Cu}_9\text{V} \) and \( \text{Cu}_{11}\text{V} \) clusters be greater than that (1 \( \mu_B \)) of \( \text{Cu}_9 \) and \( \text{Cu}_{11} \) clusters and less than that (3 \( \mu_B \)) of V atom.

The foregoing relation indicates that the big \( \text{Cu}_n\text{V} \) (\( n = 9–12 \)) clusters have a different interaction between Cu and V atoms relative to \( \text{Cu}_n\text{V} \) (\( n = 1–8 \)) clusters. As an effort to explain the magnetism, Fig. 9 gives the spin density of states (SDOS) for the global minimum structures of \( \text{Cu}_n^+ \) and \( \text{Cu}_n\text{V} \) clusters. All the ground states have an intense band between \( -5 \) and \( -2 \) eV, which consists principally of the valence \( s \) and \( d \) orbitals of the constituent atoms. It is clear from the density difference that the magnetic moment of \( \text{Cu}_n\text{V} \) clusters mostly comes from the electrons near the HOMO (\( E - E_{\text{HOMO}} = -2~0 \) eV). The \( \text{Cu}_n\text{V} \) clusters have some very small magnetic domains, which vary with the size of cluster.

To gain insight into the magnetic properties further, we have performed the natural bond orbital analysis for the lowest energy \( \text{Cu}_n\text{V} \) clusters. The local magnetic moments on V atom are 4.16 \( \mu_B \) for \( \text{CuV} \), 4.13 \( \mu_B \) for \( \text{Cu}_2\text{V} \), 3.90 \( \mu_B \) for \( \text{Cu}_3\text{V} \), 3.29 \( \mu_B \) for \( \text{Cu}_4\text{V} \), 3.82 \( \mu_B \) for \( \text{Cu}_5\text{V} \), 3.58 \( \mu_B \) for \( \text{Cu}_6\text{V} \), 3.73 \( \mu_B \) for \( \text{Cu}_7\text{V} \), 2.88 \( \mu_B \) for \( \text{Cu}_8\text{V} \), 2.33 \( \mu_B \) for \( \text{Cu}_9\text{V} \), 1.88 \( \mu_B \) for \( \text{Cu}_{10}\text{V} \), and 1.88 \( \mu_B \) for \( \text{Cu}_{12}\text{V} \), as shown in Fig. 8. Overall, with the increase of cluster size, the magnetic moments of V atoms gradually decrease. The magnetic moments of V atom in \( \text{Cu}_n\text{V} \) clusters is larger for \( n = 1–8 \) and smaller for \( n = 9–12 \) than that of free V atom. Compared to the free V atom, the change of magnetic moments of V atoms in \( \text{Cu}_n\text{V} \) clusters (see Fig. 10) should reflect the strength of the interaction between V and Cu atoms. The magnetic moment provided by Cu atoms is very small. Furthermore, Cu atoms in \( \text{Cu}_n\text{V} \) (\( n = 1, 9, 11 \) and even) clusters exhibit an antiferromagnetic alignment with respect to the V atom's magnetic moment. That is to say, the magnetic moments of these \( \text{Cu}_n\text{V} \) clusters primarily are from a paramagnetic V atom. The charge and magnetic moment on 4s, 3d, 4p and 5p orbitals of V atom in \( \text{Cu}_n\text{V} \) clusters are listed in Table 4. It can be seen from the table that the partially filled 3d orbital play a substantial role in determining the magnetism of V atom. The magnetic moment of 3d orbital is 1.81~3.98 \( \mu_B \). The 4s and 4p orbitals, which are non-magnetic for a free V atom, contribute a few of magnetic moment, apart from 4p orbital of V in \( \text{CuV} \) dimer. This may be ascribed to the internal charge transfer from 4s to 3d, 4p and 5p orbitals. Simultaneously, there are

| Clusters | V-4s | V-3d | V-4p | V-5p |
|----------|------|------|------|------|
| \( \text{CuV} \) | 0.66 | 0.18 | 4.06 | 3.98 |
| \( \text{Cu}_2\text{V} \) | 1.38 | 0.58 | 3.71 | 3.45 |
| \( \text{Cu}_3\text{V} \) | 0.49 | 0.17 | 3.85 | 3.65 |
| \( \text{Cu}_4\text{V} \) | 0.59 | 0.01 | 3.73 | 3.27 |
| \( \text{Cu}_5\text{V} \) | 0.56 | 0.1 | 3.81 | 3.61 |
| \( \text{Cu}_6\text{V} \) | 0.48 | 0.08 | 4.12 | 3.54 |
| \( \text{Cu}_7\text{V} \) | 0.47 | 0.05 | 4.37 | 3.19 |
| \( \text{Cu}_8\text{V} \) | 0.45 | 0.03 | 4.47 | 2.77 |
| \( \text{Cu}_9\text{V} \) | 0.46 | 0.02 | 4.68 | 2.26 |
| \( \text{Cu}_{10}\text{V} \) | 0.47 | 0.03 | 5.00 | 2.58 |
| \( \text{Cu}_{11}\text{V} \) | 0.46 | 0.02 | 5.41 | 1.81 |
| \( \text{Cu}_{12}\text{V} \) | 0.46 | 0.02 | 5.41 | 1.81 |

Table 4. The charge (Q) and local magnetic moment (M) of 3d, 4s, 4p, and 5p states for the V atom in the ground state \( \text{Cu}_n\text{V} \) clusters.
an interatomic charge transfer in $\text{Cu}_n \text{V}$ clusters. Namely, 0.13–0.36 electrons transfer from V atom to Cu atoms for $n = 1, 3–5$ and 0.28–3.46 electrons from Cu atoms to V atom for $n = 2, 6–12$. As we know, the d orbital can contain up to 10 electrons. If $N$ represents the sum of valence electron on V atom in $\text{Cu}_n \text{V}$ clusters, we found that $10-N$ and the magnetic moment of V atom have the same change trend as shown in Fig. 11. The charge transfer hints that the V atom in $\text{Cu}_n \text{V}$ clusters has a hybridization among $s$, $p$, and $d$ orbitals. The energy of $d$ orbital of V atom is gradually decreased with the increase of clusters size and more and more electrons are transferred to the $d$ orbital. Hence, the larger the cluster, the smaller the magnetic moment of V atom. The orbital hybridization and charge transfer should be responsible for the magnetic moment alteration of the dopant atom.

**Conclusions**

Density functional calculations have been performed for the structural, electronic, and magnetic properties of $\text{Cu}_{m+1}$ and $\text{Cu}_m \text{V}$ ($n = 1–12$) clusters. The results show that V atom in low energy $\text{Cu}_n \text{V}$ clusters tend to occupy the position with the maximum coordination number and changes the geometry of the 3D host clusters. The vibrational and photoelectron spectroscopy spectra are given to identify the most stable structures in times to come. The substitution of a Cu atom in copper clusters by a V atom enhances the binding energy of big clusters and alters the odd–even oscillations of relative stability and chemical activity of the host clusters. The ground states of copper clusters are confirmed by comparing the theoretical vertical ionization potential with experimental findings. At the same time, we predict the vertical ionization potential and electron affinity of $\text{Cu}_n \text{V}$ clusters and electron affinity of $\text{Cu}_{m+1}$ cluster. The magnetism calculation indicates that V atom in $\text{Cu}_n \text{V}$ clusters carries most of the total magnetic moment. The local magnetic moment of the doped atom decreases with the increase of cluster size because of the orbital hybridization and charge transfer.

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Acknowledgements
This project was supported by the education department of sichuan province (grant No. 15233422) and by the key scientific research fund of Xihua University (grant No. Z0820401).

Author Contributions
D.D. and B.-X.Z. conceived the idea. B.-X.Z., L.-Q.Z., Q.-W.Z. and Z.-Q.Z. performed the calculations. D.D. and B.-X.Z. wrote the manuscript and all authors contributed to revisions.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep
Competing financial interests: The authors declare no competing financial interests.
How to cite this article: Die, D. et al. Insights into the structural, electronic and magnetic properties of V-doped copper clusters: comparison with pure copper clusters. Sci. Rep. 6, 31978; doi: 10.1038/srep31978 (2016).

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