**Geometric and electronic structures of vanadium sub-nano clusters, V*n* (*n*=2-5), and their adsorption complexes with CO and O2 ligands: A DFT-NBO study**

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**Table 1s.** NBOs, orbital hybridization in percentage, energy, and shape of NBOs in α-and β-spin parts of trimer.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| NBO bonds | hA—hB% | Energy (a.u) | Occupancy | NBO picture |
| ***ρ=97.17%*** |  | ***α-spin part*** |  |  |
| σV(1)—V(2) | s5.0dx2-y295.0- s5.0dx2-y295.0 | -0.1722 | 0.96 |  |
| σV(1)—V(3) | s25.0dx2-y275.0-s25.0dx2-y275.0 | -0.1689 | 0.98 |  |
| σV(2)—V(3) | s25.0dx2-y275.0-s25.0dx2-y275.0 | -0.1689 | 0.98 |  |
| πV(1)—V(2) | dxy99.5-dxy99.5 | -0.1408 | 0.98 |  |
| πV(1)—V(3) | dxz99.0-dxz99.0 | -0.1302 | 0.99 |  |
| NB(1) V(3) | d z299.0 | -0.1099 | 0.34 |  |
| NB(2) V(3) | dxz99.0 | -0.0979 | 0.53 |  |
| NB(3) V(3) | s6.0dx2-y294.0 | -0.0622 | 0.48 |  |
| ***ρ=96.71%*** |  | ***β-spin part*** |  |  |
| σV(1)—V(2) | s7.0dyz93.0-s7.0 dyz93.0 | -0.1917 | 1.00 |  |
| σV(1)—V(3) | s48.0d z252.0-s48.0d z252.0 | -0.1862 | 0.93 |  |
| σV(2)—V(3) | s48.0d z252.0-s48.0d z252.0 | -0.1862 | 0.93 |  |
| σV(1)—V(2) | s46.0d z254.0-s46.0d z254.0 | -0.1710 | 0.85 |  |
| πV(1)—V(2) | dyz98.0-dyz98.0 | -0.1478 | 0.87 |  |
| πV(1)—V(2) | dxy99.5-dxy99.5 | -0.1448 | 1.00 |  |
| NB(1) V(1) | dxy99.0 | -0.0749 | 0.36 |  |

NB equals to non-bonding orbital.

**Table 2s**. Donor acceptor interactions of V3 cluster

(energy is in kcal/mol.) based on second order perturbation theory.

|  |  |  |
| --- | --- | --- |
| Charge transfer Ωi →Ω\*j | Occupancy Ωi →Ω\*j | E2 |
| ***α-set*** | | |
| *n*V(3)→*n*\*V(1) | 0.48-0.26 | 81.0 |
| *n*V(3)→*n*\*V(2) | 0.48-0.26 | 81.0 |
| *n*V(3)→σ\*V(1)—V(3) | 0.48-0.04 | 14.8 |
| *n*V(3)→σ\*V(2)—V(3) | 0.48-0.04 | 14.8 |
| ***β-set*** | | |
| πV(1)—V(2)→*n*\*V(3) | 0.87-0.14 | 11.8 |
| σV(1)—V(2)→*n*\*V(3) | 0.85-0.16 | 31.3 |
| σV(1)—V(3)→*n*\*V(2) | 0.93-0.03 | 14.7 |
| σV(2)—V(3)→*n*\*V(1) | 0.93-0.03 | 14.7 |

**Table 3s.** NBO description of singlet distorted tetrahedron cluster with C1 symmetry contains six σ bonds and four 3C/2e bonds for tetramer.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| NBO type | Occupancy | Energy (a.u) | hA—hB% | NBO picture |
| σV(1)-V(2) | 1.89 | -0.1859 | S32.0dxy66.0-S32.0dxz66.0 |  |
| σV(1)–V(3) | 1.89 | -0.1859 | S32.0dyz66.0-S32.0dz266. |  |
| σV(1)-V(4) | 1.89 | -0.1859 | S32.0dxz66.0-S32.0dz266 |  |
| σV(2)-V(3) | 1.89 | -0.1859 | S32.0dx2-y266.0-S32.0dxy66 |  |
| σV(2)-V(4) | 1.89 | -0.1859 | S32.0dxz66.0-S32.0dxy66 |  |
| σV(3)-V(4) | 1.89 | -0.1859 | S32.0dxz66.0-S32.0dxz66 |  |
| 3CV(1)-V(2)-V(3) | 1.94 | -0.1832 | dx2-y2-dyz-dyz |  |
| 3CV(1)-V(2)-V(4) | 1.94 | -0.1832 | dyz-dz2-dxz |  |
| 3CV(1)-V(4)-V(3) | 1.94 | -0.1832 | dz2-dz2-dyz |  |
| 3CV(1)-V(2)-V(4) | 1.94 | -0.1832 | dxy-dx2-y2-dx2-y2 |  |

**Table 4s.** Bonds and lone pair in distorted trigonal bi pyramid cluster described by the NBO methodology for pentamer.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| NBO type | Occupancy | Energy (a.u) | hA—hB% | NBO picture |
| ***α spin*** |  |  | ***%ρ=96.80*** |  |
| σV(1)-V(3) | 0.93 | -0.1836 | dz2100.0- dz2100.0 |  |
| πV(1)–V(3) | 0.82 | -0.1442 | dxz98.0- px10.0dyz90.0 |  |
| πV(1)–V(3) | 0.88 | -0.2087 | s21.0dx2-y276.0-s26.0dx2-y271.0 |  |
| πV(1)–V(3) | 0.60 | -0.1209 | s32.0dx2-y266.0- s32.0dxy66.0 |  |
| πV(2)–V(3) | 0.64 | -0.1460 | dyz99.0- pz18.0dxz82.0 |  |
| σV(2)-V(4) | 0.88 | -0.1920 | dz297.0-px34.0dz264.0 |  |
| πV(2)-V(4) | 0.80 | -0.1595 | s18.0dxy81.0- s18.0dyz81.0 |  |
| πV(2)-V(5) | 0.67 | -0.1672 | s11.0dyz87.0-s8.0px8.0dx2-y284.0 |  |
| πV(3)-V(5) | 0.60 | -0.1327 | px8.0dxz92.0- px40.0dxz60.0 |  |
| σV(4)-V(5) | 0.85 | -0.1787 | pz34.0dz264.0- pz16.0dz282.0 |  |
| πV(4)-V(5) | 0.78 | -0.1546 | s12.0dyz85.0- s20.0pz6.0dxz74.0 |  |
| πV(4)-V(5) | 0.65 | -0.1397 | s3.0px6.0dyz91.0- pz27.0dz273.0 |  |
| NB(1) V(1) | 0.57 | -0.1119 | s16.0d z284.0 |  |
| ***β spin*** |  |  | ***%ρ=95.30*** |  |
| πV(1)-V(2) | 0.45 | -0.1244 | px3.0dxz91.0- px27.0d z273.0 |  |
| σV(1)-V(3) | 0.88 | -0.1475 | px13.0d z287.0- d z298.0 |  |
| πV(1)-V(3) | 0.76 | -0.1594 | px9.0dxz91.0- pz3.0dyz97.0 |  |
| πV(1)-V(3) | 0.73 | -0.1722 | s4.0px6.0dx2-y290.0-pz3.0dx2-y297.0 |  |
| πV(1)-V(4) | 0.74 | -0.1482 | px4.0dxz96.0- dxz97.0 |  |
| πV(2)-V(3) | 0.69 | -0.1438 | px4.0 dxy96.0- px3.0 dxy97.0 |  |
| σV(2)-V(4) | 0.85 | -0.1827 | s32.0d z267.0-s13.0d z286.0 |  |
| πV(2)-V(4) | 0.72 | -0.1524 | dxz98.0- dx2-y297.0 |  |
| σV(2)-V(4) | 0.60 | -0.1733 | s11.0d z288.0-s9.0d z290.0 |  |
| σV(4)-V(5) | 0.88 | -0.1818 | s9.0d z290.0-s14.0d z283.0 |  |
| NB(1) V(2) | 0.72 | -0.1294 | d z2 |  |
| NB(1) V(5) | 0.71 | -0.1256 | dyz |  |
|  |  |  |  |  |

**Table 5s.** Donor acceptor interactions of pentamer (energy is in kcal/mol.).

|  |  |  |
| --- | --- | --- |
| Charge transfer Ωi →Ω\*j | Occupancy Ωi →Ω\*j | E2 |
| ***α-set*** | | |
| πV(1)—V(3)→σ\*V(2)—V(3) | 0.60-0.11 | 8.2 |
| σV(2)—V(4)→*n*\*V(1) | 0.88-0.22 | 11.6 |
| σV(2)—V(4)→*n*\*V(5) | 0.88-0.23 | 12.1 |
| πV(2)—V(5)→*n*\*V(3) | 0.67-0.29 | 22.6 |
| πV(2)—V(5)→*n*\*V(4) | 0.67-0.29 | 29.3 |
| σV(4)—V(5)→*n*\*V(1) | 0.85-0.22 | 14.6 |
| σV(4)—V(5)→*n*\*V(2) | 0.85-0.24 | 14.1 |
| *n*V(1)→*n*\*V(2) | 0.57-0.24 | 8.2 |
| *n*V(1)→*n*\*V(3) | 0.57-0.29 | 44.9 |
| ***β-set*** | | |
| πV(1)—V(2)→*n*\*V(3) | 0.45-0.22 | 77.5 |
| πV(1)—V(2)→*n*\*V(5) | 0.45-0.37 | 79.8 |
| πV(1)—V(3)→*n*\*V(5) | 0.73-0.37 | 23.7 |
| πV(1)—V(4)→*n*\*V(5) | 0.74-0.37 | 24.2 |
| πV(1)—V(3)→*n*\*V(5) | 0.73-0.37 | 21.3 |
| σV(2)—V(4)→*n*\*V(1) | 0.69-0.24 | 36.7 |
| σV(2)—V(3)→*n*\*V(5) | 0.60-0.37 | 52.1 |
| *n*V(5)→*n*\*V(3) | 0.72-0.22 | 13.4 |

**Table 6s.** Significant Donor acceptor interactions of V*n*CO (*n*=2-5), energy (ΔE) in β-spin part.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Complex | elongation of C―O bond (Å) | donation | E2 (kcal/mol) | back-donation | E2 (kcal/mol) |
| V2CO | 0.085 | σV(1)-C(4) → *n*\*V(2) | 91.1 | *n*O(3)→ σ\*V(2)-C(4) | 41.4 |
| V3CO | 0.119 | σV(1)-C(5) → *n*\*V(2) | 14.3 | σV(1)-V(2) → σ\*V(1)-C(5) | 14.9 |
|  |  | σV(1)-C(5) → *n*\*V(3) | 20.4 | *n*O(4)→π\*V(1)-C(5) | 41.1 |
| V4CO |  | σV(2)-C(5) → *n*\*V(3) | 131.5 | - | - |
| V5CO |  | Not considerable | - | Not considerable | - |

**Table 7s**. Number of bonds, occupancies, and distance of bond, d, (Å),

of the V*n*CO (*n*=2-5) complexes at α and β-spin sets.

|  |  |  |  |
| --- | --- | --- | --- |
| structure | V2CO | V(1)-C(4) | V(2)-C(4) |
|  | OCC | σα:0.81, *n*C: 0.81 | σβ: 0.82  σβ:0.81 |
|  | d (Å) | 2.397 | 1.929 |
| V3CO |  | V(1)-C(5) | V(3)-C(5) |
|  | OCC | σα: 0.94  σβ:0.91, πβ:0.80 | σα: 0.87 |
|  | d (Å) | 1.902 | 2.215 |
| V4CO |  | V(1)-C(5) | V(3)-C(5) |
|  | OCC | σα: 1.55,  σα: 1.47  nC: 0.86 | πα: 1.47 |
|  | d (Å) | 1.877 | 2.026 |
| V5CO |  | V(1)-C(6) | V(2)-C(6) |
|  | OCC | πα:0.63, πα:0.66  πβ:0.75 | σα:0.69 |
|  | d (Å) | 1.925 | 2.009 |

**Table 8s.** Number of bonds, occupancies, and distance of bond, d, (Å), of the V*n*O2 (*n*=2-5) complexes at α and β-spin sets.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| structure | V2O2 | V(1)-O(3) | V(1)-O(4) | V(2)-O(3) | - |
|  | OCC | σα:0.95, πα: 0.93  σβ:0.95, πβ: 0.93 | πα: 0.98, σα: 1.00, πα: 0.97  πβ: 0.98, σβ: 1.00, πβ: 0.97 | σα: 0.96  σβ: 0.96 | - |
|  | d (Å) | 1.856 | 1.630 | 1.799 | - |
| V3O2 |  | V(1)-O(4) | V(1)-O(5) | V(2)-O(5) | V(3)-O(4) |
|  | OCC | σα: 0.92, πα: 0.94  σβ:0.90 | σα: 0.95, πα: 0.90  σβ:0.87, σβ:0.84 | σα: 0.96 | σα: 0.96 |
|  | d (Å) | 1.819 | 1.867 | 1.843 | 1.811 |
| V4O2 |  | V(1)-O(5) | V(2)-O(5) | V(2)-O(6) | V(3)-O(6) |
|  | OCC | σα: 0.95, πα: 0.91  σβ:0.95, πβ: 0.91 | σα: 0.96  σβ:0.94 | σα: 0.96  σβ: 0.95, πβ: 0.89 | σα:0.95, πα: 0.91  σβ: 0.94 |
|  | d (Å) | 1.810 | 1.834 | 1.833 | 1.819 |
| V5O2 |  | V(1)-O(7) | V(1)-O(6) | V(4)-O(7) | V(3)-O(6) |
|  | OCC | σα:0.95  σβ:0.95 | σα:0.95  σβ:0.95 | σα:0.91  σβ:0.91 | σα:0.91  σβ:0.91 |
|  | d (Å) | 1.824 | 1.824 | 1.835 | 1.835 |