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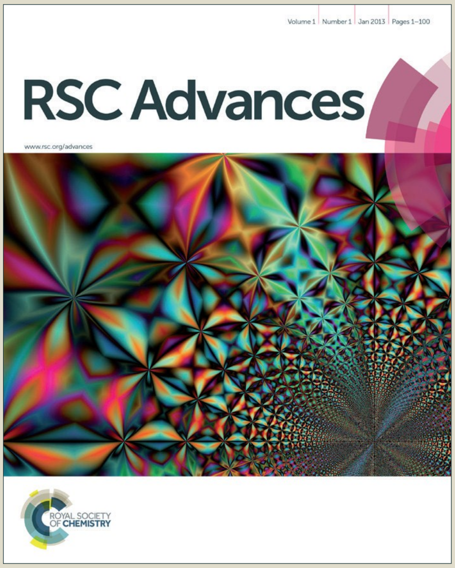

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Structural evolution, electronic and magnetic manners of small rhodium $Rh_n^{+/-}$(n=2-8) clusters: Details density functional theory study

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Abstract

Systematic investigation on the lowest energy electronic structure of neutral, cationic and anionic Rh_n (n=2-8) clusters in the gas phase are performed with all electron relativistic method using density functional theory within the generalized gradient approximation. Lowest energy structures of neutral and ionic rhodium clusters are evaluated with different multiplicities. Neutral clusters with even atoms of rhodium and ionic clusters containing odd atoms of rhodium are optimized with multiplicities (M=1, 3, 5), while neutral clusters containing odd rhodium atoms and ionic cluster having even atoms of rhodium are allowed to relax with multiplicities (M=2, 4, 6). Bond length, binding energy, coordination number, bond dissociation energy, stability function, ionization potential, electron affinity, electrophilcity, LUMO-HOMO gap, chemical hardness, dipole moment and magnetic moment are evaluated from the lowest energy geometry. These studies reveal that even atom rhodium clusters are more stable than the odd atom clusters. Calculated electronic properties such as LUMO-HOMO gap, bond dissociation energy, stability function, electron affinity and electrophilicity suggest that Rh_4 with tetrahedral geometry is the most stable among all Rh_n(n=2-8) clusters. Hence, tetrahedral Rh_4 may be considered as the magic number cluster.

Key Words: DFT, Rhodium, Magic cluster, stability

Introduction

Atomic clusters are very vital class of materials which composed of a few to hundreds of atoms. Cluster shows different physical[1] and chemical properties[2-4] from the bulk counterparts due to quantum size effects. Studies of small metal clusters provided a connecting link between molecular and bulk states. High surface to volume ratio of smaller clusters lead to the properties different from the bulk. Properties of a nanoclusters change drastically even after addition of single extra atom. In the recent years, transition metal clusters have been widely studied due to their unique catalytic and magnetic properties. In particular, nanoclusters of Pt, Pd and Rh are used as heterogeneous catalyst for hydrogenation as well as for reduction of NO, oxidation of CO and unburned hydrocarbons.[5] Rh on the other hand, is vital heterogeneous catalyst used for hydrogenation as well as dehydrogenation reactions of alcohols[6] and also for removing harmful gases.[7] Variation of magnetic moment with cluster size and high catalytic activity are the most significant characteristics of transition metal clusters. Many theoretical and experimental studies on magnetic properties of 3d transition metal clusters such as Fe, Co and Ni have been extensively performed till to date.[8-13] These investigations suggest that 3d transition metal clusters have nonzero magnetic moments while, the bulk form shows no magnetic moment.[11, 14] Due to the reduced coordination and high symmetry, clusters develop narrow d-band width that give the possibility of larger spin multiplicities in the ground state. However, a very few theoretical and experimental studies on 4d transition metal clusters are reported.[15] Out of them, Rh metal clusters have been the subject of a number of experimental and theoretical studies because of their catalytic and magnetic properties. Two very important aspects are considered to investigate the magnetic properties of metal clusters: First is to study the lowest energy geometrical structures and second is to determine their electronic properties. Most of the electronic calculations on Rh clusters have been performed either by assuming fixed geometries[16-18] or just optimizing bond lengths.[15, 19-21] Investigation of electronic structure of rhodium clusters are very challenging due to huge number of electrons and large number of achievable geometrical isomers. However, some low energy rhodium clusters are derived by density functional theory calculation. Reddy *et al.*[22] have combined the techniques of MD (molecular dynamics) with DFT and anticipated that 13 atoms Rh cluster is magnetic with magnetic moment 1.62 μ_B while, the observed value of magnetic moment per atom of Rh_{13} is found to be 0.48 μ_B.[23, 24] Jinglong *et al.*[15, 25] examined different small rhodium clusters and Li *et al.*[19] evaluated the magnetic properties of Rh_n (n= 6, 9, 13, 19, 43). Cox *et al.* reported the permanent magnetic moment of rhodium clusters with n ≤ 60-90 while, ruthenium along with palladium clusters show nonmagnetic behavior at least for cluster size greater than 13.[24, 26] Rh is the first case where magnetism is observed in the nanoclusters of a nonmagnetic solid. Remarkable size dependence of magnetic moment per atom of rhodium is observed from experimental studies. Magnetic moment of nanoclusters oscillates as a function of cluster size along with the number of atoms. Magnetic moment of rhodium cluster seems to be different from other ferromagnetic transition metal clusters such as Fe, Co and Ni, where the magnetic moments are extended over wide ranges.[27-31] Finite size effect in electronic structure and reduction of the local coordination number qualitatively reflects the enhancement of magnetism in small clusters.[24] A spin-polarized DFT study [32,33] of Ru, Rh, and Pd clusters show large magnetic moment for small clusters while, magnetic moment of Ru and Rh clusters decreases gradually on increasing the cluster size.

Some theoretical works[22, 23] reveal that Rh_4 with tetrahedral geometry is stabilized in the singlet state while; Bae *et al.*[34] showed that the high spin rhombus Rh_4 is the ground state. Magnetic moment of metal clusters changes with the changes of their geometries. Magnetic moment of Rh_{13} cluster is found to be 1.3 μ_B per atom with cage like structure[34] while, Stern-Gerlach evaluated the magnetic moment of 0.48 μ_B per atom.[24, 26] Different geometrical assumptions can clarify the obvious inconsistency between different theoretical and experimental works. Thus it is obvious that obtaining the ground state geometry is very much crucial for explaining the magnetic properties of the metal clusters.

Most of the recent investigations related to Rh clusters are motivated by the theoretical studies of Galicia[35], Reddy *et al.*[23] and the experimental works of Cox *et al*.[24,26] Wide range of magnetic moment of rhodium nanoclusters are observed from theoretical studies.[15,19,36,37] This indicates a quite strong understanding of the calculated magnetic properties of Rh with theoretical method approximation. Due to indirect experimental information and insufficient precise structural determination, the correct properties of free-standing clusters are hard to pin down. Metals do not always follow the good proportionality of magnetism with the coordination number and interatomic distances which is observed from *ab initio* calculation of Rh_2 supported on Ag (001).[38] Therefore, a methodical exploration of both the geometrical and magnetic properties are vital for isolated rhodium clusters with respect to size.

Basic attention in magnetism as well as bonding nature in correlation with the atomic structures of Rh nanoclusters are found significant for catalysis.[39] Hence, it is challenging to recognize the magnetic properties properly to understand their role in catalytic applications.

Correct representation of the electronic correlation for the large number of open shell electronic states which arise due to incomplete 4d states of Rh is challenging aspects in theoretical study.[40]

To the best of our knowledge probably for the first time a detail systematic investigation on electronic, structural and magnetic properties of neutral and ionic Rh_n(n=2-8) clusters have been done. Main focus of this study is to correlate different properties such as bond length, coordination number, binding energy, bond dissociation energy, ionization potential, electron affinity, LUMO-HOMO gap, global hardness, etc., with size and stability of the clusters. DOS and spin density values are evaluated in order to study the electronic and magnetic contribution of each atom to a cluster. A systematic survey on small rhodium clusters is done to achieve their most stable or reactive cluster on the basis of the calculated reactivity parameters. Geometry optimization of different possible structural isomers of neutral Rh_n (n=2–8) clusters are carried out with different multiplicities *i.e.*, M=2, 4, 6 for odd atom clusters and M=1, 3, 5 for even atom clusters to evaluate the stable geometry. Geometries of Rh_n^+ and Rh_n^- clusters are also fully optimized with multiplicities of 2, 4, and 6 for even atom ionic cluster, while 1, 3, 5 for odd atom ionic cluster, in order to determine the most stable geometry.

Computational Details

All the isomers of rhodium cluster are fully optimized using double numerical plus polarization (DNP) basis set implemented in DMol3 program package.[41, 42] DFT calculations are performed under generalized gradient approximation (GGA) with BLYP exchange correlation functional[43,44] which incorporates exchange functional of Becke's with the gradient corrected functional of Lee–Yang–Parr. DNP[45] basis set is chosen for geometry optimization. DNP basis set is comparable to Gaussian split-valence 6-31G** basis set. Relativistic calculations are very important for heavy metal atoms. Hence, all electron relativistic correction to valence orbitals *via* a local pseudo potential are carried out for direct inversion in a subspace method (DIIS) without symmetry constrains. In this study self consistent field (SCF) procedures are adopted with a convergence criteria of energy 1×10^{-5} Ha, maximum force gradient 2×10^{-3} Ha Å^{-1} and displacement convergence 5×10^{-3} Å on the total energy and 10^{-6} a.u. on electron density are the boundary conditions applied. All the neutral and charged isomers of rhodium clusters are optimized corresponding to low spin configurations. In order to compare energy values of ground state clusters with their higher multiplicities, symmetry restricted calculation are done at higher spin states. Vibrational frequency calculations are done to ensure the energy minima. Zero point vibrational energy correction is incorporated in all the calculated energies. For further study of higher multiplicities most of the clusters are found to retain their ground state. Absence of imaginary frequencies for all geometries suggests their energy minima. To evaluate the stability of the clusters with respect to size, binding energy per atom, the second difference of binding energy, the first vertical ionization potential, electron affinity and chemical hardness of the stable structures are determined.

The average binding energy per atom is computed from the following equation

$$BE = -\frac{E_{tot}}{n}$$

Where E_{tot} is the total energy of a cluster which is defined as $E_{tot} = E_n - nE_1$ with E_1 and E_n are the energies of a single atom and the optimized clusters, respectively, and n is the number of atoms in the cluster.

For ionic clusters, the binding energy is evaluated as

$$BE = -E_{tot}^{\pm} / n$$

Where $E_{tot}^{\pm} = E_n^{\pm} - (n-1)E_1 - E_1^{\pm}$ is the total energy of an ionized cluster where $E_1^{\pm}$ and $E_n^{\pm}$ are the energies of the single charged atom ($Rh_1^{\pm}$) and Rh_n clusters, respectively.

The dissociation energy of a cluster of size n has been calculated from

$$D(n, n-1) = E(Rh_n - 1) + E(Rh_1) - E(Rh_n)$$

Where E (Rh_1) is the energy of single atom and E (Rh_n) is the energy of optimized n atom rhodium.

Chemical hardness (η) can be defined as the second derivative of the energy (E) with respect to the number of electrons (N) at constant external potential, $\nu(\vec{r})$

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial \mathrm{N}}\right)_{\upsilon(\vec{r})}$$

Where μ, chemical potential is defined as the negative of electronegativity by Iczkowski and Margrave[46].

Using the finite difference approach[46] chemical potential, electronegativity and chemical hardness can be computed from vertical ionization potential (IP) and electron affinity (EA).

$$\mu = -\frac{IP + EA}{2}$$

$$\chi = \frac{IP + EA}{2}$$

$$\eta = \frac{IP - EA}{2}$$

According to Parr's prescription, electrophilicity index[47]is defined as

$$\omega = \frac{\mu^2}{2\eta}$$

Results and Discussion

Geometries and Energetics

In order to find out the best exchange-correlation functional to be used for the calculation, we made a comparative study of the bond length, vibrational frequency and binding energy of the rhodium dimmer using various functionals with available experimental results[48]. The comparative results are presented in Table 1. It is noticed from Table1 that among all the GGA functionals used, BLYP functional provides the best assess of all the three experimental parameters considered. Hence, we choose BLYP functional in this study.

Neutral Rh_n clusters:

The ground state for Rh atom is found to be quartet, ^4F ($4d^8 5s^1$) with energy 131524.7615 eV. Ground state geometries of neutral Rh_n (n=2-8) clusters evaluated at BLYP/DNP level are shown in Fig. 1 and all other isomers with their point group are given in supplementary information Fig S1 of ESI. Singlet multiplicity is the lowest energy state for neutral Rh_2 with symmetric point group $D_{\infty h}$ and having bond length 2.308 Å. The binding energy per atom of all the neutral clusters with different multiplicities is given in Table 2 and bond lengths are mentioned in Table S1 of ESI. It is observed from the Table 2 that the binding energy per atom of Rh_2 is calculated to be 1.5067 eV. Energy values of singlet and triplet state of Rh_2 cluster are obtained to be comparable *i.e.* the triplet state possesses 0.3660 eV higher energy than the singlet state. Variation of the binding energy per atom of neutral clusters with cluster size is shown in Fig 2. For neutral Rh_3 cluster, triangular geometry with quartet state is the lowest energy isomer having bond length of 2.448 Å bearing symmetric point group, D_{3h}. The energy difference between the doublet and the quartet state is found to be only 0.1659 eV. The binding energy per atom for the most stable Rh_3 cluster with triangular shape is 2.1276 eV. A singlet state with tetrahedral geometry is the ground state for the neutral Rh_4 cluster with average bond length and binding energy per atom are 2.518 Å and 2.5315 eV, respectively. Energy difference between triplet and singlet state is evaluated to be 0.3798 eV. Calculated binding energy per atom of Rh_4 is found to be lower than the corresponding values reported by Jinlong *et al.*[15] and Reddy *et al.*[22] However, DFT evaluated average bond length is found to be closer to the corresponding value (2.48 Å) reported by them. For the cluster containing five rhodium atoms, doublet state with square pyramidal geometry and symmetric point group C_{4v} is the lowest energy state. The average bond length and binding energy per atom of stable Rh_5 cluster are 2.532 Å and 2.7091 eV, respectively. The energy difference between the singlet and triplet state of Rh_5 cluster is 0.0778 eV only. Binding energy value is very close to the reported value 2.70 eV/atom predicted by Chien[37] (GGA-DFT) but lower than the values (3.06 and 3.13 eV/atom) showed by Jinlong *et al.*[16] and Reddy *et al.*[22] with symmetric point group D_{3h} and C_{4v}, respectively. Bond length 2.532 Å, obtained in this study is closer to the reported values (2.52 and 2.54 Å) by Jinlong *et al.*[15]and Chien.[34] Trigonal prismatic geometry for Rh_6 neutral cluster in the singlet state with symmetric point group D_{3h} is observed to be the ground state having average bond length of 2.491 Å and binding energy 2.8809 eV/atom. The energy difference between the singlet state and triplet state is found to be 0.0797 eV. Binding energy and bond length values are evaluated to be lower than the corresponding values reported by Jinlong *et al.*[15] (DV-LSDA) and Li[19] ((DV-LSDA). However, calculated binding energy value is exactly same to the binding energy obtained by Chien *et al.*[37] For Rh_7 cluster, quartet state with capped prism structure is found to be the most stable isomer with symmetric point group (C_{2v}). The binding energy per atom and the average bond length of this stable cluster are evaluated to be 2.9045 eV and 2.539 Å, respectively. Binding energy value of Rh_7 obtained is lower than the binding energy values of Jinlong *et al*[15] (3.43 eV/atom) and Reddy *et al.*[22](3.33 eV/atom). Average bond distance of 2.77 Å evaluated in this study is higher than the corresponding values reported by Jinlong *et al.*[15] and Reddy *et al.*[22] Energy difference between doublet and quartet state of Rh_7 cluster is found to be 0.0218 eV. Cubic geometry of Rh_8 having singlet state is evaluated to be most stable isomer. This isomer has a symmetric point group (O_h), having average bond length and binding energy per atom are 2.459 Å and 3.1092eV, respectively. Triplet state is recorded to be possessed slightly higher in energy (0.00370 eV) than the singlet state. The binding energy as well as the average bond distance is calculated to be lower than the values suggested by Jinlong *et al.*[15] and Reddy *et al.*[22]

Cationic (Rh_n^+) and anionic (Rh_n^-) clusters:

In the literature, a very few reports on cationic and anionic clusters of rhodium are accessible. Ground state geometries and their average bond lengths evaluated at BLYP/DNP level are shown in the Fig. 1 and Table S1 of ESI, respectively. Cationic and anionic rhodium clusters are generated by removing and adding one electron to the lowest energy neutral Rh_n clusters.

Spin unrestricted geometry optimization of these ionic clusters with different multiplicities is done. Variation of the binding energies per atom of these ionic clusters with cluster size is shown in Fig. 2 and binding energy values (eV/atom) are listed in the Table 2. Cationic (Rh_2^+) cluster in sextet state is the lowest energy state with symmetric point group $D_{\infty h}$, while, ground state for anionic (Rh_2^-) cluster is quartet with a point group $D_{\infty h}$. It is seen that average bond distance and binding energy per atom for Rh_2^+ and Rh_2^-clusters are 2.355 and 2.353 Å and 1.0707 and 1.7128 eV, respectively. Sextet Rh_2^+ is stabilized more by 0.56912 eV than the doublet state, while, quartet Rh_2^- is stabilized more by 0.26884 eV than the geometry with doublet multiplicity. The lowest energy triangular geometry with symmetry point group D_{3h} is found for $Rh_3^+$and Rh_3^- in the singlet state. It is seen from the Table S1 that the average bond distances (Rh—Rh) in Rh_3^+ and Rh_3^- are found to be 2.448 Å and 2.494 Å, respectively. Binding energy per atom for cationic cluster is 1.9935 eV while, for anionic cluster is calculated to be 2.2245 eV. Energies of Rh_3^-, in the singlet as well as in the triplet states are found to be closer. Again, doublet states of Rh_4^+ and Rh_4^- with tetrahedral geometry are found to be the ground state with T_d symmetry point group. The average bond distances of tetrahedral cationic and anionic rhodium clusters are 2.512 Å and 2.550 Å, respectively. While for cationic and anionic Rh_4 with quartet multiplicity is found to be least stable. Binding energies per atom for the ground state of $Rh_4^+$and Rh_4^- are evaluated to be 2.6381 and 2.6048 eV, respectively. Cationic and anionic Rh_5 clusters in the singlet and pentet multiplicities are evaluated to be the ground state having average bond length of 2.538 and 2.543 Å, respectively. Structure of anionic and cationic Rh_5 is evaluated to be square pyramidal with symmetric point group C_{4v}. Binding energy values per atom for Rh_5^+ and Rh_5^- are 2.8531 and 2.8069 eV, respectively. Energy difference between the triplet and singlet state of Rh_5^+ is 0.05932 eV, while, between pentet and singlet state of Rh_5^- is 0.0080 eV. A doublet state with a trigonal prismatic geometry for both Rh_6^+ and Rh_6^- clusters with a point group D_{3h} are stabilized. The average bond lengths for Rh_6^+ and Rh_6^- are calculated to be 2.484 Å and 2.497 Å, respectively. While, the quartet state of Rh_6^+ and Rh_6^- are less stabilized by 0.17796 and 0.06911 eV, respectively with respect to doublet state of respective ionic Rh_6. The binding energy per atom values of the lowest energy Rh_6^+ (3.0262 eV) and Rh_6^- (2.9966 eV) are noticed to be nearly close. Rh_7^+ and Rh_7^- with singlet multiplicity having capped prism geometry with C_{2v} symmetry are found to be the lowest energy structure. Triplet state of Rh_7^+ and Rh_7^- are evaluated to be less stable than the corresponding singlet state. The binding energies per atom for Rh_7^+ and Rh_7^- are 3.0288 and 3.0491 eV, respectively. Cubic geometry in the doublet state with symmetric point group D_{3h} is the ground state for cationic and anionic Rh_8 clusters. Table S1 reports the average Rh—Rh bond lengths for Rh_8^+ and Rh_8^- are 2.474 and 2.461 Å respectively. Binding energy per atom Rh_8^+cluster (3.2271 eV) is found to be lower than the Rh_8^- (3.2619 eV). Quartet state of $Rh_8^+$and Rh_8^- clusters are least stable. However, quartet and doublet state of ionic Rh_8 clusters are found to possess very close energy values.

Trends:

Variation of average bond length with cluster size for the most stable cluster is shown in Fig 3. It is observed from the figure that the average bond lengths increase with size in the case of smaller clusters, while no regular variation of geometrical parameters are noticed in the case of larger clusters. Variations of binding energies are plotted against cluster size is shown in Fig 2. It is quite visible from the Fig 2 that binding energy per atom of neutral and ionic (cationic and anionic) clusters increase with increasing the number of atoms and number of bonds. Hence, energy stability of rhodium cluster increases with the cluster size, while this variation is less prominent in case of larger clusters. The coordination number (α) of all the clusters is evaluated at DNP/BLYP level. The coordination number of the neutral as well as the ionic clusters is evaluated to be same. The coordination number (α) of Rh_3, Rh_4, Rh_5, Rh_6, Rh_7 and Rh_8, clusters are found to be 2.00, 3.00, 3.20, 3.00, 3.71, and 3.00, respectively. That is Rh_4, Rh_6, and Rh_8 clusters in the neutral as well as in the ionic form possesses same coordination number.

Relative stability:

To understand the relative stability of the rhodium clusters, we have evaluated the second finite difference of total energies $\Delta^2 E_b(n)$, which is the measure of stability function. The stability function is calculated from the following mathematical formulation:

$$\Delta^2 E_b(n) = 2E_b(n) - E_b(n+1) - E_b(n-1)$$

Where $E_b(n)$ is the binding energy per atom of the cluster with n atoms. Variation of stability function with cluster size of rhodium is shown in Fig 4. It is noticed from Fig 4 that highest peak is observed at n=4 for neutral as well as ionic form indicating maximum stability for neutral and ionic Rh_4 among all other cluster. Bond dissociation energies (energy required for fragmenting Rh_n cluster to Rh_{n-1} and Rh) of the most stable neutral and ionic rhodium clusters are plotted against the cluster size is shown in Fig 5. Fig 5 suggests that neutral and cationic Rh_4 and Rh_8 clusters have higher bond dissociation energies and hence, reveal higher stability. However, anionic clusters show noticeable peak at n=4, 6 and 8. It is also seen from Fig 5 that even atom rhodium clusters are comparatively more stable than the odd atom clusters. Cationic clusters are found to possess higher dissociation energies than the neutral as well as anionic clusters. Hence, higher interaction between electrons and nucleus is observed in case of cationic clusters than their neutral clusters. While anionic cluster with lower dissociation energy represents more electron-electron repulsion than nuclear electronic attraction.

Electronic properties and reactivity parameters:

A. Ionization potentials and electron affinity

Vertical ionization potential (IP) and electron affinity (EA) of rhodium clusters are evaluated based on the following mathematical expression

$$IP = E_n^+ - E_n$$

$$EA = E_n - E_n^-$$

Where E_n^+ and E_n^- are the energies of the cationic and anionic rhodium clusters at the optimized geometry of neutral cluster. Calculated ionization potential and electron affinity values of all the clusters are summarized in the Table S3 of ESI and variations of these parameters with cluster size are plotted in Fig 6. From the Fig 6, it is observed that the ionization potential decreases from Rh_2 to Rh_6 and then slightly increases to Rh_7 which again decreases towards Rh_8. Higher ionization potential values of smaller clusters reveal that nucleus held their electrons tightly giving extra stability due to closed shell electronic arrangement. It is also observed from the Fig 6 that electron affinity values decrease from Rh_2 to Rh_4 and then steadily increase from Rh_5 to Rh_8. Hence, Rh_4 has lower electron affinity than other clusters. Lower electron affinity of Rh_4 suggests higher stability due to the stable electronic configuration. Therefore, larger clusters have the tendency to attract more electrons for acquiring extra stability. Thus, the larger atomic clusters have higher affinity to accept electrons to form a negatively charged species compared to the smaller clusters.

B. LUMO–HOMO gap, global hardness, electophilicity and electronegativity:

Variation of LUMO-HOMO gap of the lowest energy isomers with cluster size is plotted in Fig 7 and the calculated values are listed in Table S2 of ESI. Even-odd oscillation of LUMO-HOMO gap is observed with respect to the cluster size (Fig 7). Neutral Rh_n exhibit larger LUMO-HOMO gap in comparison to their corresponding ionic clusters. It is also noticed that even atom clusters have higher LUMO-HOMO energy gap than the odd atom clusters. Among all the rhodium clusters investigated in this study, neutral as well as ionic Rh_4 are found to have larger LUMO-HOMO energy difference. Larger LUMO-HOMO energy gap is the measure of higher global hardness, (η) which is in return reveals higher stability. Change of global hardness with respect to cluster size is presented in Fig 8. Higher hardness values are observed for Rh_2, Rh_3 and Rh_4 Table S3 of ESI. Larger clusters have lower hardness values because band gap in higher atomic cluster is very closed due to linear combination of more atomic orbital for which electrons in Fermi regions are loosely bounded, that is why larger cluster always have the tendency to change their electronic structure.[49] Electron flows in cluster from higher potential region to lower potential region due to the chemical potential difference. Chemical potential is negative values of electronegativity. In this study, it is observed that among all stable rhodium clusters, Rh_2 cluster has the lowest chemical potential value (-4.201 eV), whereas Rh_4 (-3.492 eV) has the highest potential, which indicates that Rh_2 has higher electron accepting power than Rh_4. Higher chemical potential of a cluster exhibit lower stability because more number of electrons may be released when it interacts with species having lower chemical potential.

Variation of electronegativity with cluster size is plotted in Fig 8. It is seen from Fig 8 that electronegativity values decrease from Rh_2 to Rh_5 and then goes on increasing up to Rh_8 Table S3 of ESI. In the case of larger clusters electronegativity values increase with the increase of the number metal atoms because attraction between nucleus and inner core electron increases as with the increase of atom in a cluster nuclear charge also increases. Electrophilicity is the measure of stabilization energy required by clusters when it acquires an extra electronic charge. It is observed from Table S3 of ESI and Fig 8 that Rh_4 has lower electrophilicity values than others *i.e.* it is less prone to get electrons from surrounding, which supports the higher stability of Rh_4 cluster than its neighbours.

Magnetic properties:

A. Magnetic dipole moments

Calculated magnetic moments per atom as a function of cluster size are shown in Table 3. It is observed from the Table 3 that magnetic moment of Rh_n clusters changes discontinuously with size. Rh_4, Rh_6 and Rh_8 clusters show zero magnetic moment per atom. However, odd atomic rhodium clusters show a little magnetic moment. In Table 3, we present the magnetic moment per atom for the lowest energy structures of Rh_n(n=4-8) clusters. The magnetic moment of even atom rhodium clusters is found to be zero or nearly zero because spin up electron of one atom couples with spin down electron of another atom, where as odd atom clusters have non zero magnetic moment due to the absence of such coupling.

B. Electronic dipole moment

Variation of electronic dipole moment (in Debye) of all the stable rhodium metal clusters as a function of cluster size is shown in the Fig 9 and the calculated dipole moment values are mentioned in Table S4 of ESI. It is observed from the Fig 9 that the neutral clusters have dipole moment values closer to zero, which suggests the spherical charge distribution in the all neutral clusters. In case of ionic clusters dipole moment values are found to be higher than their corresponding neutral clusters because ionic clusters have higher delocalization of electron due to the addition or removal of electrons from neutral clusters. Polarity of the ionic rhodium clusters is also evaluated to be higher than then neutral clusters.

Molecular orbital study

Pictorial representation of molecular orbitals can be used to understand the structural properties along with stability and bonding properties of the nanoclusters. The 3D isosurface diagrams (LUMO and HOMO) of the most stable Rh_n clusters (neutral and ionic) are evaluated at BLYP/DNP level are presented in Fig 10 and Fig. 11. Isosurface diagrams of LUMO and HOMO indicate the types of orbitals involve in the formation of nanoclusters that is which type of orbitals are responsible for bond formation. Analysis of isosurface diagrams reveal that in most of the cases there is always a sideways or π overlapping between the d orbitals of rhodium atoms. In some cases constructive or sigma overlapping are also observed among bonding orbitals. As HOMO of neutral Rh_2 (b_{2u}) consists of non-bonding d_{xy} orbital but in LUMO (a_{2u}) hybridization is noticed with anti-bonding dz^2 orbital along the bond axis. HOMO of cationic Rh_2 cluster suggests the sigma bonding overlapping while in anionic cluster nonbonding overlapping is observed similar to that of neutral cluster. It is observed from the HOMO diagram of neutral Rh_3 (e') that dd_π bonding occurs from the hybridization of d_{z2} orbital oriented perpendicular to the triangular framework where as in LUMO (a_2'') some constructive overlapping is observed between four lobes of d orbitals. In cationic cluster of $Rh_{3,}$ there is anti symmetric overlapping between the d_{z2} orbital of one atom with four lobes of d orbitals of other atoms in HOMO isosurface. HOMO of anionic Rh_3 reveals pi bonding with d_{z2} orbitals but in LUMO, limited region overlapping is noticed among the orbitals. HOMO (t_1) orbital of Rh_4 consists of four lobed either d_{yz} or d_{zx} orbitals where as in LUMO (t_2) dd_π occurs in between d_{z2} orbitals. The isosurface diagrams of HOMO of cationic and anionic Rh_4 show bonding as well as perpendicular nonbonding overlapping. In neutral Rh_5 cluster HOMO (a_2) is formed by overlapping of either d_{yz} or d_{zx} orbital with d_{z2} orbital. In cationic Rh_5 limited region overlap with d_{z2} orbital is observed in HOMO whereas, mismatch overlapping among d_{x2-y2} and d_{z2} is seen in LUMO. LUMO orbital of neutral Rh_5

possesses b_1 symmetry. In neutral cluster of Rh_7 (a_1) and Rh_8 (e_u), LUMO is constituted of sigma bonding overlapping where as in Rh_6, both HOMO (e") and LUMO (a_1") are composed of nonbonding overlapping between four lobe d orbitals. In anionic Rh_6, positive bonding overlapping is observed in HOMO as well as in LUMO. For cationic Rh_7 HOMO and LUMO and Rh_8 HOMO consists of sideways limited region overlapping among perpendicular d orbitals where as in LUMO of anionic Rh_7 and Rh_8, dd_σ bonding occurs. HOMO orbital of Rh_7 and Rh_8 clusters have (t_{1u}) and (a_2) symmetry.

Density of states study

To investigate the orbital occupation per energy interval DOS study is done for neutral and ionic rhodium clusters. A few cases are picked up for our analysis purpose *viz.* neutral and ionic Rh_n clusters (n=4, 6, 8). DOS of the d orbitals of rhodium atom is partially noticeable near zero energy level which is hybridized with s and p orbitals of rhodium. Energy zero is related to the Fermi energy level. For cationic Rh_4 and Rh_8 clusters, density of state is maximum near Fermi level than the neutral clusters of the same. For cationic clusters intensity of the peak density is high at certain energy level which means that there are many states available for occupation at that energy level. Hybridization along with band width is higher for all neutral and ionic cluster of Rh_8 than Rh_4. Rh_6^- have higher mixing of orbitals where as no DOS is observed for neutral Rh_6 near Fermi level. With the increase of number of atom in cluster more overlapping occurs between orbitals of rhodium. Width of orbital band is noticed to be higher in anionic clusters than cationic and neutral clusters (Fig 12).

Spin density and deformation density analysis

Spin density and deformed electron density is shown in Fig 13 and Fig 14, respectively. It is seen from Fig 13 that the magnetic moment of Rh_4 is found to be zero because spin up density is neutralized by spin down density. Again, the spin down density is high on each vertexes which is cancelled out by the high spin up density in the middle region of the cluster which is the reason of zero magnetic moment of Rh_6. In odd atom clusters of Rh_5 and Rh_7 show nonzero magnetic moment because the spin up density is found to be higher than the spin down density. Deformation density reveals that electron density is more deformed in cationic Rh_4 than its neutral and anionic cluster. The electronic density of neutral and anionic Rh_5 cluster is evaluated to be more deformed than the cationic cluster. Again, electron density of cationic Rh_6 is more deformed than the neutral and anionic cluster of Rh_6. That is, electron density is more deformed in cationic cluster of Rh_4 and Rh_6 and in anionic Rh_5 cluster. Electron density in cationic cluster is more deformed because of the greater nuclear charge which pulls the electrons more tightly than the anionic and neutral rhodium nanoclusters.

Conclusion:

We have investigated systematically the electronic, structural and magnetic properties of neutral and ionic Rh_n (n=2-8) clusters with different multiplicities. In this study, we have evaluated different parameters such as bond length, binding energy, coordination number, stability function, bond dissociation energy, ionization potential, electron affiinity, LUMO-HOMO gap, electrophilicity, electronegativity, global hardness and magnetic properties of different possible isomers of rhodium cluster. Based on the calculated reactivity parameters such as binding energy, LUMO-HOMO gap, bond dissociation energy, electron affinity, an important inference can be drawn on the stability of the clusters. These results reveal that even atom rhodium clusters are more stable than the odd atom clusters and hence, suggest the highest stability for Rh_4. It is found that larger clusters have higher binding energy than smaller clusters in all of their neutral and ionic Rh_n. Cationic clusters possess higher stability function than neutral and anionic rhodium clusters. The highest LUMO-HOMO gap, the lowest electron affinity and electrophilicity, the highest stability function, high ionization potential and high bond dissociation energy suggest that Rh_4 is the magic cluster as these parameters are hallmark to predict the magic cluster.[51] Molecular orbital analysis suggest that bonding in Rh_n clusters in most of the cases are π overlapping between the d orbitals.

Table 1. Binding energy, vibrational frequency and bond length of Rh_2 dimmer evaluated with different functionals.

Method	Binding Energy (eV)	Frequency (cm^{-1})	Bond Length (Å)
GGA-BLYP	3.013	268	2.308
GGA-PW91	0.524	287	2.269
GGA-BOP	2.203	277	2.312
GGA-BP	2.462	286	2.288
GGAVWN_BP	2.484	286	2.286
GGA-HCTH	2.021	284	2.309
GGA-RP	2.336	279	2.308
GGA-PBE	3.321	287	2.286
Experiment	2.92±0.22	267	2.280

Table 2. Binding energies (E_b) per atom in eV of neutral, cationic and anionic Rh_n (n=2-8) with different multiplicities (M).

	Multiplicity					
Neutral Cluster size	M=1	M=2	M=3	M=4	M=5	M=6
Rh_2	1.5067		1.3235		1.5060	
Rh_3_1		1.6584		1.666		1.6644
Rh_3_2		2.0722		2.1276		2.0649
Rh_4_1	2.5315		2.5055		2.4251	
Rh_4_2	2.3471		2.3565		2.3713	
Rh_5_1		2.6337		2.6282		2.6082
Rh_5_2		2.7091		2.6935		2.6583
Rh_5_3		2.7086		2.6935		2.6640
Rh_5_4		2.7084		2.6935		2.6817
Rh_6_1	2.7393		2.7392		2.7333	
Rh_6_2	2.8307		2.8306		2.8365	
Rh_6_3	2.8307		2.8319		2.8365	
Rh_6_4	2.7135		2.7121		2.7001	
Rh_6_5	2.8809		2.8676		2.8381	
Rh_7_1		2.5676		2.5645		2.5660
Rh_7_2		2.8867		2.8917		2.8903
Rh_7_3		2.9014		2.9045		2.9026
Rh_7_4		2.8133		2.8119		2.7964
Rh_7_5		2.7869		2.7866		2.8217
Rh_7_6		2.8868		2.8917		2.8903
Rh_8_1	2.9728		2.9541		2.9612	
Rh_8_2	2.6068		2.6092		2.6103	
Rh_8_3	2.9884		2.9868		2.9825	
Rh_8_4	3.1092		3.1087		3.0796	
Rh_8_5	2.9543		2.9492		2.9403	
Rh_8_6	2.9632		2.8432		2.7890	
Rh_8_7	2.6789		2.6794		2.5978	

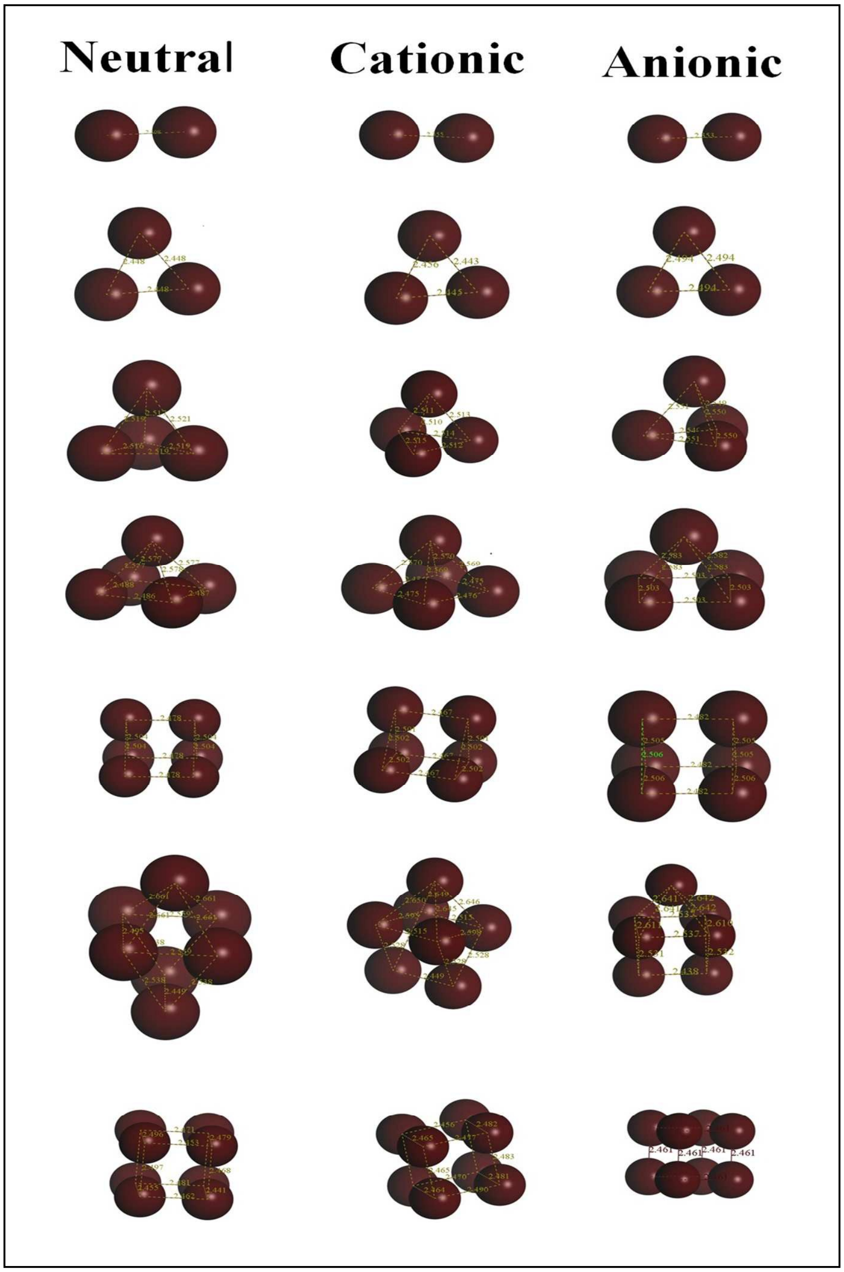
			Multiplicity			
Ionic sclusters	M=1	M=2	M=3	M=4	M=5	M=6
Rh_2^+		0.7862		0.9506		1.0707
Rh_2^-		1.5784		1.7128		1.4433
Rh_3^+	1.9935		1.9207		1.9935	
Rh_3^-	2.2245		2.2143		2.2176	
Rh_4^+		2.6381		2.5449		2.4901
Rh_4^-		2.6048		2.5297		2.4852
Rh_5^+	2.8531		2.8412		2.8082	
Rh_5^-	2.8054		2.7948		2.8069	
Rh_6^+		3.0262		2.9965		2.9557

Rh_6^-		2.9966		2.9850		2.9627
Rh_7^+	3.0288		3.0278		3.0284	
Rh_7^-	3.0491		3.0447		3.0473	
Rh_8+		3.2271		3.2171		3.1987
Rh_8^-		3.2619		3.2404		3.2285

Table 3. Magnetic moment values (μ_B) of Rh_n (n=4-8) clusters calculated at BLYP/DNP level

	Magnetic moment in this study	Magnetic moment study by Jinlonget al[16]	Magnetic moment study by Reddy et al[20]	Magnetic moment study by F. Aguilera-Granja et.al[50]
Rh_4	0	0	0	0.06
Rh_5	0.20	0.60	1.40	0.22
Rh_6	0	0	0	1.48
Rh_7	0.43	1.28	1.28	0.05
Rh_8	0	1.25	0.75	0.89

Fig.1 Stable geometries of neutral, cationic and anionic clusters derived at BLYP/DNP level



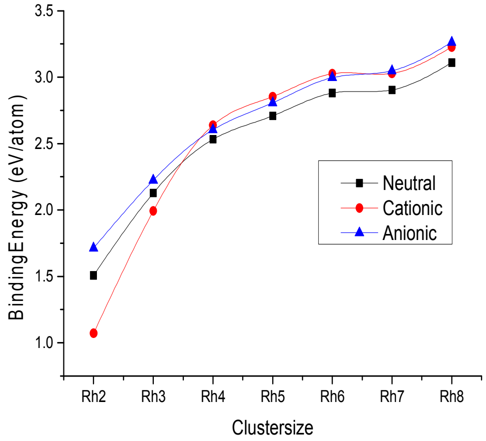


Fig 2. Binding energy (eV/atom) of neutral, cationic and anionic Rh_n clusters.

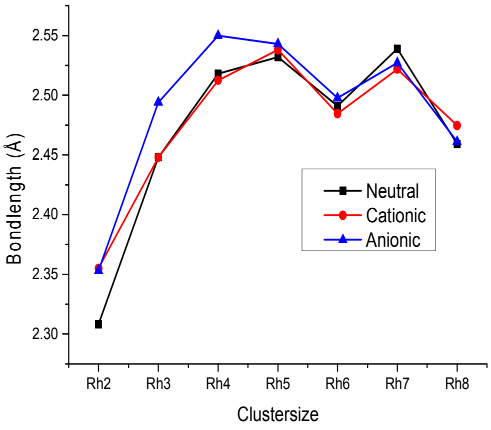


Fig 3. Bond length of neutral, cationic and anionic Rh_n clusters.

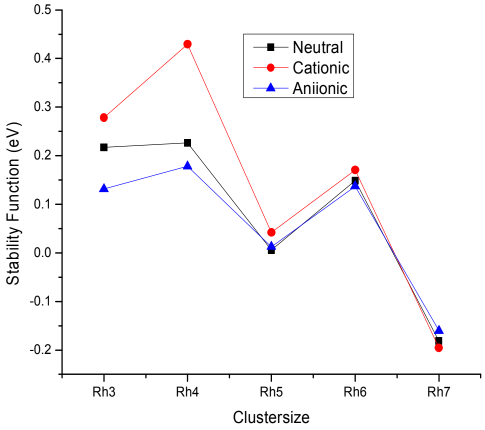


Fig 4. Stability function of neutral, cationic and anionic Rh_n

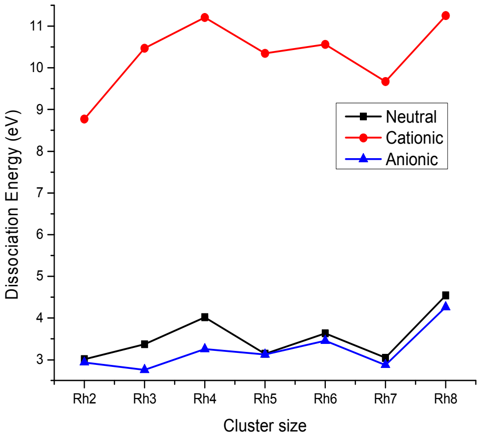


Fig 5. Dissociation energy of neutral, cationic and anionic Rh_n

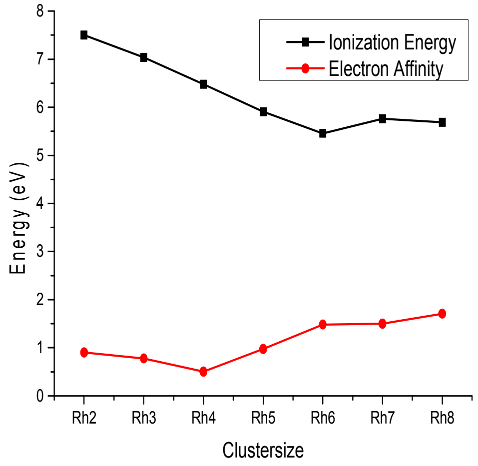


Fig 6. Ionization energy and Electron affinity of Rh_n(n=2-8)

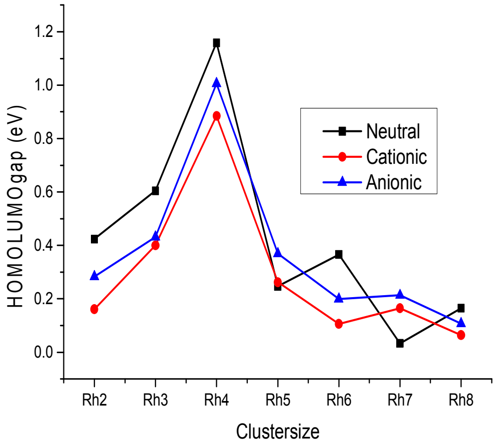


Fig 7. HOMO-LUMO gap of neutral, cationic and anionic clusters

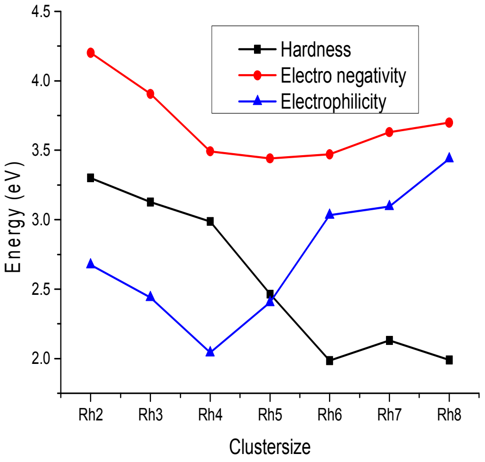


Fig 8. Chemical Hardness, Electronegativity and Electrophilicity plot of Rh_n(n=2-8).

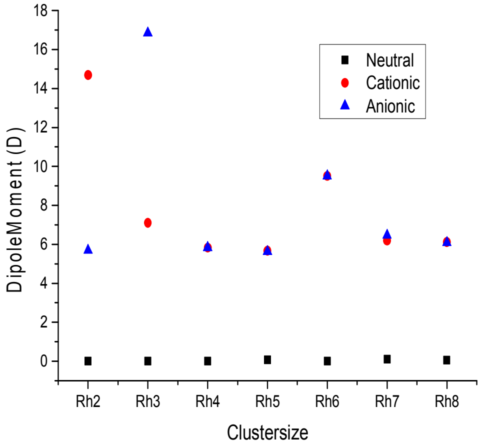


Fig 9. Dipole Moment values of neutral, cationic and anionic rhodium clusters

Fig10. 3D isosurface HOMO and LUMO diagrams of neutral Rh_n(n=2-8) clusters

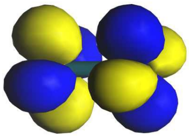
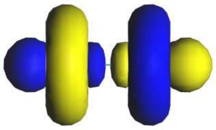
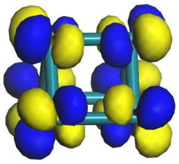
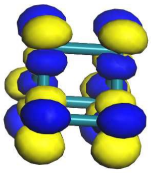
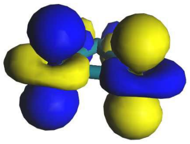
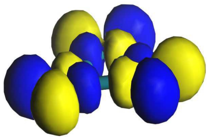
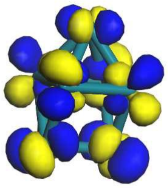
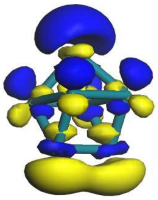
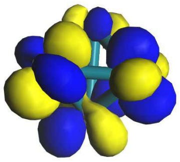
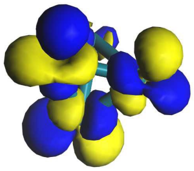
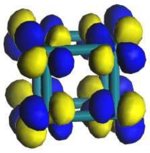
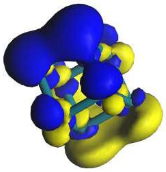
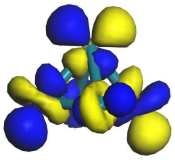
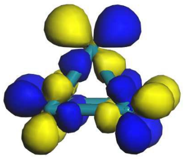
Neutral Cluster	HOMO	LUMO	Neutral Cluster	HOMO	LUMO
Rh_2			Rh_6		
Rh_3			Rh_7		
Rh_4			Rh_8		
Rh_5					

Fig11. 3D isosurface HOMO and LUMO diagrams of cationic and anionic Rh$_n$(n=2-8) clusters

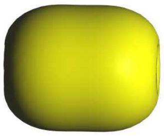
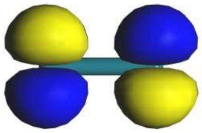
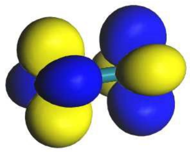
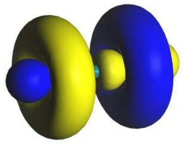
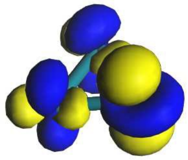
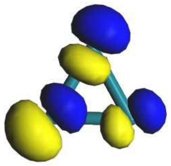
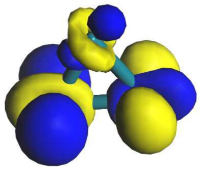
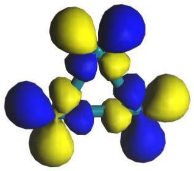
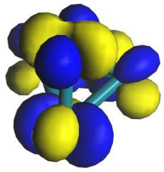
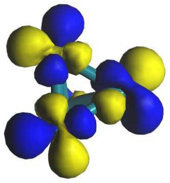
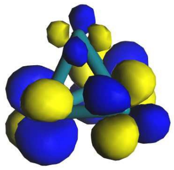
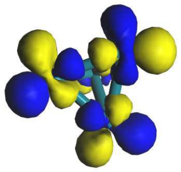
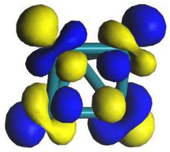
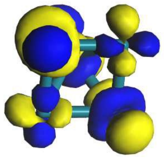
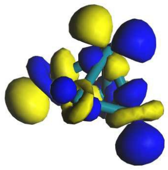
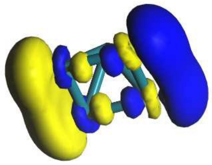
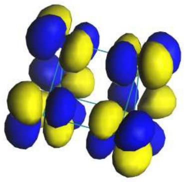
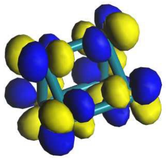
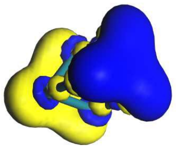
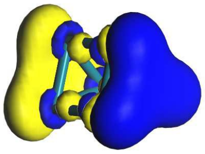
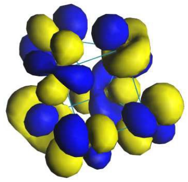
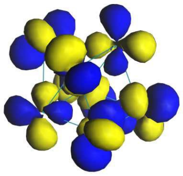
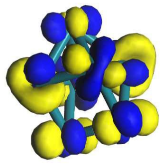
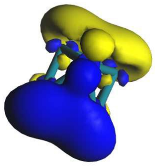
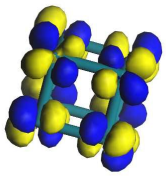
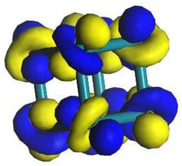
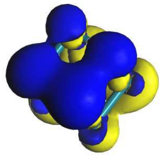
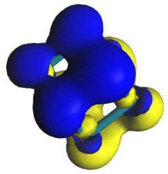
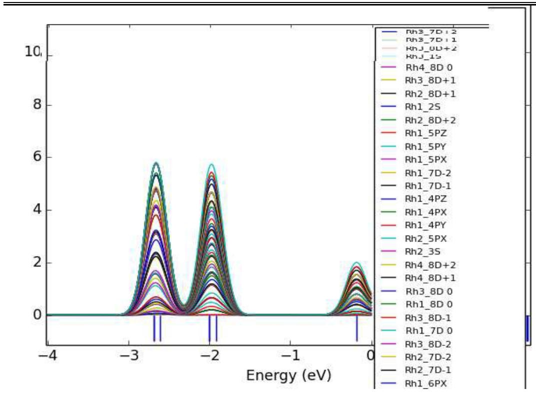
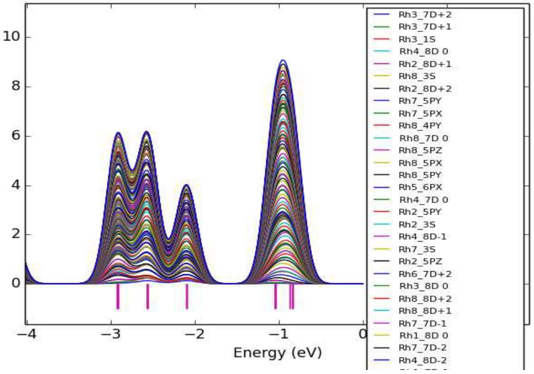
	Cationic Cluster		Anionic Cluster	
	HOMO	LUMO	HOMO	LUMO
Rh$_2$				
Rh$_3$				
Rh$_4$				
Rh$_5$				
Rh$_6$				
Rh$_7$				
Rh$_8$				

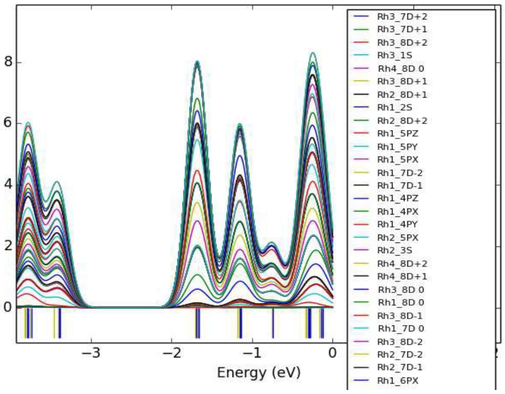
Fig 12. DOSs of all higher and lower energy s, p and d orbitals of rhodium atoms for neutral and ionic Rh_n (n=4, 6, 8) clusters. (all D ± n orbital refers to upper and lower energy orbital of D state, n=0,1,2).



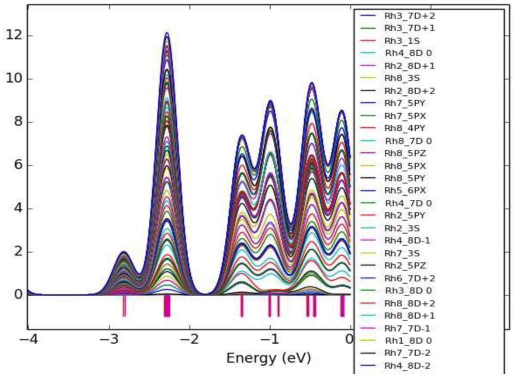
All energy s, p and d orbital DOS of Rh_4



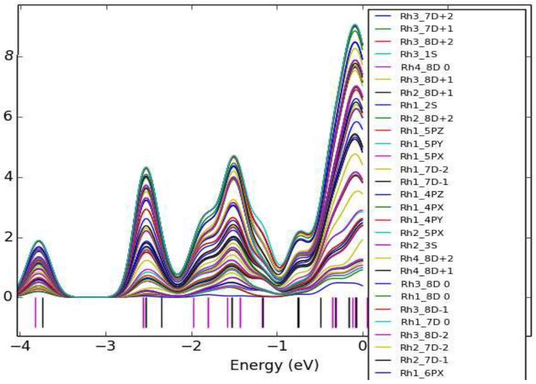
All energy s, p and d orbital DOS of Rh_8



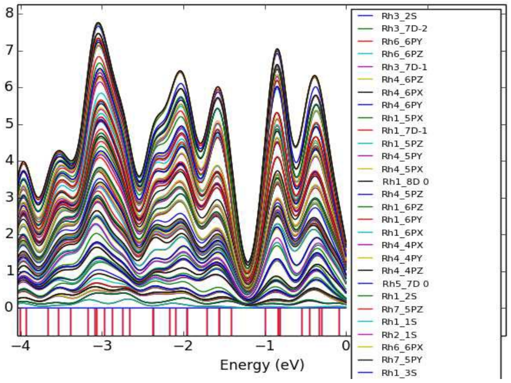
All energy s, p and d orbital DOS of Rh_4^+



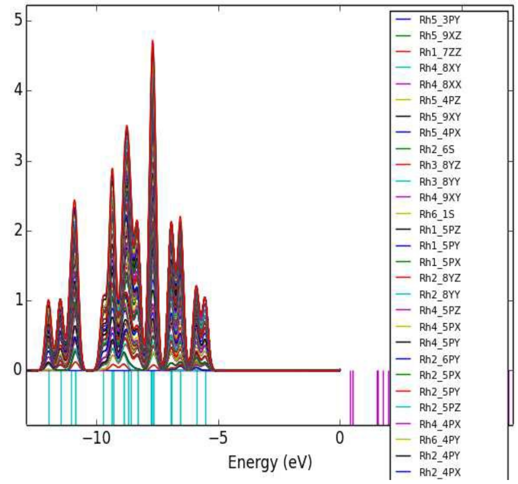
All energy s, p and d orbital DOS of Rh_8^+



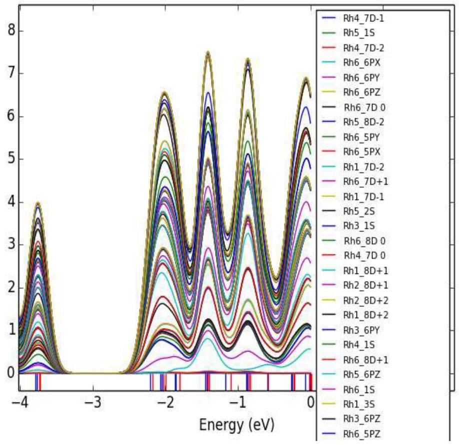
All energy s, p and d orbital DOS of Rh_4^-



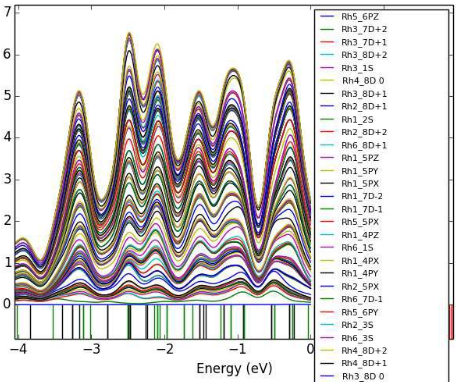
All energy s, p and d orbital DOS of Rh_8^-



All energy s, p and d orbital DOS of Rh_6

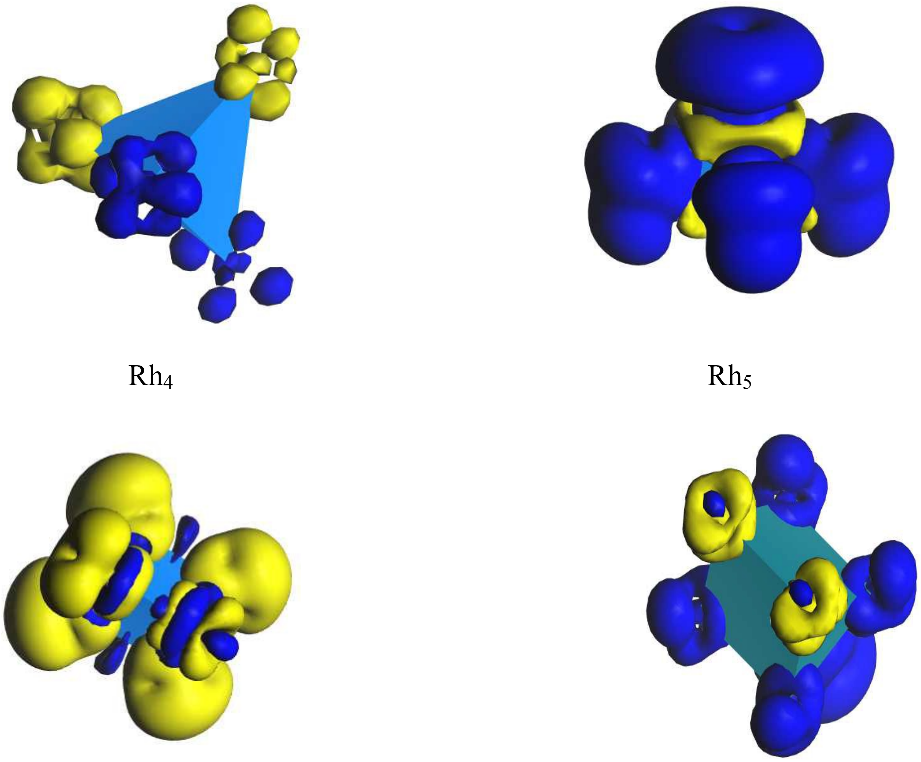


All energy s, p and d orbital DOS of Rh_6^+



All energy s, p and d orbital DOS of Rh_6^-

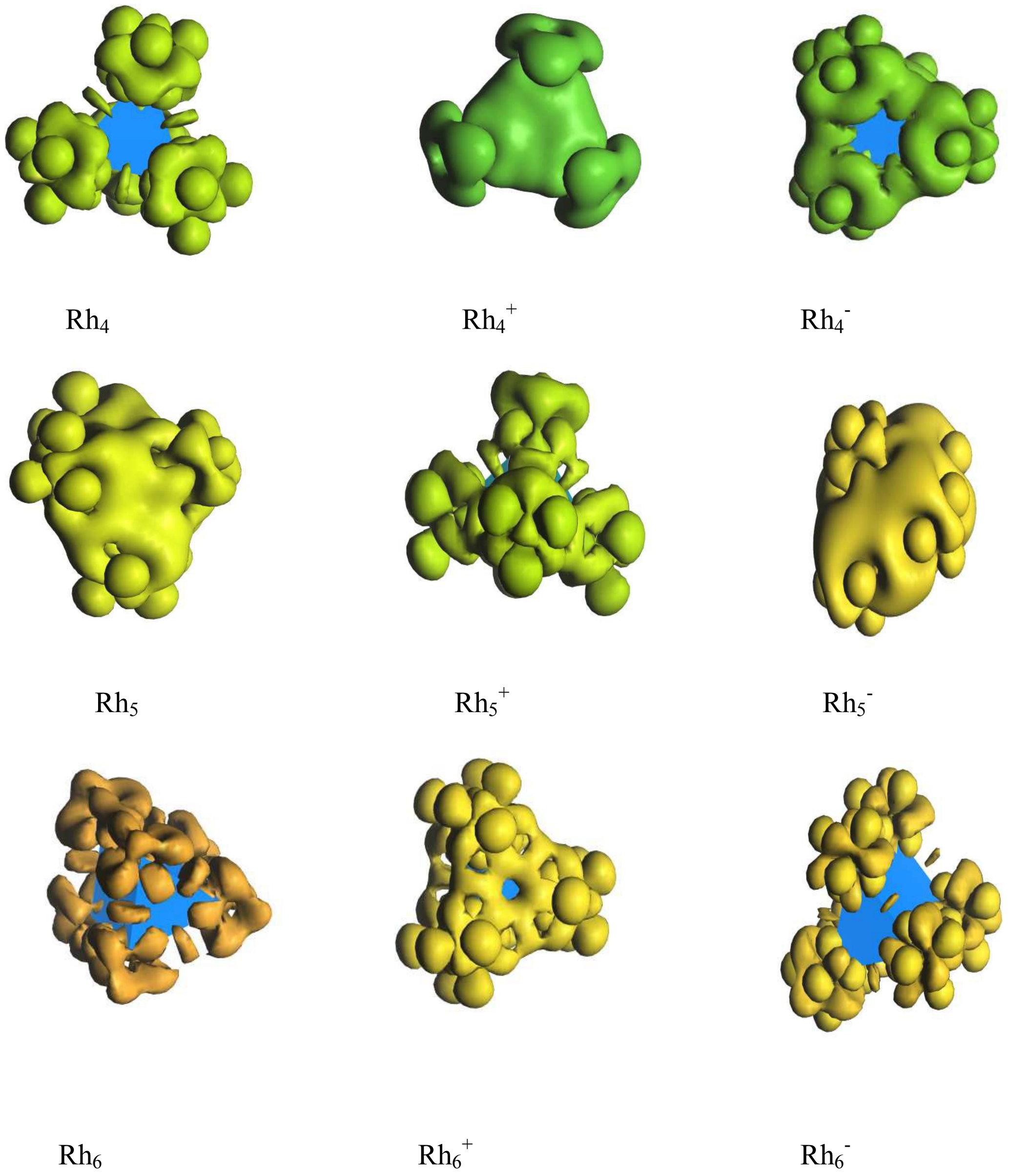
Fig 13. Calculated spin density of Rh_n (n=4, 5, 6, 7) clusters. (Blue and yellow colour represent spin up and spin down density)



Rh_4 Rh_5

Rh_6 Rh_7

Fig 14. DFT evaluated deformation electron density of neutral and ionic Rh_n(n=4,5,6) clusters



Rh_4 Rh_4^+ Rh_4^-

Rh_5 Rh_5^+ Rh_5^-

Rh_6 Rh_6^+ Rh_6^-

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Structural evolution, electronic and magnetic manners of small rhodium $Rh_n^{+/-}$(n=2-8) clusters: Details density functional theory study

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We have evaluated the stable electronic structure as well as magnetic properties of all neutral and ionic Rh_n(n=2-8) clusters using density functional theory. This study reveals that Rh_4 is the magic cluster based on the calculated reactivity parameters.