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STABILITY AND SPECTROSCOPIC PROPERTIES OF NEGATIVE IONS

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STABILITY AND SPECTROSCOPIC PROPERTIES OF NEGATIVE IONS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, at Virginia Commonwealth University.

by

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M.S. in Physics
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Negative ions play an important role in chemistry as building blocks of salts and oxidizing agents. Halogen atoms, due to their ability to attract electrons, readily form negative ions. Considerable interest exists in the design and synthesis of new negative ions called superhalogens whose electron affinities are much higher than those of halogen atoms. This thesis deals with the design of such species. Using density functional theory I have studied two classes of superhalogens. First one involves d^1 transition metal (Sc, Y, La) atoms surrounded by Cl while the second one involves simple metals (Na, Mg, Al) surrounded by pseudohalogens such as CN. Geometry, electronic structure, and electron affinity of these species containing up to 5 ligands have been calculated. Studies reveal a fundamental difference between the interaction of transition and metal atoms with electronegative ligands. In addition, pseudohalogens can be used to synthesize a new class of superhalogens.
Chapter 1: Introduction

1.1 Overview

There is considerable interest in studying negative ions not only because they are among the best known oxidizing agents [1] but also they play an important role in atmospheric chemistry by acting as nucleation centers [2]. Among the elements in the Periodic Table, halogen atoms are the most electronegative because they possess a hole in the outermost p-shell (ns\(^2\)np\(^5\) electronic configuration), which can readily accommodate an electron in order to close the np shell. An extra electron attachment to a halogen atom results in the negatively charged ion whose total energy is significantly lower than that of the corresponding neutral. Consequently, the halogen atoms possess the highest electron affinities [3] (3.0–3.6 eV) among all the elements, with Cl having the largest value (~ 3.6 eV). However, the EA of a polyatomic system may exceed the 3.6 eV atomic limits due to collective effects.

In 1962, Bartlett synthesized the first chemically bound Xenon in Xe\(^+\) [PtF\(_6\)]\(^-\) [Ref:4]. He estimated the electron affinity of PtF\(_6\) to be at least 6.76 eV [5]. This milestone work started the Chemistry of Nobel Gases, which previously have been considered as absolutely inert atoms. Since then, numerous molecules with high EAs were used to synthesize a wide variety of new chemical compounds, in which very strong oxidizers were required. Later Gutsev and Boldyrev...
[6, 7], termed this class of molecules as superhalogens and gave the formula for such species, $\text{MX}_{(m+1)/k}$, where $m$ is the nominal valence of the metal atom $M$ and $k$ is the valence of the electronegative ligand $X$. The resulting superhalogen anions have extremely high electron detachment energies due to the delocalization of the extra electron over the electronegative atoms. The EAs of many superhalogens have been estimated both theoretically [8, 9, 10, 11, 12] and experimentally [13, 14, 15]. First experiment to verify this assignment for superhalogens was carried out by Wang and coworkers [16].

Superhalogens are used in the synthesis of many new materials including organic metals and organic superconductors [17] many of which are highly energetic. Some superhalogen anions are commonly found as building blocks in condensed phase materials and gas phase molecules. The electron affinities of some of these superhalogens can be as high as 14 eV. Such large electron affinities suggest that these species can be used to extract electrons from the core orbital’s of some atoms and form new compounds that otherwise do not exist.

1.2 Motivation and Current Work

Exploring various new superhalogen species is primarily focused on studying molecular clusters which are capable of forming strongly bound anions. The purpose of these efforts is to provide reliable data and predictions considering the possible use of such compounds as electron acceptors in the production of organic superconductors, as well as the role they can play in synthesis (e.g., in the oxidation of counterpart systems with high ionization potentials).
1.2.1 The onset of Super halogen Behavior of \( d^1 \) Transition metal chloride clusters

While considerable amount of work on superhalogen involving sp metals have been carried out [18, 19, 20, 21, 22, 23, 24] work on transition metal containing superhalogens are limited [25, 26].

A systematic study of the electron affinity of transition metals as a function of halogen content, however, can reveal interesting physics and chemistry. This is because the partially filled d-electrons can contribute to the valence of transition metals due to the small gap between d and s orbitals. For example, Manganese with an orbital configuration of \( 3d^54s^2 \) is known to exhibit oxidation states ranging from -3 to + 7. Thus, it is a priori not clear for what composition of halogen atoms \( MX_n \) clusters will exhibit superhalogen behavior. In addition, how would this behavior change from 3d to 4d to 5d elements?

Recently photoelectron spectroscopy experiments have been carried out for \( MCl_4 \) (\( M = \text{Sc, Y, La} \)) and their vertical detachment energies have been measured [27, 28]. These are rather large, in the range of 7 eV, and clearly show that they behave as superhalogens. However, experiments containing lesser number of Cl atoms have not yet been performed, and so it is not clear how this superhalogen property evolves. To gain a detailed understanding of how each addition of chlorine to \( d^1 \) transition metal changes its electron affinity we carried out a systematic study of the equilibrium geometry, electronic structure, vertical detachment energies, and electron affinities of \( (MCl_n; M = \text{Sc, Y, La}; n = 1–5) \) clusters using density functional theory. The computational procedure and the results are discussed in Chapter 3.
1.2.2 Singly and doubly charged anions of chloride and pseudohalogen clusters:

Numerous investigations have been carried out on singly negative atomic and molecular ions both experimentally and theoretically. But the information on free doubly negative charged atomic and molecular charge is scarce. Multiply charged anions, on the other hand, mostly exist in solutions, on surfaces, or as building blocks of condensed matter systems where they are stabilized by charges on counter ions. Since the stability and electronic properties of multiply charged anions in the above systems are influenced by the medium they exist in, their fundamental understanding without the influence of the environment can only be achieved in the gas phase. The most important question concerns the critical size of a gas phase multiply charged anion. In these systems the Coulomb repulsion between the added charges has to be balanced by the binding energy of the constituent atoms that hold them together. An unstable multiply charged anion in the gas phase can either eject an electron or fragment into binary species to stabilize itself.

There have been several reports on doubly charged negative ions of fairly large organic molecules [29, 30, 31, 32]. For example, a long lived stable organic dianion is the dimer of benzo[cd] pyren-6-one, a large organic ketone. It was the first long-lived doubly charged negative ion to be observed in the gas phase [29]. Several theoretical [32, 33, 34] and experimental [35, 36] investigations have been carried out in search of small stable dianions. The smallest known long lived dianions thus far are found to be the alkali trihalide AX$_3^-$ (A= Li, Na, K and X=F or Cl) whose existence has been predicted theoretically by Scheller and Cederbaum.
[33, 34] and experimentally verified [37]. The dianionic earth alkaline tetrahalides EX$_4^{2-}$ (E=Be, Mg, Ca and X=F or Cl) have also been predicted in 1991 [37,38] theoretically and later verified experimentally [36].

We address both the issues of designing superhalogens with different electronegative ligands and using these concepts to study the critical size for the stability of their dianions in the gas phase. In the first part we use Cl as a ligand and present a systematic study of the structure, stability, and spectroscopic properties of neutral, single and doubly charged negative ions of MCl$_n$ (M= Na, Mg, Al) clusters. In the second part, we replace the Cl ligand by psuedohalogen or halogenoid (–CN or –NC). The purpose of using the pseudohalogen is to understand how the geometry, electronic structure and the stability of the dianions change as the size of the ligand increases. The computational procedure and the results are discussed in Chapter 4.
Chapter 2: Theoretical Method

All calculations have been carried out using density functional theory (DFT) with B3LYP hybrid functional for exchange and correlation (XC) potential. The accuracy of the DFT-based results is verified by carrying selected calculations using other ab initio quantum-chemical methods such as MP2 (second order Moller-Plesset Perturbation), CCSD(T) (Coupled Cluster with single and double excitations).

2.1 Introduction

The quest for a practical theory to calculate the electronic properties of an N-electrons system is almost a century old. A theoretical path towards this goal was first proposed by Schrödinger in 1927, using the concept of wave mechanics as a tool.

According to Schrodinger, the electronic properties of much particle system can be determined from its wave function $\Psi$, the solution of the time-independent Schrödinger equation:

$$\hat{H} \, \Psi = E \, \Psi$$  \hspace{1cm} (2.1)

where $\hat{H}$ is Hamiltonian operator and $E$ is an Eigen value.

Hamiltonian operator $\hat{H}$ is a differential operator that acts on the total wave function and can be written as [39]
\[
H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla^2_i - \frac{\hbar^2}{2M_A} \sum_{A=1}^{M} \nabla^2_A e^2 \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + e^2 \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + e^2 \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{r_{AB}}
\]  

(2.2)

where \(i\) and \(j\) run over \(N\) electrons and \(A, B\) run over \(M\) nuclei. \(Z_A\) and \(Z_B\) are atomic number, \(M_A\) and \(m_e\) are the mass of nucleus and electron respectively, \(\hbar = \frac{\hbar}{2\pi}\) where \(\hbar\) is the Planck’s constant. The first two terms are kinetic energy (T) of electron and nuclei respectively. The third term (potential energy term) is attractive electrostatic interaction between the nuclei and electrons (\(V_{Ne}\)). The fourth and fifth terms are potential energy due to electron–electron (\(V_{ee}\)) and nucleus–nucleus interaction respectively. Both terms are repulsive in nature. Here the Laplacian operator \(\nabla^2_q\) is defined as sum of differential operators.

\[
\nabla^2_q = \frac{\partial^2}{\partial x^2_q} + \frac{\partial^2}{\partial y^2_q} + \frac{\partial^2}{\partial z^2_q}
\]  

(2.3)

The exact solution \(\Psi\) for the equation (2.1), however has been a challenge to many, for most of the last century. The electronic structure studies of large clusters and solid having interesting phenomena, like chemisorptions study are computationally very expensive and hence demand simplified schemes.

The major step toward simplifying the above problem is by the application of Born–Oppenheimer approximation [40]. This approximation is valid, only when the ratio of electron to nuclear mass is considerable small. Therefore, the kinetic energy of the nucleus is assumed to be zero and repulsive potential energy due to nucleus–nucleus interactions can be assumed to be
almost constant. Thus, the complete Hamiltonian is given by equation (2.2) reduces to so called electronic Hamiltonian $H_{ele}$ is given by:

$$H_{ele} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 - e^2 \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + e^2 \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} = T + V_{Ne} + V_{ee} \quad (2.4)$$

The attractive potential $V_{Ne}$ is often termed as external potential $V_{ext}$ in density functional theory.

Now, the main task of the electronic structure calculation is reduced to solving the electronic Schrödinger equation.

However, it can be exactly solved only for a single electron system. Approximations are required to solve multi-electron systems because of the complexity of electron–electron interaction in much particle system.

### 2.2 – Hartree approximation

In this approximation [41], the one–N electron problem is separated into N–one electron Schrödinger equations. Here the Hamiltonian has the form:

$$H = \sum_{i=1}^{N} h(i) \quad (2.5)$$

where $h(i)$ is the operator describing kinetic energy and potential energy of electron i and is defined as

$$h(i) = -\frac{\hbar^2}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + e^2 \sum_{j=1}^{N} \frac{1}{r_{ij}} \quad (2.6)$$
The wave function is a simple product of spin orbital wave functions for each electron and is defined as Hartree product wave function.

The Hartree product [42] wave function is given by:

$$\Psi^{hp}(x_1, x_2, \ldots, x_n) = \chi_i(x_i) \chi_j(x_j) \ldots \chi_k(x_k)$$

(2.7)

where $\chi_i$ is spin orbital $i$ (solution of one particle Schrödinger equation), $x_i$ is position and spin of electron $i$. The function uses Hartree equation. The Hartree equation is an eigenvalue equation of the form:

$$h(i) \chi_j(x_i) = \varepsilon_j \chi_j(x_i)$$

(2.8)

Schrödinger equation for whole system is of the form:

$$H\psi^{hp} = E\psi^{hp}$$

(2.9)

Here eigenvalue, $E$ is sum of spin orbital energies of each spin orbitals appearing in $\psi^{hp}$

$$E = \varepsilon_i + \varepsilon_j + \ldots + \varepsilon_k$$

(2.10)

The Hartree method provides a great foundation for numerically approximating many body systems. However, it has some drawbacks. The important one is that the total wave function is not anti-symmetric under interchange of electron coordinates and doesn’t obey the Pauli Exclusion Principle.

2.3 – Hartree- Fock approximation

In Hartree –Fock [42,43] approximation, the total wave function of the N-electron system is approximated by an anti-summarized product of N one-electron wave functions $\chi_i(x_i)$. This
product is usually represented by a determinant called \textit{Slater determinant} $\psi_{SD}$ \cite{44}. Here the correlated electron-electron repulsion is not specifically taken into account, only its average effect is included in the calculation.

$$\psi_{SD}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_N) & \chi_2(x_N) & \cdots & \chi_N(x_N) \end{vmatrix}$$ \hspace{1cm} (2.11)

Where $\frac{1}{\sqrt{N!}}$ is the normalization factor. $\chi_i(x_i)$ is called spin orbital of particle $i$.

In the Hartree-Fock (HF) approximation, the antisymmetry property of electrons is accounted. $\Psi(x_1, x_2)$ is antisymmetric with respect to the interchange coordinates of electron one and two.

$$\Psi(x_1, x_2) = -\Psi(x_2, x_1)$$ \hspace{1cm} (2.12)

The Slater determinant obeys Pauli Exclusion Principle. When two electrons are assigned to the same spin orbital, i.e. $\chi_1$ and $\chi_2$ is same, then the determinant will be zero.

The Hartree-Fock equation is an eigenvalue equation of the form:

$$f(i)\chi_j(x_i) = \varepsilon_i\chi_j(x_i) \quad (i = 1, \ldots, N)$$ \hspace{1cm} (2.13)

where $\varepsilon_i$ is eigen solutions of $N$ number of equations, $\chi_j$ is spin orbital $j$ and $f(i)$ is an effective one-electron operator, called the \textit{Fock} operator, of the form:

$$f(i) = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + v_{HF}^{HF}(i)$$ \hspace{1cm} (2.14)
where \(v^{HF}(i)\) is *Hartree-Fock potential* (average repulsive potential experienced \(i^{th}\) electron due to remaining N-1 electrons). Thus, the complicated two-electron repulsion operator \(1/r_{ij}\) in the Hamiltonian is replaced by the simple one-electron operator \(v^{HF}(i)\) where the electron-electron repulsion is taken into account only in an average way. \(v^{HF}(i)\) has following two components:

\[
v^{HF}(i) = \sum_{j} J_{i}(x_i) - K_{j}(x_j)
\]  

(2.15)

where \(J\) and \(K\) are Coulomb and exchange operators, respectively.

The total energy for the HF approximation is given as below:

\[
E_{HF} = \langle \psi_{SD} | H | \psi_{SD} \rangle = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (J_{ij} - K_{ji}) = \sum_{i=1}^{N} \varepsilon_i - \langle \psi_{SD} | \mathcal{V}_{ee} | \psi_{SD} \rangle
\]

(2.16)

where the Coulomb integral (due to pair-wise Coulomb interaction between the \(i^{th}\) electron and the other electrons in all occupied spin orbitals) is given by:

\[
J_{ij} = \langle ii | jj \rangle = \int dx_i dx_j \frac{\hat{\chi}_i(x_i) \hat{\chi}_j(x_j)}{r_{ij}}
\]

(2.17)

and exchange integral, exchange of two variables within spin orbitals, is given by:

\[
K_{ij} = \langle ij | ji \rangle = \int dx_i dx_j \frac{\hat{\chi}_i^*(x_i) \hat{\chi}_j(x_j) \hat{\chi}_j^*(x_j) \hat{\chi}_i(x_i)}{r_{ij}}
\]

(2.18)

However, due to the Coulomb and Exchange terms appearing in the Hartree-Fock (HF) Hamiltonian, solving the Schrödinger equation involves calculating large number of two-electron integrals. Hence the HF method requires greater computational effort, compared to that for
Hartree method. Moreover, the HF approximation doesn’t take into account the short-range (\textit{dynamical}) correlation between the electrons. This is due to the fact that the wave function \( \psi \) is represented as a rigid single \textit{Slater determinant} which makes the electrons interact with the average potential due to other electrons, instead of pair wise interactions. Hence, this method fails in describing the bond strengths, giving energies with an error of about 1 percent.

In order to include the \textit{dynamical correlation}, the many-body wave function is represented by a linear combination of \textit{Slater determinants}. The Configuration Interaction (CI) method or multi-configuration expansion includes these multi-determinantal wave functions. Many types of calculations begin with a Hartree–Fock calculation and subsequently correct for electron-electron repulsion, referred to also as electronic correlation. Møller–Plesset perturbation theory (MP\(_n\)) and coupled cluster theory (CC) are examples of these post-Hartree–Fock methods. However, due to these required large number of the configurations, it become computationally expensive to employ this Post Hartree-Fock method for large systems. Hence the application of these methods is usually limited to relatively smaller molecules/clusters, where an accurate representation of the electron system is possible.

Several promising approximations have been developed to incorporate the energy and also to balance the computational time/cost with accuracy of the results. Thomas and Fermi, proposed a different method, in which, instead of the wave function \( \psi \), the total electron charge density \( \rho \) was considered. The electron charge density of an N particle system is given by:

\[
\rho(r) = N \int dx_1 \ldots \int dx_N \psi^* (x_1, \ldots , x_n) \psi (x_1, \ldots , x_n) \quad (2.19)
\]
This theory can be seen as the starting points towards the development of *Density Functional Theory* (DFT).

### 2.4 Density Functional Theory (DFT)

DFT is a quantum mechanical method used in physics and chemistry to investigate the electronic structure of many-body systems and is based on the fact that electron density can be used to describe the fundamental properties of an N-electron system. In 1964, Hohenberg and Kohn [45] proved that the ground state energy of an N-electron system can be represented as functionals of electron density, $\rho$ that depends only on three spatial coordinates. It lays the groundwork for reducing many-body problem of N electrons with 3N spatial coordinates to 3 spatial coordinates, through the use of functional of electron density.

#### 2.4.1 Hohenberg-Kohn Formulation

Under the Born-Oppenheimer approximation, the Hamiltonian of an N-electron system can be represented as:

$$
H = \sum_{i=1}^{N} \left( \frac{-\nabla_i^2}{2} + \sum_{i=1}^{N} V(\vec{r}_i) + \frac{1}{2} \sum_{i<j}^{N} \frac{1}{r_{ij}} \right)
$$

Where $V(\vec{r}_i)$ known as external potential, is the potential created by the nuclei over electron $i$, and is given by:

$$
V(\vec{r}_i) = -\sum_{A=1}^{M} \frac{Z_A}{r_{iA}}
$$
The ground state electronic energy for this system can be determined by the minimization of the functional $E[\Psi]$, using the variational principle

$$E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

(2.22)

Hence, for an N-electron system, the external potential $V(\vec{r})$ completely fixes the Hamiltonian; Thus $N$ and $V(\vec{r})$ determine all the ground state properties. According to Hohenberg-Kohn theorems, the ground state electron density $\rho$, instead of $N$, $V(\vec{r})$, determines the properties of the system, hence every observable can be represented as a functional of $\rho(\vec{r})$.

The Density Functional Theory is based on two famous lemma due to Hohenberg and Kohn. The first lemma states that: The external potential $V(\vec{r})$, can be determined within a trivial additive constant, by the electron density $\rho(\vec{r})$. A simple proof of this theorem is based on the minimum energy principle for the ground state, was provided by Hohenberg and Kohn in their work. The total energy, therefore, can be represented in terms of the electron density $\rho$ as:

$$E[\rho] = T[\rho] + V_{Ne}[\rho] + V_{ee}[\rho]$$

(2.23)

where $T[\rho]$ is the kinetic energy, $V_{Ne}[\rho]$ is the potential energy due to the electron-nuclei interaction, and the third term $V_{ee}[\rho]$ represents the potential energy due to the electron-electron interactions. The above equation can be rewritten as:

$$E[\rho] = \int \rho(\vec{r})V(\vec{r})d\vec{r} + F_{HK}[\rho]$$

(2.24)

where $F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]$
where the $V_{ee}[\rho]$ can be written as sum of two parts: $J[\rho]$, the Coulomb electrostatic interaction between electron and $E_{\text{non-classical}}[\rho]$, the non-classical part, called Exchange-Correlation energy. It is to be noted here that the $F_{\text{HK}}$ doesn’t depend on the external potential $V$, and hence is a universal functional and is identical for every system.

The second lemma of Hohenberg-Kohn deals with the variational principle. It states: For any trial density $\tilde{\rho}(\vec{r})$, such that $\tilde{\rho}(\vec{r})d\vec{r} \geq 0$ and $\int \tilde{\rho}(\vec{r})d(\vec{r}) = N$,

$$E_{\text{ground}} \leq E[\rho(\vec{r})]$$  \hspace{1cm} (2.26)

Hence, the energy of the system is represented and minimized with respect to the electron density $\rho$. As the functional $F_{\text{HK}}$ is a universal functional, if we can construct an approximate form of the functional, it can be applied to any real system. The earliest approximation for this functional was provided by Thomas [1927], Fermi [1928] and Dirac [1930], even before the advent of Hohenberg-Kohn theorems. Kohn and Sham in 1965, modified this equation by introducing the orbital and by a clever mixing of the interacting and non-interacting terms and paved the way for practical application of DFT.

### 2.4.2 Kohn-Sham Equations

In Kohn-Sham [46] density functional theory, one imagines that a system of independent non-interacting electrons moving in a common, one body potential $V_{\text{eff}}$ (one electron potential) yields the same density as the “real” fully-interacting system. A set of independent orbitals $\Phi_i$ (Kohn-Sham orbitals) satisfy the following independent single particle Schrödinger equation:
\[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r}))\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r}) \]  
(2.27)

where the first term is the kinetic energy of the non-interacting electrons defined as \((T_S[\rho])\).

The local one-body potential \(V_{\text{eff}}\) (one electron potential) is derived from the non-interacting density:

\[\rho(\vec{r}) = \sum_{i=1}^{N} \left| \varphi_i(\vec{r}) \right|^2 \]  
(2.28)

The above single-particle Schrödinger equations are valid for systems with interacting particles, which satisfy:

\[V_s(\vec{r}) \equiv V_{\text{eff}}(\vec{r}) = V_C + V_{xc}(\vec{r}) - V_{Ne} = \int \frac{\rho(\vec{r})}{\vec{r}_{12}} d\vec{r}_{12} + V_{xc}(\vec{r}_{i}) - \sum_{A=1}^{M} \frac{Z_A}{\vec{r}_{iA}} \]  
(2.29)

where \(V_C\) is the classical Coulomb potential, \(V_{xc}\) is exchange-correlation potential and \(V_{Ne}\) or \(V_{ext}\) is external energy due to nuclei-electron interaction. \(V_{xc}\) is simply defined as the functional derivative of \(E_{xc}\) with respect to \(\rho\), i.e.,

\[V_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \]  
(2.30)

Then we express the total electronic energy of the real, fully interacting system as,

\[E[\rho(\vec{r})] = T_S[\rho] + J[\rho] + E_{xc}[\rho] + E_{Ne}[\rho] \]

\[= -\frac{1}{2} \sum_{i=1}^{N} \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \int \left| \varphi_i(\vec{r}_{ij}) \right|^2 \left| \varphi_j(\vec{r}_{ij}) \right|^2 d\vec{r}_{ij} + E_{xc}[\rho(\vec{r})] - \sum_{A=1}^{M} \sum_{i=1}^{N} \frac{Z_A}{\vec{r}_{iA}} \left| \varphi_i(\vec{r}_{i}) \right|^2 d\vec{r}_{i} \]  
(2.31)

where the first term is the kinetic energy of a non-interacting system \((T_S[\rho])\), the second
term is the classical electrostatic electron-electron repulsion energy \( J[\rho] \), the third term is exchange-correlation energy of particle \( E_{xc}[\rho] \), and the last term is energy due to nuclei-electron interaction \( E_{Ne}[\rho] \). The kinetic energy is represented in terms of corresponding orbital instead of electron density \( \rho \).

### 2.4.3 Exchange-Correlation Functional

The exact form of exchange-correlation energy \( (E_{xc}) \) is difficult to obtain. Hence, in DFT, one uses an approximate form for \( E_{xc} \), which may give accurate results. \( V_{xc} \) depends on the electron density at every point. \( E_{xc} \) can be treated in two parts:

\[
E_{xc}[\rho(\vec{r})] = E_x[\rho] + E_c[\rho] = \int \rho(\vec{r})\varepsilon_x \, d\vec{r} + \int \rho(\vec{r})\varepsilon_c \, d\vec{r}
\]  

(2.32)

where \( E_x \) is the exchange energy of the Slater determinant of Kohn-Sham orbital in equation (2.27). \( E_c \) is the correlation energy, \( \varepsilon_x \) is exchange energy per particle and \( \varepsilon_c \) is correlation energy per particle. In general, the contribution of exchange energy, \( E_x \) is larger than the correlation energy \( E_c \).

#### 2.4.3.1 Local Density Approximation (LDA)

This is the first approximation made to \( E_{xc} \). It is based on the homogenous electron gas. In this approximation, the electron density is assumed to be a slowly varying function of \( \vec{r} \). The exchange energy, \( E_x \) in LDA approximation is defined as:

\[
E_{x}^{LDA} = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho(\vec{r})^{2/3} \, d\vec{r}
\]  

(2.33)

where exchange energy per particle is,
Therefore, the corresponding local exchange potential is given as:

\[ V_{x}^{LDA}(\rho) = \frac{\partial E_{x}^{LDA}}{\partial \rho} = -\left( \frac{3}{\pi} \right)^{1/3} \rho(\vec{r})^{1/3} \]  

The most widely used LDA functional is the VWN (Vosko, Wilk and Nusair) \[47\] correlation functional which is given in the form of:

\[ E_{c}^{VWN} = \frac{A}{2} \left[ \ln \frac{x^2}{X(x)} + \frac{2b}{Q} \tan^{-1} \frac{Q}{2x-b} - \frac{bx_0}{X(x_0)} \left( \ln \frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q} \tan^{-1} \frac{Q}{2x-b} \right) \right] \]  

where \( x = r_s^{1/2} \) ( \( r_s \): effective volume containing one electron), \( X(x) = x^2 + bx + c \), and \( Q = (4c-b^2)^{1/2} \) and \( A, x_0 \) and \( c \) are constants.

The LDA exchange-correlation energies are insufficiently negative (by about 10%) for almost all atoms. The LDA is a reliable, moderate-accuracy approximation. However, LDA is not accurate enough for most chemical applications, which require the determination of energy differences with considerable accuracy. It overestimates bonding and in turn underestimates equilibrium volume; underestimate bond gap; gives too large bulk modulus.

**2.4.3.2 Generalized Gradient Approximation (GGA)**

Several attempts have been made to improve the LDA, and one of the most important is the inclusion of gradient corrections in the \( E_{xc} \). Here the functional are dependent on both the density \( \rho \) and its gradient, \( \nabla \rho \). Gradient-corrected functional is of the following form:

\[ E_{c}^{GGA} [\rho] = \int \rho(\vec{r}) E_{xc}[\rho(\vec{r}), \nabla(\vec{r})] d\vec{r} \]  

\[ \epsilon_{s}^{LDA}[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho(\vec{r})^{1/3} \]  

(2.44)
Becke proposed a correction to the LDA exchange energy that has the correct asymptotic behavior \((1/r)\) (in the LDA exchange the density has an exponential dependence on \(r\) in the asymptotic region). The gradient corrected exchange functional due to Becke (B88) \([48, 49]\) is given as:

\[
E_x^{B88} = E_x^{LDA} + \Delta E_x^{B88}
\]  
\[(2.48)\]

Where \(\Delta E_x^{B88} = -\beta \rho^{1/3} \frac{x^2}{1 + 6\beta x \sinh^{-1} x} \)  
\[(2.49)\]

where \(\beta\) is a parameter determined from atomic data, and \(x = \frac{\nabla \rho}{\rho^{4/3}}\)

2.5 B3LYP Hybrid Density Functional

In 1993, Becke \([48,49]\) gave a gradient corrected exchange functional, which is a combination of both the exact HF exchange and DFT exchange energies, hence termed hybrid functional. In the B3LYP hybrid functional scheme, the non local HF is mixed with the energy functional of Generalized Gradient Approximation (GGA). Here, the Perdew-Wang \([50]\) gradient-corrected correlation energy, which was used in the original work of Becke, is replaced with the Lee-Yang-Parr correlation energy \([51]\). It is a combination of the Slater40 [LDA exchange], HF and Becke’s gradient correction for exchange and with Lee, Yang and Parr gradient corrected correlation functional. The B3LYP has the form:

\[
E_{xc}^{B3LYP} = E_x^{LDA} + a_0 (E_x^{HF} - E_x^{LDA}) + a_x \Delta E_x^{B88} + E_c^{VWN} + a_c (E_c^{LYP} - E_c^{VWN})
\]  
\[(2.50)\]

where \(a_0 = 0.20, a_x =0.72\) and \(a_c =0.81\) are semi-empirical coefficients, determined by
fitting to experimental data. Here the LDA of Vosko, Wilk, and Nusair[47] is used for \( E_{x}^{\text{LDA}} \) and \( E_{x}^{\text{VWN}} \). \( E_{x}^{\text{HF}} \) is the exact non-local HF exchange energy. \( E_{x}^{\text{B88}} \) and \( E_{x}^{\text{LYP}} \) are the Becke’s and Lee-Yang-Parr’s gradient corrections for the local exchange and correlation energies, respectively.

### 2.6 Basis Sets

The molecular orbitals \( \Psi_{i} \) are represented as linear combination of a finite set of predefined N- one electron functionals, known as basis functions, \( \chi_{\mu} \).

\[
\Psi_{i} = \sum_{\mu=1}^{N} C_{\mu i} \chi_{\mu}
\]

(2.51)

where \( C_{\mu i} \) are molecular orbital expansion coefficients, \( \chi_{\mu} \) is the \( \mu \)-th orbital and N is number of atomic orbitals. Often basis functions are atomic orbitals in Linear Combination of Atomic Orbitals.

There are two types of basis functions commonly used in the electronic structure calculations. They are *Slater Type Orbitals (STOs)*[52] and *Gaussian Type Orbitals (GTOs)*[53]. The Slater Type Orbitals are given as:

\[
\chi(r, \theta, \phi) = N r^{n-1} e^{-\zeta r} Y_{l,m}^{\theta,\phi}
\]

(2.52)

where \( N \) is normalization constant, \( \zeta \) is called "Slater orbital exponent". \( (r,\theta,\phi) \) are spherical coordinates, and \( Y_{l,m} \) are the conventional spherical harmonics. These functions are accurate as they reflect exponential decay of the wave function. However solving the three- and four-centered integrals with STOs are extremely expensive in SCF calculations.
To circumvent this problem GTOs basis functions come into picture. In cartesian coordinates GTOs can be written as:

$$\chi(x, y, z) = N x^{l_x} y^{l_y} z^{l_z} e^{-\zeta^2}$$  \hspace{1cm} (2.53)

where $l_x$, $l_y$ and $l_z$ determines the angular part of orbital and $\zeta$ represents the radial part of the function.

The use of Gaussian-Type orbitals (GTOs) reduces the computational cost but has some drawbacks. The $e^{-r^2}$ dependence, results in a zero slope at the nucleus.

Contracted basis sets were used to reduce computational expense of large number of basis functions describing each of the atomic orbitals. The Contracted basis functions, have fixed contraction and coefficients. $\chi_{\mu}^{CGF}$ can be written as:

$$\chi_{\mu}^{CGF} = \sum_{i=1}^{L} d_{i\mu} \chi_{i}^{GF} (\zeta_{i\mu}, r)$$  \hspace{1cm} (2.54)

where $d_{i\mu}$ is a contraction coefficient, L is the length of the contraction, and $\zeta_{i\mu}$ is a contraction exponent.

Now, equation (2.51) can be rewritten as:

$$\psi_i = \sum_{\mu=1}^{N} C_{i\mu} \chi_{\mu}^{CGF}$$  \hspace{1cm} (2.55)

The widely used minimal basis set can be represented as STO-nG basis. In this basis set, each STO is given by contraction of n primitive GTOs. For example, 6-311G acronym implies that the valence basis functions are contractions of three primitive Gaussians (the inner function) and
one, one primitive Gaussians (the outer functions), whereas the inner shell functions (core orbital) are contraction of six primitive Gaussians. Polarization functions and diffuse functions are added to improve the basis set. Polarization functions (represented as *) enhance the ‘flexibility’ of atoms to form chemical bonds whereas diffuse functions (represented as +) improve the predicted properties of species with extended electron density such as anion. For example 6-31G** denotes that d-type functions is added to heavy atoms (left *), and p-type functions is added to hydrogen (right *). Similarly, in 6-31++G; diffuse functions are added to hydrogen (right +) and heavy atoms (left +).
Chapter 3

Computational Procedure, Results and discussion
Of
d\(^1\) transition metal chloride clusters

3.1 Validation of Computational Procedure

We carried out all the computations using density functional theory (DFT) with
generalized gradient approximation (GGA) as well as hybrid functional for exchange and
correlation (XC) potential. We have used BPW91[54-56] for the hybrid functional. Similarly we
have used 6-311+G(d) and 6-311+G(3df) basis sets for Cl and Sc and SDD basis set for Y and
La. Calculations were carried out using the GAUSSIAN 03 package[57]. In Table 1 we compare
the calculated ionization potentials and electron affinities of Sc, Y, La and Cl atoms for different
basis sets and exchange correlation functionals.
Table 1: Comparison of calculated IP (Ionization Potential) and EA (Electron Affinity) of Sc, Y, La and Cl with experimental data [58]:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Sc</th>
<th>Y</th>
<th>La</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IP  (eV)</td>
<td>IP  (eV)</td>
<td>IP  (eV)</td>
<td>IP  (eV)</td>
</tr>
<tr>
<td>Properties</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>6.54</td>
<td>6.38</td>
<td>5.58</td>
<td>12.97</td>
</tr>
<tr>
<td>BPW91/SDD</td>
<td>6.31</td>
<td>6.17</td>
<td>5.35</td>
<td>12.96</td>
</tr>
<tr>
<td>B3LYP/SDD</td>
<td>6.65</td>
<td>6.33</td>
<td>5.69</td>
<td>13.02</td>
</tr>
<tr>
<td>BPW91/6-311+G(d)</td>
<td>6.16</td>
<td>-</td>
<td>-</td>
<td>12.98</td>
</tr>
<tr>
<td>B3LYP/6-311+G(d)</td>
<td>6.56</td>
<td>-</td>
<td>-</td>
<td>13.07</td>
</tr>
<tr>
<td>BPW91/6-311+G(3df)</td>
<td>6.16</td>
<td>-</td>
<td>-</td>
<td>12.98</td>
</tr>
<tr>
<td>B3LYP/6-311+G(3df)</td>
<td>6.56</td>
<td>-</td>
<td>-</td>
<td>13.07</td>
</tr>
</tbody>
</table>

By comparing these with experimental results [59] we chose to use the B3LYP functional for the remaining calculations. For each cluster, MCl\textsubscript{n} (M = Sc, Y, La; n = 2–5) several initial geometries were used with chlorine bound both molecularly (Cl\textsubscript{2}) and atomically (Cl). Optimizations were carried out without any symmetry constraint. All the optimizations are followed by frequency calculations to confirm that the structures represent genuine minima in the potential energy surface. We have calculated the total energies as a function of spin multiplicities to obtain the preferred spin configurations of the neutral and anionic species. Thus, complete conformational search has been done at SDD/6-311+G(d) basis set level and the lowest energy isomers were re-optimized at SDD/6-311+G(3df) level. The vertical detachment energy,
VDE (the energy difference between the anion and its neutral at the anionic geometry) and electron affinity, EA (the energy difference between the ground states of the anion and its corresponding neutral) were calculated so that these can be compared with available experimental data involving photoelectron spectroscopy.

3.2 Results

Here we have discussed the geometries, electronic structure, and electron affinities of MCl\(_n\) (M = Sc, Y, La; n = 1–5) separately.

3.2.1 MCl (M= Sc, Y, La)

In Figure 1 we provide the geometries of ScCl, YCl, and LaCl molecules. The bond lengths and charges obtained from the natural bond orbital (NBO) analysis are listed for the neutral. In the parentheses corresponding results are given for the anions.

![Figure 1. Structures of MCl (M = Sc, Y, La) at B3LYP/SDD/6-311+G(3df).](image)

As seen from the above figure, the bond lengths for both the neutrals and anions increase from Sc to La as can be expected from the size of the Sc, Y and La atoms. The charge transfer from the metal atoms to Cl in the neutral molecule is about the same for all the three metals and
indicates that the bonding is dominated by ionic interaction. In the anions, the extra electron goes to neutralize the positive charge on the metal atoms and consequently the bond lengths are larger than those in the neutrals.

To obtain the preferred spin multiplicity of the ScCl, YCl and LaCl we calculated the total energies of the lowest two spin states, namely singlet and triplet for the neutrals and doublet and quartet for the anions. Spin triplet state of neutral ScCl is 0.24 eV lower in energy than the singlet state. The ground state spin multiplicity of YCl is a singlet which lies lower in energy than the triplet by 0.57 eV. For neutral LaCl, on the other hand, both singlet and triplet states are energetically nearly degenerate with the triplet only 2 eV higher in energy than the singlet. The degeneracy in the preferred spin is lifted in the anions. The preferred spin states for the ScCl, YCl and LaCl are all doublets which lie 0.95, 0.94 and 1.13 eV, respectively, lower in energy than from the spin quartet states.

The computed electron affinities (EAs) and vertical detachment energies (VDEs) for two different basis sets are given in Table 2. We note that improving the basis sets only has marginal effect on the VDE and EA which are uniformly small in all cases. No experimental data are available to compare with our calculated results.
Table 2: EA of MCl and VDE of MCl (M = Sc, Y, La).

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>ScCl</th>
<th>YCl</th>
<th>LaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(d)</td>
<td>1.19</td>
<td>1.24</td>
<td>0.73</td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(3df)</td>
<td>1.16</td>
<td>1.20</td>
<td>0.68</td>
</tr>
</tbody>
</table>

3.2.2 MCl$_2$ (M= Sc, Y, La)

The equilibrium geometries of all neutral and anionic MCl$_2$ clusters (M = Sc, Y, La) are given in Fig. 2 below along with their respective bond lengths and NBO charges.

Figure 2. Structures of MCl$_2$ (top row) and MCl$_2^-$ (bottom row) (M = Sc, Y, La) at B3LYP/SDD/6-311 + G(3df).
Note that all neutral clusters are bent structures while the ScCl$_2^-$ and YCl$_2^-$ have linear structures. The geometry of LaCl$_2^-$, however, is a bent structure although the Cl–La–Cl bond angle in the anion is larger than that of the neutral. The bond lengths are similar to those in MCl and the anion bonds are larger than their corresponding neutrals. In neutral MCl$_2$ cluster, charge is transferred from the metal atoms to Cl, thus making the bonding predominantly ionic. When the extra electron is added to the anion, it preferentially goes to neutralize the positive charge on the metal atoms. The preferred spin states for neutral ScCl$_2$, YCl$_2$, and LaCl$_2$ clusters are doublet with the quartet states lying, respectively, 4.19, 4.59 and 4.50 eV higher in energy. This drastic rise in energy from doublets to quartets is due to the non-availability of electrons in valence orbitals that can be unpaired after the preferred two-center two-electron (2c–2e) bonds are formed. For the anions, however, the additional electron available for bonding reduces the energy difference between singlets and triplets; the triplets are only 0.08, 0.64, 0.36 eV higher than the singlets in ScCl$_2^-$, YCl$_2^-$, and LaCl$_2^-$, respectively.

The EA and VDE values are given in Table 3. We note that these values are again small, although they are slightly larger than those of their MCl (see Table 2) counterparts. Again, no experimental data are available to compare with our calculated results.
Table 3: EA of MCl\textsubscript{2} and VDE of MCl\textsubscript{2}\textsuperscript{-} (M = Sc, Y, La).

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>ScCl\textsubscript{2}</th>
<th>YCl\textsubscript{2}</th>
<th>LaCl\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(d)</td>
<td>1.50</td>
<td>1.61</td>
<td>1.68</td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(3df)</td>
<td>1.41</td>
<td>1.52</td>
<td>1.58</td>
</tr>
</tbody>
</table>

3.2.3 MCl\textsubscript{3} (M= Sc, Y, La)

The equilibrium geometries of neutral ScCl\textsubscript{3}, YCl\textsubscript{3}, and LaCl\textsubscript{3} are given in Fig. 3. The geometries of their anions are similar to those of their neutrals, which is trigonal planar. Thus, in Fig. 3 we have given the bond lengths and NBO charges of the anions in parentheses. The bond lengths between metal atoms and Cl are similar to those seen in Figs. 1 and 2. The ground state spin configurations of the neutral clusters are all singlets while those for the anions are doublets. The spin triplet states of the neutrals are 3.68, 3.98 and 4.28 eV, respectively, higher in energy than the singlets in ScCl\textsubscript{3}, YCl\textsubscript{3}, and LaCl\textsubscript{3}. Correspondingly, the quartet states of the anions are 4.77, 4.98 and 4.92 eV higher in energy than the spin doublet states.
We note that in neutral MCl$_3$ clusters, charge is transferred from the metal atom, M to Cl and this charge transfer increases from Sc to La. This is consistent with the decreasing ionization potential as one proceeds from Sc to La (see Table 1). In the anions, significant portion of the extra electron goes to the metal site.

MCl$_3$ is the most stable species as it consumes all its valence electrons when interacting with three Cl atoms and all the three bonds are classic two-center two-electron bonds. It should be kept in mind that in solids with composition MCl$_3$, metals have higher coordination; 6 for ScCl$_3$ [60] and YCl$_3$ [61] and 9 for LaCl$_3$ [62]. The high ionic nature of the bonding is apparent from the high charge for Cl in gas phase calculation and also negligible change in atomic charge of Cl in MCl$_n$ series. The VDE and EA values of ScCl$_3$, YCl$_3$, and LaCl$_3$ are given in Table 4. These values only show a marginal increase over those in Tables 2 and 3. Once again, no experimental results are available to compare with our calculated results.

**Figure 3.** Structures of MCl$_3$ (M = Sc, Y, La) at B3LYP/SDD/6-311 + G(3df).
3.2.4 MCl₄ (M= Sc, Y, La)

MCl₄ represents the first neutral cluster having electron deficient bonding. This is reflected in the geometry of the neutral clusters which are shown in Fig. 4.

Here the electron deficiency resulted in multicenter bonding with one Cl–M–Cl bond angle being around 60º while the other bond angles are around 120º. The clusters have C₂ᵥ symmetry. The bond lengths between the metal atom and Cl are relatively unchanged from those described earlier for the bonds involving electron sufficient bonding, but the electron deficient bonds are lengthened. Similarly the atomic charges on chlorines involved in electron deficient bond are remarkably less. When an extra electron is attached, the geometries of MCl₄⁻ change significantly. The Cl–M–Cl bond angle that is around 60º changes to 109º. Unlike in MCl₃ (n ≤ 3) clusters, the charge on the metal atoms remains nearly the same in both anion and neutral clusters.

**Table 4**: EA of MCl₃ and VDE of MCl₃⁻ (M = Sc, Y, La).

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>ScCl₃</th>
<th>YCl₃</th>
<th>LaCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(d)</td>
<td>2.15</td>
<td>2.43</td>
<td>1.94</td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(3df)</td>
<td>2.01</td>
<td>2.28</td>
<td>1.77</td>
</tr>
</tbody>
</table>
Figure 4. Structures of $\text{MCl}_4$ (top row) and $\text{MCl}_4^-$ (bottom row) at $(\text{M} = \text{Sc, Y, La})$ B3LYP/SDD/6-311+G(3df).

Note that Sc, Y, and La atoms have a maximal valence of 3, and hence can accommodate at best three Cl atoms using the conventional bonding mechanism. The anion, having sufficient electrons form four two-center two-electron bonds and possesses tetrahedral geometry. Compared to the electron deficient bonds in neutral, the bond lengths of $\text{MCl}_4^-$ are shorter. The extra electron in the anionic clusters is distributed uniformly over four Cl atoms (see the NBO charges in Fig. 4). This has dramatic effect on the electron affinities which are shown in Table 5.
Table 5: EA of MCl₄ and VDE of MCl₄⁻ (M = Sc, Y, La).

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>ScCl₄</th>
<th></th>
<th></th>
<th>YCl₄</th>
<th></th>
<th></th>
<th>LaCl₄</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(d)</td>
<td>6.11</td>
<td>6.35</td>
<td>6.21</td>
<td>6.47</td>
<td>5.99</td>
<td>6.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(3df)</td>
<td>5.96</td>
<td>6.32</td>
<td>6.03</td>
<td>6.39</td>
<td>5.90</td>
<td>6.43</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The vertical detachment energies (and electron affinities) of ScCl₄, YCl₄, and LaCl₄ calculated at the B3LYP level of theory with SDD/6-311+G(3df) basis sets are respectively 6.32 (5.96), 6.39 (6.03) and 6.43 (5.90) eV. The corresponding experimental values are 7.14 (6.84), 7.31 (7.02) and 7.38 (7.03) eV [63, 64]. We note that the calculated values are about 1 eV smaller than the corresponding experimental values. This is mainly attributed to the inadequate electron correlation in density functional theory. Recently Dixon and coworkers [65,66] incorporated various corrections to get highly reliable electron affinities of metal hexafluoride. Besides extrapolating to complete basis set at CCSD(T), additional corrections for relativistic effect and spin orbit coupling were included in their approach.

We note that these electron affinities are not only substantially larger than those seen in MClₙ (n ≤ 3) clusters, but also they are larger than that of Cl atom which is 3.62 eV. Thus, these clusters can be identified as superhalogens. As in the case of MCl₃, higher spin states of both neutral and anion are higher in energy. The quartet states of neutral MCl₄ are 3.73, 4.12 and
4.32 eV higher in energy than the doublet ground states for M = Sc, Y and La. The triplet states of the corresponding anions are higher than the singlet ground states by 4.29, 4.61 and 4.64 eV.

3.2.5 MCl₅ (M= Sc, Y, La)

We have examined the possibility of whether a fifth Cl atom can be attached to both neutral and anion MCl₄ clusters since further addition of Cl can only worsen the electron deficiency nature of neutral MCl₄. We found that this is indeed possible and in Fig. 5 we provide the geometries of neutral and anionic MCl₅ (M = Sc, Y, La) clusters. The equilibrium geometry of neutral MCl₅ clusters show that three of the Cl atoms are chemically bound, while two of them form a molecular-like structure and are weakly coordinated to the MCl₃ portion of the cluster. In the anion, the bond between the molecularly coordinated chlorine atoms break and all the five Cl atoms are chemically bound.
Despite our best efforts, which includes optimization by calculating the force constant at every step, a small imaginary frequency of -10 cm$^{-1}$ for YCl$_5^-$ and -24 cm$^{-1}$ for LaCl$_5^-$ could not be eliminated at the B3LYP/SDD/6-311+G(3df) level of theory. This imaginary vibration mode appears to be spurious but involves the side to side wagging of the two chlorine atoms at the top.

The preferred spin multiplicities of neutral and anionic MCl$_5$ clusters are respectively singlets and doublets. The triplet states of neutral MCl$_5$ clusters are 0.44, 0.33 and 0.30 eV higher in energy than the corresponding singlet states for Sc, Y, and La, respectively.

**Figure 5.** Structures of MCl$_5$ (top row) and MCl$_5^-$ (bottom row) (M = Sc, Y, La) at B3LYP/SDD/6-311 + G(3df).
This marginal increase in energy is remarkable from the point of view of chemical bonding since the energies of triplet MCl$_3$ (see above) and Cl$_2$ (1.51 eV at B3LYP/6-311 + G* level) are quiet high. The doublet states of the anions are lower in energy than the quartet states by 4.04, 4.59 and 4.61 eV for Sc, Y, and La, respectively.

In Table 6 we provide the calculated vertical detachment energies and electron affinities of ScCl$_5$, YCl$_5$ and LaCl$_5$ clusters.

<table>
<thead>
<tr>
<th>Method/Basis set</th>
<th>ScCl$_5$</th>
<th>YCl$_5$</th>
<th>LaCl$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(d)</td>
<td>5.35</td>
<td>6.29</td>
<td>5.61</td>
</tr>
<tr>
<td>B3LYP/SDD/6-311+G(3df)</td>
<td>4.98</td>
<td>6.21</td>
<td>5.22</td>
</tr>
</tbody>
</table>

Note that the electron affinities are larger than that of the Cl atom, and hence these clusters can also be classified as superhalogens. However, they are smaller than those in MCl$_4$ clusters (see Table 5). More interestingly, we note that there is significant difference between VDE and EA values. This arises due to considerable difference between the structures of the anions and their neutrals. No experimental results are available to compare with our calculated results.
3.3 Summary of the above calculations

Using density functional theory and generalized gradient approximation for exchange and correlation potential we have systematically studied the equilibrium structure, stability, electronic structure, vertical detachment energies and electron affinities of ScClₙ, YClₙ, and LaClₙ (n = 1–5) clusters. For a given Cl composition our results are similar for Sc, Y and La. However, results vary strongly as Cl atoms are attached successively. In neutral MClₙ clusters, chlorine atoms are bound chemically for n ≤ 3. In neutral MCl₅ clusters two of the Cl atoms bind weakly in a quasi-molecular fashion while the other three bind chemically. In MCl₄ clusters, on the other hand, two of the Cl atoms tend to be much closer than the others. In the anionic MClₙ clusters all Cl atoms bind chemically until n ≤ 4. The partial bond between two Cl atoms in MCl₄ breaks once an extra electron is attached.

In Fig. 6 we summarize the stability of the neutral and anionic MClₙ clusters against fragmentation to chlorine atom or molecule.
This is studied by calculating the fragmentation energies as defined below:

\[ \Delta E_{\text{atomic}} = E[MCl_{n-1}] + E[Cl] - E[MCl_n] \]

\[ \Delta E_{\text{molecular}} = E[MCl_{n-2}] + E[Cl_2] - E[MCl_n] \]

In the case of the anion, we calculate these energies using the equations,

\[ \Delta E_{\text{atomic}} = E[MCl_{n-1}] + E[Cl^-] - E[MCl_n^-] \]

\[ \Delta E_{\text{atomic}} = E[MCl_{n-1}] + E[Cl] - E[MCl_n^-] \]

\[ \Delta E_{\text{molecular}} = E[MCl_{n-2}] + E[Cl_2] - E[MCl_n^-] \]

Here, the extra electron can be carried by either the Cl atom or the MCl\(_{n-1}\) cluster. The preferred path corresponds to the channel for which \( \Delta E_{\text{atomic}} \) is lower.

The lowest fragmentation energies for both neutral and anion MCl\(_n\) clusters are shown in Figure 6(A) and (B) respectively. As can be seen, up to \( n = 3 \) the lowest path for fragmentation
for neutral clusters is by ejecting a Cl radical. About 5 eV of energy is required for breaking the MCl bond indicating that 2c-2e M—Cl bond is preferred over 2c-2e Cl—Cl bond. However, being electron deficient, the energy required to expel a Cl atom is drastically reduced for MCl₄. The preferred decomposition path for MCl₅ is to Cl₂ and MCl₃.

Given the high electron affinity of Cl, the preferred decomposition path for the MClₙ⁻ anions is by ejecting a Cl⁻ ion. This is the preferred path until n = 4. It may be noted that despite the high electron affinity of Cl, decomposition to Cl⁻ is endothermic, a consequence of the strong M—Cl bond. Because of the extraordinary stability of MCl₄⁻ the lowest decomposition path for MCl₅⁻ is to MCl₄⁻ and Cl.

The electron affinity of MClₙ clusters are plotted in Figure 7 as a function of Cl content. The EA values increase marginally until the valence of the metal atoms is consumed which in this case are three. Beyond that the EA values rise sharply indicating the onset of superhalogen behavior.

![Graph](image)

**Figure 7.** Electron affinities of MClₙ (M = Sc, Y, La) at B3LYP/SDD/6-311 + G(3df).
The small increase in electron affinities for \( n \leq 3 \) and its abrupt increase at \( n = 4 \) is consequence of how the extra electron’s charge is distributed. These are summarized in Figure 8. We note that for \( n \leq 3 \), the extra charge in the \( \text{MCl}_n^- \) clusters goes to the metal atom site and hence the electron affinities do not change much. However for \( n \geq 4 \), the extra charge is distributed over the Cl atoms and hence the electron affinity rises sharply.

![Figure 8. NBO atomic charges at B3LYP/SDD/6-311 + G(3df) level on metal atom in \( \text{MCl}_n \) series; (A) \( \text{M} = \text{Sc} \), (B) \( \text{M} = \text{Y} \), and (C) \( \text{M} = \text{La} \).](image)
Chapter 4

Computational Procedure, Results and Discussion
Of
Singly and Doubly Charged Anions of Metal Chloride and Pseudohalogen Clusters

4.1 Validation of Computational Procedure

All calculations have been carried out using density functional theory (DFT) with B3LYP hybrid functional for exchange and correlation (XC) potential [67, 68]. The accuracy of the DFT-based results is verified by carrying selected calculations using other ab initio quantum-chemical methods such as MP2 (second order Moller-Plesset Perturbation), CCSD(T) (Coupled Cluster with single, double excitations, and perturbative treatment of triple excitations) and comparing our results with available prior theoretical [69-72] and experimental [73-75] results. In all our calculations we have used 6-311++G(3df) basis sets which are known to provide excellent agreement between calculated and experimental results [76-79]. All other procedures are similar to that mentioned previously in section 3.1.
4.2 Results

In the following section A, we discuss the structure, stability, and spectroscopic properties of neutral, singly charged and doubly charged anions of NaCl$_n$ ($n \leq 3$), MgCl$_n$ ($n \leq 4$) and AlCl$_n$ ($n \leq 5$) clusters. Similar results where the Cl atoms are replaced by pseudohalogen are described in section B.

4.2.A Metal-Chloride Clusters MCl$_n$ (M=Na, Mg, Al):

(i) NaCl$_n$ ($n \leq 3$)

Equilibrium Geometries:

In Figure.9 we provide the ground state optimized geometries of neutral, singly and doubly charged anions of NaCl$_n$ ($n \leq 3$) clusters. The bond lengths and NBO charge are also given in the figure. The bond length of the anionic NaCl is elongated compared to that in the neutral. In the neutral NaCl$_2$, the number of the Cl atoms exceeds the valence of the Na atom, and therefore in accordance with VSEPR (Valence Shell Electron Pair Repulsion) theory it has a bent shape due to the presence of one lone pair of electrons. NaCl$_2^-$, on the other hand, becomes a linear chain as the electron deficiency of Cl atom is fulfilled by the addition of an extra electron.
Figure 9: Optimized geometries of neutral (left), anionic (middle) and dianionic (right) NaCl$_n$ clusters at B3LYP/6-311++G(3df) level of theory.

The geometry of doubly charged NaCl$_2$ anion remains almost identical to that of NaCl$_2^-$, but found to be unstable as the repulsive interaction between the two extra electrons overwhelms the binding energy of the molecule. Its lack of stability will be discussed later by studying the fragmentation channel. In neutral NaCl$_3$ cluster, as Na can afford only one electron to the Cl atom, the other two Cl atoms binds quasi-molecularly with only one of them bound to the Na atom giving it an adduct type structure NaCl$^+$ Cl$_2$. 
Note that the bond length between the chlorine atoms is 2.15 Å which is nearly similar to the bond length of the Cl₂ molecule (2.01 Å) calculated at the same level of theory as for this cluster. In NaCl₃⁻, due to the availability of an extra electron, all the Cl-atoms bind chemically to the Na atom with two of the Cl atoms coming close together. As NaCl₃⁻ is still an electron deficient cluster, it needs one more electron to fulfill the valence shell of all the Cl atoms. On addition of an extra electron to the anionic NaCl₃, the resulting dianion possesses a perfectly trigonal planar geometry and the extra electron is delocalized among all the Cl atoms.

**Stability and Fragmentation:**

The stability of neutral, anionic and dianionic clusters of NaClₙ (n ≤ 3) is determined by calculating the least energy needed to fragment the cluster among all possible channels. We define these fragmentation energies as:

\[
\Delta E_{\text{neutral}}(n) = E(\text{NaCl}_n) - E(\text{NaCl}_{n-m}) - E(\text{Cl}_m) \quad \text{m} \leq 2 \quad (1)
\]

For calculating the corresponding fragmentation energies of the anion and dianion, one has to further consider which fragment carries the extra charge(s) or if the electron is autoejected. Thus, we define,

\[
\Delta E_{\text{anion}}^1(n) = E(\text{NaCl}_n^-) - E(\text{NaCl}_{n-m}^-) - E(\text{Cl}_m) \quad \text{m} \leq 2 \quad (2)
\]

\[
\Delta E_{\text{anion}}^2(n) = E(\text{NaCl}_n^-) - E(\text{NaCl}_{n-m}^-) - E(\text{Cl}_m^-) \quad \text{m} \leq 2 \quad (3)
\]

\[
\Delta E_{\text{anion}}^3(n) = E(\text{NaCl}_n^-) - E(\text{NaCl}_n^-) - e^- \quad (4)
\]

\[
\Delta E_{\text{dianion}}^1(n) = E(\text{NaCl}_n^{2-}) - E(\text{NaCl}_{n-m}^{2-}) - E(\text{Cl}_m^-) \quad \text{m} \leq 2 \quad (5)
\]

\[
\Delta E_{\text{dianion}}^2(n) = E(\text{NaCl}_n^{2-}) - E(\text{NaCl}_{n-m}^-) - E(\text{Cl}_m^-) \quad \text{m} \leq 2 \quad (6)
\]
\[ \Delta E_{\text{dianion}}^n = E(\text{NaCl}_n^{2-}) - E(\text{NaCl}_n^-) - e^- \quad m \leq 2 \] (7)

The preferred channel for fragmentation and the corresponding energies are given in Table -7.

<table>
<thead>
<tr>
<th></th>
<th>Neutral</th>
<th>Mono-anion</th>
<th>Di-anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel</td>
<td>(\Delta E) (eV)</td>
<td>Channel</td>
<td>(\Delta E) (eV)</td>
</tr>
<tr>
<td><strong>NaCl</strong> (\rightarrow) <strong>Na + Cl</strong></td>
<td>4.06</td>
<td><strong>NaCl</strong> (\rightarrow) <strong>NaCl + e^-</strong></td>
<td>0.86</td>
</tr>
<tr>
<td><strong>NaCl(_2)</strong> (\rightarrow) <strong>NaCl + Cl</strong></td>
<td>1.31</td>
<td><strong>NaCl(_2)(^-)</strong> (\rightarrow) <strong>NaCl + Cl</strong></td>
<td>2.2</td>
</tr>
<tr>
<td><strong>NaCl(_3)</strong> (\rightarrow) <strong>NaCl + Cl(_2)</strong></td>
<td>0.54</td>
<td><strong>NaCl(_3)(^-)</strong> (\rightarrow) <strong>NaCl(_2) + Cl</strong></td>
<td>1.26</td>
</tr>
</tbody>
</table>

We see that among neutral NaCl\(_n\) clusters, NaCl is the most stable one as can be expected from ionic bonding argument. Among the mono-anion series, NaCl\(_2\)\(^-\) is the most stable cluster due to its closed shell structure. The dianion of NaCl\(_2\) is unstable against auto-ejection of an electron while the dianion of NaCl\(_3\) is unstable against fragmentation into NaCl\(_2\)\(^-\) and a Cl\(^-\) ion. However, the frequencies are positive indicating that these structures correspond to local minima in the potential energy surface. NaCl\(_3\)\(^-\) is metastable and can be seen in the experiment due to finite lifetime.
Electron Affinities (EA) and Vertical Detachment Energies (VDE)

The EAs of neutrals and VDEs of anions are calculated using DFT as well as MP2 and CCSD(T) methods. The VDEs are also calculated by the direct method i.e with using Outer Valence Green's Function (OVGF) method. The results are given in Table-8. We see that the results based on DFT agree with those with quantum chemical methods within 0.2 eV which currently is the accuracy of DFT-based methods.

Table-8: EA of NaCl\textsubscript{n} and VDE of NaCl\textsubscript{n}\textsuperscript{−} with 6-311++G(3df) basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>NaCl</th>
<th>NaCl\textsubscript{2}</th>
<th>NaCl\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA(eV)</td>
<td>VDE(eV)</td>
<td>EA(eV)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.86</td>
<td>0.91</td>
<td>4.58</td>
</tr>
<tr>
<td>MP2</td>
<td>0.68</td>
<td>0.71</td>
<td>4.78</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>0.69</td>
<td>0.72</td>
<td>4.68</td>
</tr>
<tr>
<td>OVGF</td>
<td>0.73</td>
<td></td>
<td>5.89</td>
</tr>
</tbody>
</table>

In case of NaCl cluster, the EAs and VDEs values are quite close to each other, which is consistent with minimal changes in the neutral and anionic geometries. On the contrary, the EA and VDE values are very different in NaCl\textsubscript{2} and NaCl\textsubscript{3} clusters due to the large difference between their corresponding geometries. The results compare well with earlier theoretical [90, 91] and experimental value [91] on NaCl\textsubscript{2} cluster. Note that the EA value of NaCl\textsubscript{2} is significantly higher than that of Cl\textsuperscript{−}, thus making it a superhalogen. Although NaCl\textsubscript{3} remains as a superhalogen, its EA is less than that of NaCl\textsubscript{2} due to its filled shell.
**Charge Distribution:**

One of the ways to understand the stability of NaCl\textsubscript{n} clusters and origin of the superhaogen behavior of NaCl\textsubscript{2} and NaCl\textsubscript{3} clusters is to analyze the charge distribution both in neutral and anionic states. This was done by calculating the charge on Na and Cl atoms as a function of n by using the natural bond orbital analysis. As seen from Figure.9 the charge on Na atom in neutral NaCl\textsubscript{n} clusters is same for n \leq 3 irrespective of how the Cl atoms are bound to it and the transferred charge is distributed among the Cl atoms. When an extra electron is added, it goes to the Na atom in NaCl, but in NaCl\textsubscript{2} and NaCl\textsubscript{3} the electron is distributed over the Cl atoms. Consequently, the electron affinity increases sharply. In NaCl\textsubscript{2} dianion, both the electrons reside on the Cl atom while Na remains electrically neutral. The electrostatic repulsion makes NaCl\textsubscript{2} dianion unstable. The case is different for NaCl\textsubscript{3}. Here the charge on Na atom is nearly +1 and each of the Cl atoms carries an extra electron. The electrostatic interaction between Na\textsuperscript{+} and Cl\textsuperscript{-} atoms provide metastability for the NaCl\textsubscript{3} dianion.

**(ii) MgCl\textsubscript{n} (n \leq 4)**

**Equilibrium Geometries:**

The ground state optimized geometries of neutral, singly and doubly charged clusters of MgCl\textsubscript{n} (n \leq 4) are displayed in Figure.10 with the bond lengths and the NBO charges. In MgCl\textsubscript{2} cluster, the charge on Mg in neutral MgCl\textsubscript{2} is +1.65e and the transferred charge is equally shared by both the Cl atoms. Consequently, it is a linear chain. However, on addition
of electrons to the neutral, the resulting anion and dianion have bent structures. The bond lengths are elongated due to the presence of a lone pair as per VSEPR theory.

![Figure 10](image)

**Figure 10:** Optimized geometries of neutral (left), anionic (middle) and dianionic (right) MgCl$_{n}$ clusters at B3LYP/6-311++G(3df).

The energy difference between the anionic and dianionic cluster of MgCl$_2$ is found to be 2.76 eV. In MgCl$_3$ cluster, there is also a significant geometrical change between the mono-
anion and the neutral. In the neutral, as the number of Cl atoms exceeds the nominal valence of Mg atom, the bond lengths between Mg and two Cl atoms are stretched. On the other hand in MgCl$_3^-$ the third electron required to fill in the shells of three Cl atoms is supplied by the added electron giving it a perfect trigonal planar geometry. Upon addition of an extra electron the resulting dianion is again unstable as most of the charges are taken by the Mg atom and the large Coloumb repulsion dominates its binding energy. The energy difference between the anionic and dianionic MgCl$_3$ is found to be nearly 3 eV. In MgCl$_4$ cluster, the situation is very similar to that for NaCl$_3$. Due to its electron deficient nature, the two Cl atoms bind quasi-molecularly with a bond length 2.05 Å resulting in an adduct-like structure. Whereas in the anion, as Mg atom can only afford to lose two electrons the extra electron is distributed among all the Cl atoms and the bond between the quasi-molecularly bound Cl atoms breaks while the bonds between Mg and corresponding Cl atoms stretch to 2.47 Å. As the anionic cluster needs one more electron to fulfill the valence of all the Cl atoms, the resulting dianion has a perfect tetrahedral geometry. Its energy is lowered by 1.07 eV as compared to its anion.

**Stability and Fragmentation:**

The stability of neutral, anionic and dianionic clusters of MgCl$_n$ are determined by calculating the fragmentation energies as defined in Eqs. (1) – (7). The preferred channels and the corresponding fragmentation energies are given in Table 9.
Note that energy needed to fragment MgCl\(_2\) is the highest among the neutral clusters and hence is the most stable species. MgCl\(_4\) dissociates into MgCl\(_2\) and a Cl\(_2\) molecule while the smaller clusters eject only a Cl atom.

**Table-9:** Preferred fragmentation channels and energies of MgCl\(_n\) clusters.

<table>
<thead>
<tr>
<th>Neutral</th>
<th>Mono-anion</th>
<th>Di-anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel</td>
<td>ΔE (eV)</td>
<td>Channel</td>
</tr>
<tr>
<td>MgCl (\rightarrow) Mg + Cl</td>
<td>3.21</td>
<td>MgCl(^-) (\rightarrow) Mg + Cl(^-)</td>
</tr>
<tr>
<td>MgCl(_2) (\rightarrow) MgCl + Cl</td>
<td>4.66</td>
<td>MgCl(_2)(^-) (\rightarrow) MgCl(_2) + e(^-)</td>
</tr>
<tr>
<td>MgCl(_3) (\rightarrow) MgCl(_2) + Cl</td>
<td>1.09</td>
<td>MgCl(_3)(^-) (\rightarrow) MgCl(_2) + Cl(^-)</td>
</tr>
<tr>
<td>MgCl(_4) (\rightarrow) MgCl(_2) + Cl(_2)</td>
<td>0.28</td>
<td>MgCl(_4)(^-) (\rightarrow) MgCl(_3)(^-) + Cl</td>
</tr>
</tbody>
</table>

On the other hand, MgCl\(_3\)\(^-\) is the most stable cluster among the mono-anionic clusters. While MgCl\(_2\)\(^-\) prefers to eject an electron, the other anions either eject a Cl\(^-\) atom for \(n = 1\) and 3 or a Cl atom for \(n = 4\). The latter is due to the fact that the MgCl\(_3\) is a superhalogen which will be discussed later. All the dianions of MgCl\(_n\)\(^2-\) are thermodynamically unstable against auto-ejection of an electron or Cl\(^-\), but for \(n = 2\)\(-\)4, they belong to the local minima in the potential energy surface. Hence, these are metastable.
Electron Affinities (EA) and Vertical Detachment Energies (VDE):

The EAs of the neutrals and VDEs of the anions calculated using different theoretical models are given in Table 10. The experimental data is only available for the VDE of MgCl$_3^-$ [92]. The theoretical values are available only for MgCl$_3$ clusters [92, 93].

**Table-10**: EA of MgCl$_n$ and VDE of MgCl$_n^-$ with 6-311++G(3df) basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>MgCl</th>
<th>MgCl$_2$</th>
<th>MgCl$_3$</th>
<th>MgCl$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA(eV)</td>
<td>VDE(eV)</td>
<td>EA(eV)</td>
<td>VDE(eV)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>1.61</td>
<td>1.74</td>
<td>1.15</td>
<td>1.87</td>
</tr>
<tr>
<td>MP2</td>
<td>1.30</td>
<td>1.45</td>
<td>1.0</td>
<td>1.69</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>1.53</td>
<td>1.68</td>
<td>1.52</td>
<td>1.72</td>
</tr>
<tr>
<td>OVGF</td>
<td>1.65</td>
<td>1.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expt</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Note that results based on MP2 and CCSD(T) methods agree well with available experimental data. From our data, we found that the values of EAs and VDEs are quite similar for MgCl$_n$ clusters and it gradually increases as the number of Cl content increases. The EA values significantly increase for MgCl$_3$ and MgCl$_4$ which indicates the onset of superhalogen behavior. Note that the difference between EA and VDE is especially large for MgCl$_4$, around 2 eV. This due to a large geometry change (see Figure 10).
**Charge Distribution:**

In order to understand the nature of bonding, we analyzed the charge on Mg atom as a function of n, where n is the number of Cl atoms for neutral, anion and dianionic species using natural bond orbital analysis (NBO). The results are displayed in Figure 10. We found that in all the neutral clusters the bonding is basically ionic in nature. On addition of an electron to the neutral cluster, the charges prefer to reside on Mg atom for n ≤ 2. When n exceeds the maximal valence of Mg atom (n > 2), the charge prefers to reside on the Cl atoms rather than on Mg which causes the EA to rise sharply. In neutral MgCl$_4$, the charge transfer is no longer possible and subsequently two Cl atoms bind quasi-molecularly. When one more electron is added to the anionic MgCl$_n$ cluster for 1<n < 3, most of the charges are transferred to Mg atom. In MgCl$_4$ dianion the extra charge is delocalized among all the Cl atoms rather than staying on the Mg atom. This makes it stable against Coulomb repulsion due to its high binding energy. It can be noted from Fig.2 that the charges in the neutral, anion and the dianion are nearly the same at n = 4.

**(iii) AlCl$_n$ (n ≤ 5)**

**Equilibrium Geometries:**

The ground state optimized geometries of neutral, mono-anion of AlCl$_n$ (n=1-5) and the dianions of AlCl$_n$ (1<n ≤5) clusters are given in Figure.11 with their bond lengths and NBO charges. Unlike the clusters discussed before, the geometries of the neutral and the mono-anionic AlCl$_n$ clusters are very similar for n ≤ 5. The differences are larger for n ≥ 4 as Al is trivalent and each Cl atom needs an electron to close its shell.
Figure 11: Optimized geometries of neutral (left), anionic (middle) and dianionic (right) AlCl$_n$ clusters at B3LYP/6-311++G(3df).
In the neutral AlCl\textsubscript{4} cluster, two of the Cl atoms bind to the Al atom with bond lengths of 2.24 Å while the other two have a shorter bond length of 2.09 Å. AlCl\textsubscript{4}\(^-\), on the other hand, has a perfect tetrahedral geometry as the extra electron can fill the shell of the Cl atom resulting in a closed shell structure. In the neutral AlCl\textsubscript{5} cluster, the two Cl atoms are bound in a quasi-molecular form having a bond length of 2.02 Å resulting in an adduct like structure AlCl\textsubscript{3}*Cl\textsubscript{2} which is very similar to those seen in NaCl\textsubscript{3} and MgCl\textsubscript{4} clusters. In AlCl\textsubscript{5}\(^-\), the extra electron is not enough to fill the shells of all the Cl atoms. Consequently the quasi-molecular bond between the two Cl atoms in neutral AlCl\textsubscript{5} cluster is stretched to 2.71 Å. The geometries of dianions are similar as those of their corresponding mono-anionic clusters except for \(n = 5\). AlCl\textsubscript{5}\(^-\) forms a closed shell cluster and all the Cl atoms are chemically bound to the Al atom. It is the only stable species among all the dianions of AlCl\textsubscript{n} clusters against auto ejection of an electron.

**Stability and Fragmentation:**

The preferred fragmentation channel and corresponding dissociation energies of the neutral, anion and dianion of AlCl\textsubscript{n} clusters are given in Table 11.

We note that AlCl and AlCl\textsubscript{3} clusters are among the most stable neutral clusters. In the mono-anions, AlCl\textsubscript{4}\(^-\) is the most stable species. All dianions studied here are unstable against either auto-ejection of the electron or Cl\(^-\) ion. However, the frequencies associated with the dianion geometries are positive and hence they belong to minima in the potential energy surface, and are metastable.
Table-11: Preferred fragmentation channels and energies of AlClₙ clusters.

<table>
<thead>
<tr>
<th>Neutral</th>
<th>Mono-anion</th>
<th>Di-anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel</td>
<td>ΔE (eV)</td>
<td>Channel</td>
</tr>
<tr>
<td>AlCl → Al + Cl</td>
<td>5.10</td>
<td>AlCl⁻ → AlCl + e⁻</td>
</tr>
<tr>
<td>AlCl₂ → AlCl + Cl</td>
<td>2.94</td>
<td>AlCl₂⁻ → AlCl + Cl⁻</td>
</tr>
<tr>
<td>AlCl₃ → AlCl₂ + Cl</td>
<td>4.80</td>
<td>AlCl₃⁻ → AlCl₃ + e⁻</td>
</tr>
<tr>
<td>AlCl₄ → AlCl₃ + Cl</td>
<td>0.88</td>
<td>AlCl₄⁻ → AlCl₃ + Cl⁻</td>
</tr>
<tr>
<td>AlCl₅ → AlCl₄ + Cl</td>
<td>0.18</td>
<td>AlCl₅⁻ → AlCl₄⁺ + Cl</td>
</tr>
</tbody>
</table>

Electron Affinities (EA) and Vertical Detachment Energies (VDE):

The EAs of the neutral and the VDEs of the anions calculated using different levels of theory are given in Table 12.

Table-12: EA of AlClₙ and VDE of AlClₙ⁻ with 6-311++G(3df) basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>AlCl</th>
<th>AlCl₂</th>
<th>AlCl₃</th>
<th>AlCl₄</th>
<th>AlCl₅</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.19</td>
<td>0.30</td>
<td>2.36</td>
<td>2.91</td>
<td>1.44</td>
</tr>
<tr>
<td>MP2</td>
<td>-0.01</td>
<td>0.13</td>
<td>2.09</td>
<td>2.74</td>
<td>1.22</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>0.07</td>
<td>0.20</td>
<td>2.26</td>
<td>2.89</td>
<td>1.26</td>
</tr>
<tr>
<td>OVGF</td>
<td>0.21</td>
<td>2.91</td>
<td>2.73</td>
<td>7.04</td>
<td>6.95</td>
</tr>
</tbody>
</table>
No experimental values are available for these clusters. Note that the results obtained using DFT-B3LYP agrees well with those obtained from quantum chemical approaches. The EAs are small for AlCl. This is because the 3p\(^1\) electron of Al joins with the 3p\(^5\) shell of Cl making it a closed shell and leaving Al with a filled 3s\(^2\) shell. The electron affinity of AlCl\(_2\) increases sharply, but decreases for AlCl\(_3\). This odd-even effect is again the result of shell closure. AlCl\(_4\) with an electron affinity of 5.88 eV is a superhalogen. Our results agree well with the theoretical value of the VDE of AlCl\(_4^-\) cluster calculated by S Skurski and coworkers [94] using the OVGF method. The EA of AlCl\(_5\) is higher than that of Cl, but smaller than that of AlCl\(_4\) due to even number of electrons.

**Charge Distribution:**

The charge on neutral, anionic and dianionic clusters are displayed in Fig.3. Unlike in the case of NaCl\(_n\) clusters, the charge on Al atom never reaches +3 irrespective of how many Cl atoms are attached to it. However, it increases from (+0.69e) in neutral AlCl to (+1.46e) in AlCl\(_3\). This represents more covalent nature of the bonding. In AlCl\(_4^-\) the extra charge is distributed among all the four Cl atoms and AlCl\(_4\) becomes a superhalogen. The charges on the Cl atoms range from (0.47e) to (0.81e), except in the case of AlCl\(_4\) and AlCl\(_5\) where the quasi-molecular Cl atoms carry very little extra charge.
**4.2.B. Metal-Cyanide MXₙ (M=Na, Mg, Al and X= -CN or –NC) Clusters:**

In the following section, we carried out a systematic study of psuedohalogen clusters. As the name suggest, psuedohalogens mimic the chemistry of halogen atoms and are composed of multi-atom species. They form (i) strong bound univalent radical, (ii) a singly charged anion, and (iii) a pseudohalogen-hydrogen acid, etc [80]

The term pseudohalogen was first introduced by Birkenback in 1925 [81] and further developed in a series of papers [82-84]. The purpose of choosing CN pseudohalogen is due to its high electron affinity (~ 4.05 eV) compared to Cl (~ 3.68 eV), calculated at the same level of theory. In addition, the resulting anions have very large electronic stabilities [85], due to which they are important in chemical synthesis and have versatile applications in the production of polyurethanes [86], a wide range of copolymers and abrasion-resistance polymers [87], semiconductor photoreceptors [88] and solid polymer electrolytes [89].

In the following we will discuss each cluster individually. In every cluster it is found that the bond length between N and C in all these clusters varies in the range (1.15-1.20 Å) which is very similar to the bond length between C-N (~ 1.17 Å) calculated at the same level of theory, which indicates that the species consisting of -NC functional group is bound to the metal atoms.

(i) NaXₙ (X= -NC, n ≤ 3)

In Figure.12, we provide the ground state optimized geometries of neutral, singly and double charged anion of NaXₙ (n ≤ 3) clusters along with bond lengths and NBO charges. All clusters have been studied with both –CN and –NC ligand attached to the metal atom. We found
that although the minimum energy geometries correspond to clusters when N-atom is bound to the metal atom, in most of the cases the cyanide and isocyanide groups are energetically nearly degenerate.

Figure 12: Optimized geometries of neutral (top), anionic (middle) and dianionic (bottom) of Na(NC)$_n$ clusters at B3LYP/6-311++G(3df).

The geometries of CN pseudohalogenes interacting with Na are similar to that of metal chloride clusters of Na except for the neutral NaNC and Na(NC)$_2$ and the anionic Na(NC)$_3$. When the number of ligand exceeds the valence of Na, the CN moieties dimerize. This can be seen in neutral Na(NC)$_2$ and Na(NC)$_3$ and in anionic Na(NC)$_3$. However on addition of extra
electrons to these clusters, the electron deficiency of the clusters can be overcome. Note that the geometry of the dianion of Na(NC)$_3$ is perfectly trigonal planar which is completely different from that of the anion and is dynamically stable. This will be explained later.

The preferred channel for fragmentation and the corresponding energies are given in Table 13.

**Table-13**: Preferred fragmentation channels and energies of Na(NC)$_n$ clusters.

<table>
<thead>
<tr>
<th>Channel</th>
<th>ΔE (eV)</th>
<th>Channel</th>
<th>ΔE (eV)</th>
<th>Channel</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNC → Na + NC</td>
<td>4.32</td>
<td>Na(NC)$_2^-$ → NaNC + e$^-$</td>
<td>0.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(NC)$_2$ → Na + (NC)$_2$</td>
<td>0.43</td>
<td>Na(NC)$_3^-$ → NaNC + (NC)$^-$</td>
<td>2.26</td>
<td>Na(NC)$_2^-$ → Na(NC)$_2^-$ + e$^-$</td>
<td>-1.94</td>
</tr>
<tr>
<td>Na(NC)$_3$ → NaNC + (NC)$_2$</td>
<td>0.33</td>
<td>Na(NC)$_3^-$ → Na(NC)$^-$ + (NC)$_2$</td>
<td>1.56</td>
<td>Na(NC)$_3^-$ → Na(NC)$_3^-$ + e$^-$</td>
<td>-1.44 0.12</td>
</tr>
</tbody>
</table>

Among all the neutral clusters, NaNC is the most stable species due to its high fragmentation energy. While Na(NC)$_2$ and Na(NC)$_3$ prefer to dissociate by producing (NC)$_2$ dimer. In the anionic clusters, Na(NC)$_2^-$ is the most stable species among the anions. The dianion of Na(NC)$_2$ and Na(NC)$_3$ are metastable due to their positive frequencies. It can be noted that the fragmentation product of the dianions of NaCl$_n$ and Na(NC)$_2$ are similar, but its fragmentation energies are -1.88 eV and -1.44 eV respectively, which indicates that Na(NC)$_3$ dianion is more stable than NaCl$_3$ dianion.

Our results for the electron affinities (EA) of neutral and vertical detachment energy (VDE) of anion for Na(NC)$_n$ clusters are given in Table 14.
Table 14: EA of Na(NC)$_n$ and VDE of Na(NC)$_n^-$ with 6-311++G(3df) basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>NaNC</th>
<th>Na(NC)$_2$</th>
<th>Na(NC)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA(eV)</td>
<td>VDE(eV)</td>
<td>EA(eV)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.90</td>
<td>1.06</td>
<td>3.89</td>
</tr>
<tr>
<td>OVGF</td>
<td>0.88</td>
<td>5.86</td>
<td>2.20</td>
</tr>
</tbody>
</table>

The data show that both EA and VDE rise sharply at $n=2$ and drop at $n=3$. At $n=2$, the cluster is a superhalogen. Basically in superhalogens, the charge no longer goes to the metal atom. Instead, it is transferred to the electronegative ligand and the charges on the metal atom in both neutral and anion clusters are nearly same. This is not the case for neutral Na(NC)$_2$. This is due to the small electron affinity of NCCN dimer (~ 0.53 eV calculated at the same level of theory). For $n=3$ the geometries of both the neutral and the anion are quite similar (as shown in Fig.12). Due to the dimerization of CN there is a drop in the EA at $n=3$ and hence it does not behave as a superhalogen. (Its EA could have been high if the –NC ligands are not allowed to dimerize. But those clusters do not belong to a genuine minimum as is evidenced by an imaginary frequency). In case of dianion of Na(NC)$_2$, the negative charge is mostly transferred to Na in order to neutralize its positive charge while in the dianion of Na(NC)$_3$, the extra charges are distributed equally among all the ligands resulting in a perfect trigonal planar geometry. Due to this reason, it is more stable than that of its corresponding anion.
(i) $\text{MgX}_n$ ($X=\text{-NC}$, $n \leq 4$)

In Figure.13, we provide the ground state optimized geometries of neutral, singly charged and double charged anion of $\text{Mg(NC)}_n$ ($n \leq 4$) along with the bond lengths and NBO charges.

In these clusters, the N atom of CN preferentially binds to the central atom Mg due to its high electron negativity compared to that of C atom.
In MgNC cluster, both the geometries of neutral and anion are similar and the bonding is ionic in nature. As Mg can afford 2 electrons, the neutral Mg(NC)₂ is linear whereas both the anions and dianions are bent due to the lone pair of electron as per VSEPR theory. Whereas in case of Mg(NC)₃, the neutral geometry is very different than that of its anionic and dianionic counterpart. In the neutral cluster, due to electron deficiency, the two –NC ligands dimerize, whereas in Mg(NC)₃⁻, the added electron along with the two valence electrons of Mg are enough to fill the shells of the three –NC ligands. Consequently, the geometry of Mg(NC)₃⁻ is a perfect trigonal planar. The extra electron resides on the Mg atom to neutralize its positive charge. On the other hand, as Mg atom can afford maximum 2 electrons, the two –NC clusters dimerize in both neutral and anionic clusters of Mg(NC)₄. This is because the binding energy of (NC)₂ is
very high (~ 6.30 eV). In the dianion, all the –NC ligands are bound to Mg forming a perfect tetrahedral geometry, due to its closed shell structure.

The dianions of Mg(NC)\textsubscript{n} for \(n \geq 3\) are thermodynamically unstable since the Coulomb repulsion between the extra electrons dominate the binding energies of the clusters. The preferred channel for fragmentation and the corresponding energies are given in Table -15.

**Table-15**: Preferred fragmentation channels and energies of Mg(NC)\textsubscript{n} clusters.

<table>
<thead>
<tr>
<th>Neutral Channel</th>
<th>(\Delta E) (eV)</th>
<th>Mono-anion Channel</th>
<th>(\Delta E) (eV)</th>
<th>Di-anion Channel</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgNC→ Mg + NC</td>
<td>3.39</td>
<td>Mg(NC)\textsuperscript{-}→ Mg + (NC)\textsuperscript{-}</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>Mg(NC)\textsubscript{2}→ Mg + (NC)\textsubscript{2}</td>
<td>1.91</td>
<td>Mg(NC)\textsuperscript{2-}→ MgNC + (NC)\textsuperscript{-}</td>
<td>2.41</td>
<td>Mg(NC)\textsuperscript{2-}→ Mg(NC)\textsuperscript{3+} + e\textsuperscript{-}</td>
</tr>
<tr>
<td>Mg(NC)\textsubscript{3}→ MgNC + (NC)\textsubscript{2}</td>
<td>0.74</td>
<td>Mg(NC)\textsuperscript{3-}→ Mg(NC)\textsuperscript{2+} + (NC)\textsuperscript{-}</td>
<td>3.46</td>
<td>Mg(NC)\textsuperscript{3-}→ Mg(NC)\textsuperscript{3+} + e\textsuperscript{-}</td>
</tr>
<tr>
<td>Mg(NC)\textsubscript{4}→ Mg(NC)\textsuperscript{2+}(NC)\textsubscript{2}</td>
<td>0.70</td>
<td>Mg(NC)\textsuperscript{4-}→ Mg(NC)\textsuperscript{2+} + (NC)\textsuperscript{2}</td>
<td>2.00</td>
<td>Mg(NC)\textsuperscript{4-}→ Mg(NC)\textsuperscript{3+} + (NC)\textsuperscript{-} + e\textsuperscript{-}</td>
</tr>
</tbody>
</table>

Among all the neutrals, MgNC is the most stable species against fragmentation. At first, this may seem surprising since Mg is divalent. However, CN psuedohalogens gain considerable binding energy after dimerization (~ 6.30 eV). For the same reason all other neutral clusters prefer to dissociate by ejecting (NC)\textsubscript{2}. Among the anions, Mg(NC)\textsubscript{3} is the most stable species. All anions except for \(n = 4\) prefer fragmentation by ejecting a NC ion, whereas Mg(NC)\textsubscript{4} anion
prefers to dissociate into Mg(NC)$_2^-$ and (NC)$_2$. The negative charge resides on Mg(NC)$_2$ due to the small EA of (NC)$_2$ ligand. The dianion of Mg(NC)$_2$ and Mg(NC)$_3$ prefer to auto eject an electron and are highly unstable due to their large fragmentation energies. Whereas the dianion of Mg(NC)$_4$ is stable against auto ejection of an electron. This process liberates +0.93 eV of energy. However, it is found to be metastable against dissociation into Mg(NC)$_3^-$ and (NC)$^-$ and is thermodynamically more stable than that of its anionic counterpart.

The electron affinities (EA) of neutral and vertical detachment energy (VDE) of anion for Mg(NC)$_n$ clusters are summarized in Table 16.

Table 16: EA of Mg(NC)$_n$ and VDE of Mg(NC)$_n^-$ with 6-311++G(3df) basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>MgNC</th>
<th>Mg(NC)$_2$</th>
<th>Mg(NC)$_3$</th>
<th>Mg(NC)$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA(eV)</td>
<td>VDE(eV)</td>
<td>EA(eV)</td>
<td>VDE(eV)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>1.76</td>
<td>1.91</td>
<td>1.64</td>
<td>2.44</td>
</tr>
<tr>
<td>OVGF</td>
<td>1.90</td>
<td>2.43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We found that there is a sudden rise of EA at $n = 3$ and hence Mg(NC)$_3$ is a superhalogen. There is a quite large energy difference in between EA and VDE values for $n = 3$ which is due to significant changes in the geometries of the neutral and anion. On addition of electron to the neutral clusters, most of the charges are transferred to Mg until $n = 2$. Beyond this it is distributed over the pusedohalogenes. Due to this reason, the charges on the Mg atom, in both neutral and anion for $n \geq 3$ are found to be similar (as shown in Fig.13). It can also be noted that
the charges on Mg for \( n = 4 \) in neutral, anionic and dianionic clusters are similar. Whereas the EA as well as VDE drops in both neutral and anion, the –NC ligand dimerizes.

(i) \( \text{AlX}_n \) (\( X = \text{-NC}, \ n \leq 5 \))

In Figure 14, we provide the ground state optimized geometries of neutral, singly charged and doubly charged anion of \( \text{AlX}_n \) (where \( n \leq 5 \)) along with the bond lengths and NBO charges.
These pseudohalogen clusters are very different as compared to all the Na and Mg clusters. In AlX cluster, the energies of the clusters are nearly degenerate (around 0.3 eV in neutral and 0.03 eV in anion) whether C or N atom is attached bound to the metal atom. The geometries are given based on the minimum energy structure. In AlX₂, due to the presence of lone pair of electron, the geometries of neutral, anion and dianion are bent in shape, while in the dianion, C atom is bound to Al rather than N. On the other hand, in AlX₃, the neutral has a very stable geometry as the 3 valence electrons of Al are shared by the ligands giving it a perfectly trigonal geometry. When an extra electron is added, C atom preferentially binds to Al in both the anion and dianion. As the Al-atom can at most provide 3 electrons for bonding, CN prefers to dimerize when the number of ligands exceed the maximal valence of Al. This can be seen from
the geometries of neutral AlXₙ cluster. When the electron deficiency is fulfilled by adding an electron, the anion assumes tetrahedral symmetry and Al(CN)₄⁻ is found to be most stable species. In the dianion, the C-atom is preferably binds to Al. For n=5, the neutral and anion have very similar geometry, while the dianion has a trigonal bipyramidal geometry. It is found to be the most stable species among all the dianions. Thus, we conclude that in all the neutral clusters N atom is preferably binds to Al due to its higher electronegativity compared to C. In the dianions, however, C atom binds to Al due to the availability of extra charge. The anions show different bonding mechanism than the neutral.

The preferred channel for fragmentation and the corresponding energies are given in Table 17.

<table>
<thead>
<tr>
<th>Neutral</th>
<th>Mono-anion</th>
<th>Di-anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlNC→ Al + NC</td>
<td>5.25</td>
<td>AlCN→ AlCN + e⁻</td>
</tr>
<tr>
<td>Al(NC)₂ → Al + (NC)₂</td>
<td>2.25</td>
<td>Al(NC)₂⁻ → AlNC + (NC)⁻</td>
</tr>
<tr>
<td>Al(NC)₃ → AlNC + (NC)₂</td>
<td>2.23</td>
<td>Al(CN)₃⁻ → Al(CN)₃ + e⁻</td>
</tr>
<tr>
<td>Al(NC)₄ → Al(NC)₂ + (NC)₂</td>
<td>0.38</td>
<td>Al(NC)₄⁻ → Al(NC)₃ + (NC)⁻</td>
</tr>
<tr>
<td>Al(NC)₅ → Al(NC)₃ + (NC)₂</td>
<td>-0.07</td>
<td>Al(NC)₅⁻ → Al(NC)₄ + (NC)⁻</td>
</tr>
<tr>
<td>Al(NC)₅ → Al(CN)₅⁻ + e⁻</td>
<td>1.55</td>
<td>Al(CN)₅⁻ + e⁻</td>
</tr>
</tbody>
</table>

Table-17: Preferred fragmentation channels and energies of AlXₙ (X= -CN or –NC) clusters.
Among all the neutral clusters, AlNC is the most stable species having high fragmentation energy. All other neutral clusters prefer to dissociate by ejecting \((\text{NC})_2\). In the case of anions, \(\text{Al(NC)}_4^-\) is the most stable species due its superhalogen behavior. This will be explained shortly. While \(\text{AlCN}^-\) and \(\text{Al(CN)}_3^-\) auto eject an electron, \(\text{Al(NC)}_5^-\) prefers to fragment to \(\text{Al(NC)}_3^-\) and \((\text{NC})_2^-\). On the other hand, the dianionic clusters for \(n \leq 4\) auto eject an electron while, \(\text{Al(NC)}_5^{2-}\) fragments into \(\text{Al(NC)}_4^-\) and \((\text{NC})^{-}\), since \(\text{Al(NC)}_4^-\) is the most stable species among the anions. The dianion of \(\text{Al(NC)}_5\) is found to be thermodynamically stable as compared to its anionic counterpart.

The EA and VDE of \(\text{AlX}_n\) clusters are mentioned in Table 18.

**Table 18:** EA of \(\text{AlX}_n\) (X= -CN or –NC) and VDE of \(\text{AlX}_n^-\) with 6-311++G(3df) basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>(\text{AlX})</th>
<th>(\text{AlX}_2)</th>
<th>(\text{AlX}_3)</th>
<th>(\text{AlX}_4)</th>
<th>(\text{AlX}_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
<td>VDE (eV)</td>
<td>EA (eV)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.57</td>
<td>0.86</td>
<td>2.81</td>
<td>3.35</td>
<td>2.38</td>
</tr>
<tr>
<td>OVGF</td>
<td>0.73</td>
<td>3.51</td>
<td>3.51</td>
<td>3.51</td>
<td>7.96</td>
</tr>
</tbody>
</table>

Due to the structural similarity between the neutrals and anions, there is a small energy difference between the EA and VDE. The charges are transferred to the Al atom till its valence is consumed i.e till \(n = 3\). But as the number of ligands exceeds the valence of Al, the charges no longer reside on the Al atom and are distributed over the CN ligands. Consequently, the EA increases abruptly at \(n = 4\). This is similar to what was seen in \(\text{AlCl}_n\) clusters. The charge on Al
in neutral Al(CN)$_4$ is (+2.04e) whereas in the anion it is (+1.97e). In Al(CN)$_5$ clusters, due to dimerization of CN in both the neutral and anion, the value of EA drops. However, its dianion has a closed shell structure. Its energy is lower by ~ 2.7 eV from that of its anion, thus making it stable.
Chapter 5
Conclusion

A systematic theoretical study of the stability and spectroscopic properties of $d^1$ transition metals (Sc, Y and La) interacting with Cl atoms and simple metal atoms (Na, Mg, Al) interacting with Cl as well as CN moieties was carried out using gradient corrected density functional theory. The objective of my study was to find ways in which electronegative species with electron affinities much higher than those of Cl can be designed and synthesized. Our results led to the following conclusions:

1. The $d^1$ transition metals (Sc, Y and La) behave as superhalogens when the number of Cl atoms exceeds the maximal valence of these atoms, namely 3.

2. For simple metal atoms (Na, Mg, Al), superhalogen behavior is also observed when the number of Cl atoms exceed the normal valence of Na, Mg, and Al, namely 1, 2, and 3.

3. CN moieties which are known as pseudohalogens can also form the building blocks of a new class of superhalogens. However, unlike halogens, they provide considerable challenge in designing superhalogens. First, CN can bind to a metal atom as cyanide (i.e. CN) or as an isocyanide (i.e. NC). Second, cyanogen which is a $(CN)_2$ dimer has very large binding energy compared to that of $Cl_2$. Consequently, as the number of CN moieties bound to a metal atom increases, the most stable configuration may not be the one where the CN moieties are bound individually, but rather structures where CN moieties dimerize and then bind to the metal atom.
In this case, they may not form superhalogens. This is what our systematic studies of CN moieties bound to Na, Mg, and Al reveal. For Na, up to two CN moieties can be bound individually and Na(CN)$_2$ is a superhalogen. Beyond this, CN moieties dimerize and the electron affinity of Na(CN)$_3$ drops below that of Cl. Similar systematic is seen for Mg and Al except the number of CN moieties bound to these metal atoms that exhibit superhalogen behavior is 3 for Mg and 4 for Al.

The stability and electronic properties of the dianions were also studied in the gas phase. The results show that while some the dianions of the clusters studied here are stable against auto ejection of electron but they are all metastable against fragmentation. However, when compared between the halogens and pseudohalogens bound to a metal atom, the dianions composed of pseudohalogens are more stable than those composed of halogens. This is because the second electron in a dianion containing CN moieties finds a larger phase space to delocalize as opposed to those containing Cl. The results compared well with available experimental and theoretical data. The studies reveal that there are a number of ways where new superhalogens can be created and these can be useful in synthesizing new salts and oxidizing agents.
References:


