Endohedrally Doped II-VI Hollow Nanoclusters

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Chapter 1

Introduction

1.1 Nanoscience and Nanotechnology

There are different ways of approaching nanoscience and nanotechnology. They may be seen as the science and technology arising from the study and manipulation of matter at the atomic and molecular scale. They also can be understood as the science and technology of designing, producing, and using structures and devices having one or more dimensions no larger than 100 nm. The properties of these new materials differ significantly from those of their bulk counterparts, due to their different structures and strong quantum confinement [1]. Another important feature is that, being small objects, nanostructured materials have a very high surface/volume ratio. Thus, the surface energy contribution is not negligible and usually strongly size dependent. Since the properties of nanomaterials vary with the size of the nanoparticle, materials with modified properties can, in principle, be obtained. The development of nanoscience and nanotechnology have led to the discovery of new phenomena and applications [2, 3, 4, 5].

Nevertheless, regardless the current success of nanotechnology, it was claimed to be a not viable proposition by the theoreticians in the first half of the last century. Erwin Schrödinger concluded that “atoms must no longer be regarded as identifiable individuals” [6], and Werner Heisenberg, who stated the indetermination principle, thought that “atoms form a world of potentialities of possibilities rather than one of things or facts” [7]. That is, it was thought that atoms were not entities with individual nature. However, nowadays we know that atoms may be manipulated individually [8]. As it was pointed out by the Nobel Prize winner Richard Feynmann [9, 10], “There is plenty of room at the bottom”. Indeed, recent spectacular growth of nanotechnology supports the predictions of some of the pioneers in the field, such as Arthur von Hippel [11] and K. Eric Drexler [12, 13].

As mentioned above, the purpose of the nanoscience and nanotechnology is to understand, control and manipulate objects of a few nanometers in size. This field nowadays extends through physics, chemistry, medicine and engineering, and addresses a huge number of important issues, ranging from basic science to a variety of technological applications. There are many important developments in nanotechnology, concerning nanoelectronics, nanowires, nanomechanics, nanobiomedicine and new and revolutionary techniques have been developed, such as the atomic force microscope (AFM), the scanning tunneling microscope (STM), and others. Nanoelectronics and nanowires have provided novel broad possibilities for the development of smaller and faster chips and other machines. As an example, transistors as small as 20 nm were developed at the French Atomic Energy Commission’s Electronic, Technological and Instrumentation Laboratory (LETI) in Grenoble [14]. Semiconductor nanoparticles have a broad variety of applications in nanobiotechnology [2, 3] due to their optical properties. For instance, nanomaterial-based optical sensors may be used for the continuous, real-time monitoring of diverse analytes including drugs, proteins in general and antibodies in particular, DNA and viruses [15] have been developed. In addition to this, semiconductor nanocrystals have been synthesized and evaluated for the study and detection subcellular processes. The ability to make nanomaterials water soluble and to bind them to biomolecules to facilitate selective binding of these nanoscale fluorescent structures to specific subcellular structures has led to promising applications [16]. Future work focus not only in the improvement of the mentioned above imaging, labelling and sensing applications, but also in the development of specific nanomaterials with therapeutic properties. In this vein, magnetic nanoparticles have been already employed for the hyperthermic tumoral regression [17].

Among nanostructured materials, nanoclusters may be considered as the smallest nanostructures. Nanoclusters are aggregates of atoms or molecules of nanometric size, containing a number of constituent particles, ranging from
∼ 10 to 10^6 [18]. They may be neutral or charged. They may be held together by very different kinds of forces: strong attraction between oppositely charged ions (e.g. in NaCl clusters), van der Waals attraction (as in He and Ar clusters), covalent chemical bond (Si clusters) or a metallic bond (as in Na and Cu clusters). One of the best known ‘new’ clusters or nanostructures are the so called fullerenes discovered in 1985 by R. F. Curl, R. E. Smalley and H. W. Kroto [19]. They performed an experiment to simulate the formation of long-chain carbon molecules in interstellar space and circumstellar shells. In order to do so, they evaporated graphite surfaces by laser ablation, and analyzed the masses of the resulting structures in a mass spectrometer. They found a very stable C_{60} structure, and based on Richard Buckminster Fuller’s work, they proposed C_{60} to be hollow structures built by 12 pentagons and 20 hexagons, where all atoms are located at the surface of the structure (see 1.1), and baptized this molecule as fullerene. Later on, other carbon fullerenes of different sizes, and other carbon structures like carbon nanotubes were synthesized.

![Figure 1.1: The fullerene C_{60}, discovered in 1985 by Kroto and co-workers.](image)

C_{60} molecules interact with each other to form the so-called fullerites [20, 21]. Fullerites are molecular solids where each C_{60} is linked to others by van der Waals interactions. These are weak interactions, and, therefore, the distance between fullerenes is much larger than in C-C covalent bonds, 3 Å vs 1.4 Å, respectively. Hence, one may see these fullerites as solid structures built by smaller building blocks, i.e., C_{60} molecules are the building blocks that are assembled to form fullerites. Fullerites are a new solid phase of carbon, with properties different to those of other carbon solid phases, such as diamond and graphite.

The properties of fullerites, and also those of their basic constituents, may be altered by doping. In general, as their bulk counterparts, nanoclusters can also be doped in order to modify their properties at will. Concretely, in hollow structures such as fullerenes, there are three different ways of doping. i) The replacement of one or more atoms by others, which leads to the so-called heterofullerenes. The first one was produced by Smalley’s group in 1991 [22]. ii) Exohedral doping, where atoms are placed outside the cage. For instance, by doping with alkali metals, fullerites that show superconductive properties have been synthesized [23, 24, 25]. iii) Endohedral doping, where atoms or molecules are trapped inside the nanocluster. Endohedral fullerenes [26, 27, 28, 29, 30, 31] were the first endohedrally doped nanoparticles described in the literature.

Other fullerene-like cage hollow structures were later studied both theoretically and experimentally. Metallic clusters of gold, tin and lead, or semiconducting clusters of silicon, germanium, III-V and II-VI materials have been widely studied in the literature. Hollow structures of materials such as Mg_{12}O_{12}, Zn_{12}O_{12}, B_{12}N_{12} and Zn_{12}S_{12} have shown the ability of building up new solid structures without substantially alter their nature [32, 33, 34, 35], although the interaction between the basic constituents is stronger than that in fullerites. Conversely, these hollow cages are also able to trap atoms inside, leading to new endohedral structures of gold [36], tin [37, 38], lead [39, 40] and germanium [41, 42] have been reported recently.

Among all these structures, the ones bases on III-VI semiconducting nanoclusters are of special interest for this work.
1.2 II-VI Semiconducting Nanoclusters

Interest in II-VI compound semiconductors has grown spectacularly in recent years due to their paramount technological potential. Their special semiconductor properties make these compounds suitable for applications such as photovoltaic solar cells, optical sensitizers, photocatalysts, quantum devices or nanobiomedicine.

Concretely, hollow nanoclusters of these elements have been widely studied in the literature both theoretically and experimentally[43, 44, 45, 46, 47, 48, 49, 50, 51]. However, studies of the properties of endohedral compounds made of these hollow nanoclusters are scarce [52, 53, 54, 35]. In ref [53] Matxain et. al. characterized (X@Zn$_i$S$_4$)$_{q=0,\pm 1}$ compounds, with X being alkali metals or halogens. In this work, it was observed that alkali metals transferred an electron to the cage, while halogen atoms withdrew an electron from the cage leading to charged ions inside the cage. Moreover, encapsulation of halogen atoms resulted in endohedral nanoclusters with enhanced electron affinity relative to the guest halogen atom (4.5 eV compared to 3.5 eV). These nanoclusters ought, therefore, to be considered as superhalogens in the same vein as the Al@Al$_{12}$ cluster for which recent research has confirmed its predicted [55] high electron affinity (EA) of 3.20 eV as well as its ability to ionize spontaneously into (Al@Al$_{12}$)$^+$ even in the gas phase [56]. The Cl and Br endohedral nanoclusters studied in ref [53] have electron affinities substantially larger than Al@Al$_{12}$. Hence, they are expected to have even a stronger superhalogen character. Furthermore, the electron affinities of the halogen endohedral nanoclusters and the ionization energies of the alkali endohedral nanoclusters of Zn$_i$S$_4$ are rather similar rendering them good candidates to form cluster-assembled materials under mild conditions since large ionization energy/electron affinity (IE/EA) differences would yield substantial heat release during assembling that might destroy the assembled material as it is formed.

Such solids, based on X@Zn$_i$S$_{12}$ structures, have been recently theoretically characterized[35]. They have face-centered cubic (fcc) crystal lattice structure, and interestingly, the band gap is decreased from 3.66 eV found in wurtzite to 2.2 eV in the bare solid and even further, to 1.8 eV, in the doped solids. These solids may be seen as semiconducting materials with smaller band gaps than the solids found in nature, namely, wurtzite and zincblende. Ab initio quantum dynamics calculations further confirmed the thermal stability of the calculated structures. Moreover, the predicted metastability of the fcc structures was supported by the predicted energy barriers toward collapsing into wurtzite, which were found to be larger than 6 eV.

As mentioned in the subsection 1.1, doping these nanoclusters with first-row transition-metals can allow the design of nanoclusters that would combine the appropriate optical properties and magnetic properties to be used in nanomedicine not only in the improvement of the cited imaging, labelling and sensing applications, but also in the development of specific nanomaterials with therapeutic properties. Matxain et. al. [54] characterized the first-row TM@Zn$_i$S$_4$ endohedral compounds, for i=12 and 16. They observe that these clusters act as a host protecting the spins of the trapped dopant transition-metal atom, giving rise to the atomic magnetism. It is well-known that the local properties of a dopant transition-metal atom strongly depend on their vicinal environment. For these particular endohedral nanoclusters, the interaction between the trapped dopant transition-metal atoms and the Zn$_i$S$_4$ hosts is weak, allowing them to behave atomic-like and keep their spin states unaltered. Moreover, preliminary quantum molecular dynamics calculations carried out on these endohedrally-doped nanoclusters were very supportive of the thermal stability of the characterized structures. Those with optimum geometries having the trapped transition atom at the center of mass of the nanocluster, presented a deep enough confinement well as to retain the dopant atom around its equilibrium position.

In view of these results, the design of new building blocks of endohedrally doped II-VI materials appears to be very promising. In this work, we want to push further with the design of new building blocks based on these materials. Concretely, we present here in Chapter 2 the characterization of endohedrally doped X@Cd$_i$S$_4$ materials with X=Na, K, Cl and Br, and in Chapter 3 we focus on the thermal stability of endohedrally doped TM@Zn$_i$S$_4$ clusters, TM being first-row transition-metals.

The potential technological applications of these new designed materials in a large variety of fields, like solar cells, heterogeneous catalysis, molecular transport, optical sensors, nanobiomedicine and so on, makes the searching of new building blocks for such materials worthwhile. Within this context, the theoretical investigations reported herein could help, or guide, experimentalists toward such a goal.

In order to perform all this work we make use of the powerful quantum chemistry methods and programs. Let us remind briefly the methods used throughout this work.

...
1.3 Methods

The theory of quantum mechanics, developed in the twenties of the last century [57, 58, 59], changed the viewpoint of physicist over the microscopic world. Before it, all attempts that tried to explain the stability of atoms failed. Bohr explained the stability of the simplest atom, hydrogen, by fixing that electrons were in stationery orbits around the nucleus. An electron needs a quantum of energy in order to move from one stationary orbit to another. In other words, the energy is quantized, and not continuous. In quantum mechanics this statement arises from the theory.

At the beginning the theory was mainly the playground of physicists, but it soon found applications in chemistry, creating what is called quantum chemistry. Over the years quantum chemistry has become a very important tool for chemists in order to calculate, understand and predict molecular properties.

1.3.1 Born-Oppenheimer Approximation

In principle, all the information of a molecule may be obtained from its wave function. In order to know it, we ‘only’ have to solve the Schrödinger equation (here in its time independent form):

\[ \hat{H}\Psi = E\Psi \] (1.1)

where the Hamiltonian \( \hat{H} \) contains the kinetic energy terms of the electrons and the nuclei, the interactions between the nuclei, the electrons, and the nuclei-electrons.

Eq. (1.1) can be written also as follows:

\[ (\hat{T}_N + \hat{V}_{NN} + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne})\Psi_{tot}(\{R_\alpha\}, \{r_i\}) = E_{tot}\Psi_{tot}(\{R_\alpha\}, \{r_i\}) \] (1.2)

Since nuclei are much heavier than electrons, on the time-scale of electron motion nuclei can be considered as stationary objects, fixed at certain positions in space. Based on this idea, the Born-Oppenheimer approximation [60] decouples nuclear and electronic motions, where the nuclei move into the potential created by the electrons and the nuclei. Thus, a simplified Schrödinger equation which does not treat nuclear motion is solved for electrons only. The so-obtained electronic wave function and energy depends on the nuclear positions as on the external parameters.

\[ \hat{H}_e\Psi_e = E_e\Psi_e \] (1.3)

\[ (\hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne} + V_{NN})\Psi_e(\{r_i\}; \{R_\alpha\}) = E_e\{R_\alpha\}\Psi_e(\{r_i\}; \{R_\alpha\}) \] (1.4)

In the Born–Oppenheimer picture, the nuclei move on a potential energy surface (PES) which is a solution to the electronic Schrödinger equation. Nuclear motion is treated in a separate Schrödinger equation, which employs the electronic energy obtained as a potential energy function:

\[ (\hat{T}_N + E_e)\Psi_N(\{R_\alpha\}) = E_{tot}\Psi_N(\{R_\alpha\}) \] (1.5)

Unfortunately, Eq. (1.4) can only be cast into a closed analytical form for one electron systems, i.e., the hydrogen atom. Therefore, approximate methods have been developed:

1. Wave-function based methods: variational (configurational interaction, direct expansion of \( \Psi \) in some suitable basis) and many-body perturbation theory.

2. Density functional theory (DFT).

3. Quantum Monte-Carlo.

It is beyond the scope of this section to develop a full description of these methods, so refer the interested reader to the literature devoted to these topics. See for example [61, 62, 63, 64, 65].

Wave-function based methods were the earliest developed ones. Two of these methods have been widely used throughout the years, the Valence Bond (VB) method and the Molecular Orbital (MO) method. The VB method was formulated in 1927 by Heitler and London [66]. The MO method was developed a bit later by Hund [67], Mulliken [68] and others. This theory became the most popular due to its quantitative power, which come from the use of orthogonal orbitals, in opposition to the VB theory which plays with non-orthogonal orbitals.

One of the first developed molecular orbital method was the Hartree-Fock method [69, 70], where the wave function is an antisymmetricized product of one-electron orbitals. The electrons are treated as moving in a mean field due to the nucleus and the remaining electrons. The main drawback of this method is that correlation of electrons with opposite spins is neglected. There are different ways in which this correlation can be taken into account. One of them are the perturbational methods such as Moller-Plesset [71] theory (denoted as MPn, where n is the order of the perturbation). In these methods the electron correlation is treated as a perturbation of the HF problem. In the Configuration-Interaction (CI) method [72, 73] the wave function is expressed as a linear combination of configurations to provide a better variational solution to the exact many-electron wave function. There are other more sophisticated methods such as Coupled Cluster [74, 75, 76], Multi-Reference Configuration Interaction (MR-CI) or Complete-Active-Space (CAS) methods [77, 78], which are very useful tools to study electronic properties of both ground and excited states.

Quantum Monte Carlo methods have been shown to be very powerful in the calculation of the electronic properties of ground states [79, 80, 81] or excited states [82, 83] of many systems. They have not been used in this work, and we refer the reader to more detailed papers [65, 84].

Density matrix based methods has emerged in recent years [85, 86, 87, 88, 89] as an alternative method to conventional ab initio approaches and density functional theory (DFT) for considering the electronic correlation. A major advantage of the NOF method is that the kinetic energy and the exchange energy are explicitly defined using the one-particle reduced density matrix (1-RDM) and do not require the construction of a functional. The unknown functional in a 1-RDM theory only needs to incorporate electron correlation.

Mainly all the work presented in this thesis has been carried out within the density-functional framework. In the following subsection these methods are described in more detail.

1.3.2 Density Functional Theory

The Density Functional Theory formalism replaces the N-electron wave function by a much simpler electron density $\rho(\vec{r})$ which is a function of the three spatial variables. Then, the electronic state, the energy and all the electronic properties of a system can be described in terms of this $\rho(\vec{r})$ [63, 64].

Hohenberg and Kohn [90] proved that the electronic properties of a system with a nondegenerate ground state are uniquely determined by the electron density $\rho(\vec{r})$. Hence, the ground-state energy $E_0$ is a functional of $\rho(\vec{r})$, and therefore, if we know the ground-state electron density it is possible to calculate all the ground-state electronic properties from $\rho$ once we have been able to set all the appropriate functional dependencies. They also established an energy variational principle for the energy functional, analogous to the variational principle for wave functions. Thus, knowing the exact form of the $E[\rho]$ functional, we can search for the ground state density (as it is the case for the wave function). However, since the exact form of the functional is unknown, Kohn and Sham [91] developed an indirect approach to this functional, the Kohn-Sham method, and DFT turned into a practical tool for rigorous calculations. They showed that the exact ground-state purely electronic energy $E_0$ of an N-electron molecule with ground-state electron probability density $\rho$ is given by:

$$E^{KS} = -\frac{1}{2} \sum_{i=1}^{N} <\psi_i(1)|\nabla_1^2|\psi_i(1)> + \int v(r)\rho(1)d\vec{r}_1 +$$

$$+ \frac{1}{2} \int \int \frac{\rho(1)\rho(2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho]$$

where $v(r) = -\sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}}$ is the external potential due to the nuclei, $\psi_i$ are the Kohn-Sham orbitals, and the $E_{xc}[\rho]$ is the exchange-correlation energy.
In the Kohn-Sham procedure, the exact ground state $\rho$ can be found from the Kohn-Sham orbitals according to,

$$\rho = \sum_{i=1}^{N} |\psi_i|^2$$  \hspace{1cm} (1.7)

and the Kohn-Sham orbitals are found by solving the one-electron equations

$$\hat{F}_{KS}(1)\psi_i(1) = \varepsilon_i\psi_i(1)$$ \hspace{1cm} (1.8)

being the Kohn-Sham operator $\hat{F}_{KS}$

$$\hat{F}_{KS} = -\frac{1}{2}\nabla_i^2 + v(1) + \sum_{j=1}^{n} J_j(1) + V_{xc}(1)$$ \hspace{1cm} (1.9)

where $J$ is the Coulomb operator, and $V_{xc}$ is called the exchange-correlation potential. $\hat{F}_{KS}$ is like the Fock operator in HF equations, except that the exchange operators are replaced by $V_{xc}$, which handles the effects of both the exchange and electron correlation.

These equations are iteratively solved. Starting from a guess density, $\hat{F}_{KS}$ is built and the set of equations, Eq. (1.8), solved. The solution then is transferred to $\hat{F}_{KS}$, in order to build a new $\hat{F}_{KS}$. This process is repeated until convergence is achieved.

The physical significance of the Kohn-Sham orbitals is still under debate. Some authors claim that they do not have any significance other than in allowing the exact $\rho$ to be calculated from Eq. (1.7). Likewise, the Kohn-Sham orbital energies should not be confused with molecular orbital energies. However, others based on the fact that the exact Kohn-Sham orbital energy for the HOMO is just the negative of ionization potential [92, 93], and due to the fact that the set of Kohn-Sham equations remind us, as in the HF case, the independent particle model, they associate to the Kohn-Sham orbitals a similar physical significance and legitimacy than to the HF canonical orbitals. In recent publications it is shown the results obtained from molecular orbitals obtained from DFT are quite similar to the molecular orbitals from standard MO-LCAO methods, and that one can extract a lot of useful information about molecular systems from analysis of their MOs even if the density functional methods are used [92, 94].

However, there is one more problem: the exchange-correlation functional $E_{xc}[\rho]$ and hence the exchange-correlation potential $v_{xc}[\rho; \vec{r}]$ is not known except for the case of the uniform electron gas. Fortunately, approximate functionals have been developed. One simple approximation is the so called local density approximation (LDA). The idea is to consider each volume element with local density $\rho(\vec{r})$ to be a homogeneous electron gas. From this point of view the approximation would be expected to be accurate if the density varies slowly in space. Then, $E_{xc}[\rho]$ is given by

$$E^{LDA}_{xc}[\rho] = \int \rho(\vec{r})\varepsilon_{xc}(\rho)d\vec{r}$$ \hspace{1cm} (1.10)

where $\varepsilon_{xc}(\rho)$ is the exchange plus correlation energy per electron in a homogeneous electron gas with electron density $\rho$. An accurate expression for $\varepsilon_{xc}(\rho)$ was found by Vosko, Wilk and Nusair [95]. Application of this expression leads to the local density approximation (LDA), or local spin density approximation (LSDA) [96], if one uses different orbitals and densities $\rho^\alpha$ and $\rho^\beta$ for electrons with different spins. Of course, in the case of molecules these are only approximations to the true functionals, since $\rho$ is far from being homogeneous. One might hope to improve the approximation by introducing an expansion in terms of gradients of the density. These methods are called generalized gradient approximations (GGA), and are of great importance in the study of molecules, where the electron density can not be considered as homogeneous. Recently, several new GGA functionals have been develop, both, from first principles but also highly parametrized ones using fits to exact data on atoms and small molecules. Most recently, so called meta-GGA functionals were proposed, where besides the local density and its gradient also the laplacian (or the kinetic energy density) enters the equations.

Density functional methods have proved to give excellent results in most chemical systems [97], with results comparable to those given by CPU intensive electron-correlation methods. However they frequently overestimate bond
dissociation energies [98]. The hybrids of HF and DFT theories increment the accuracy of the dissociation energy as was validated by Johnson et al. [99]. The hybrid [100] Becke 3 combined with the correlation functional Lee-Yang-Parr (B3LYP) [90, 101, 102] has become one of the most popular one, having the following form:

\[
(1 - a_0)E_{x}^{LSDA} + a_0E_{x}^{HF} + a_xE_{x}^{BS8} + a_cE_{c}^{LYP} + (1 - a_c)E_{c}^{VWN}
\]

being the values of the parameters \( a_0 = 0.20, a_x = 0.72 \) and \( a_c = 0.81 \). This functional is known as the Becke’s 3 parameter functional, B3LYP.

Since density-functional calculations do not use the exact \( E_{xc} \) they are not, strictly speaking, ab-initio calculations. However, they do not use parameters fitted to experimental data, hence they lie closer in spirit to ab-initio calculations than to semiempirical ones. One of the main advantages of these methods is that with a similar computational cost to HF methods, they include some kind of electron correlation, being the major drawback that the correlation effects cannot be sorted out precisely. They are already mixed from the beginning with the uncorrelated solution. Besides, there is not any systematic way to improve the calculations by applying more and more sophistication, so the results must be accepted as they stand. In spite of these facts, DFT have been found to yield good results for ground state properties of various chemical systems, with a quality comparable to MP2 results , or even better in some cases. Due to their relative low computational cost, DFT is the method of choice for large systems, for which the inclusion of electron correlation by MP or CI methods is prohibitive.

### 1.3.3 Quantum Molecular Dynamics

Molecular dynamics (MD) is a form of computer simulation in which atoms and molecules are allowed to interact for a period of time, giving a view of the motion of the particles. One convenient approach to include the electronic structure in molecular dynamic simulations consists in straightforwardly solving the static electronic structure problem in each molecular dynamics step given the set of fixed nuclear positions at that instance of time. This is what we do in the Born-Oppenheimer molecular dynamic simulations: Born-Oppenheimer molecular dynamics follows the adiabatic time evolution of a sistem, dividing time into series of timesteps. In order to solve the Newton’s equations of motion, electrons are treated quantum mechanically (solving the electronic equation by means of density functional theory) and nuclei classically.

Thus, we solve the static electronic structure problem in each molecular dynamics step given the set of fixed nuclear positions at that instance of time. Hence, the electronic structure part is reduced to solving a time-independent quantum problem, namely by solving the time-independent Schrodinger equation, concurrently to propagating the nuclei via classical molecular dynamics.

The resulting Born-Oppenheimer molecular dynamics method is propagated for the electronic ground state by

\[
F = -\frac{dE}{dR} = ma = m\frac{d^2R}{dt^2} = -\nabla_{\varphi} \min_{\varphi_0} \{<\Psi_0|H_e|\Psi_0>\}
\]

where the minimum of \( <H_e> \) has to be reached in each Born-Oppenheimer molecular dynamics step according to Eq. (1.12).

As we use Density Functional Theory as outlined before to solve the electronic problem, the total ground-state energy of the interacting system of electrons with classical nuclei fixed at positions \( \{R_{\alpha}\} \) can be obtained as the minimum of Kohn-Sham energy:

\[
\min_{\varphi_0} \{<\Psi_0|H_e|\Psi_0>\} = \min_{\{\varphi_i\}} E^{KS}[\{\varphi_i\}]
\]

where the Kohn-Sham energy is defined in Eq. (1.6) and \( \{\varphi_i\}_{i=1}^k \) being the Kohn-Sham orbitals according to Eq. (1.8).
1.3.4 Basis Sets

In both wave function based methods and density functional theory a set of functions to span the molecular orbitals are needed. These sets of function are the so called basis sets. The choice of an appropriate basis set is an essential requirement for the success of the calculation. However, we have to balance the precision of the basis set and its size, since increasing the size of the basis set the calculation cost becomes more expensive.

In the characterization of the structures we have used the Contracted Gaussian Functions (CGF), which are the most used in quantum chemistry calculations. They consist of linear combinations (contractions) of Gaussian functions (primitives),

\[ \varphi_{CGF}^\mu(|\vec{r} - \vec{R}_A|) = \sum_{p=1}^{L} d_{p\mu} g(\alpha_{p\mu}, |\vec{r} - \vec{R}_P|) \]  

where the exponent of the primitives \( \alpha_{p\mu} \) and the contraction coefficients \( d_{p\mu} \) are optimized for the different elements.

Additionally, for the quantum molecular dynamic simulations, we have used numerical linear combination of atomic orbitals basis set. These orbitals are zero beyond a certain radius. Within this radius, the atomic basis orbitals are products of a numerical radial function and a spherical harmonic, namely, for atom \( I \) located at \( R_I \), where \( r_I = r - R_I \),

\[ \phi_{Ilmn}(r) = \phi_{Iln}(r_I)Y_{lm}(\hat{r}_I) \]

It must be pointed out that usually all-electron basis sets are used, which means that all electrons are considered in the basis set. However, in some cases due to the large number of electrons and the consequently prohibitive cost of the calculation, some of the electrons (the core electrons) are removed from the calculation and only the outer electrons are considered. In this case the outer electrons feel the averaged potential due to the core electrons and the nuclei.
Chapter 2

Structure and Stability of the Endohedrally Doped \( (X@Cd_{i}S_{i})^{q=0, \pm 1}_{i=4, 9, 12, 15, 16}, X= Na, K, Cl, Br, \) Nanoclusters


Abstract  Endohedral \( (X@Cd_{i}S_{i})^{q=0, \pm 1}_{i=4, 9, 12, 15, 16} \) structures have been characterized by means of the Density Functional Theory, with \( X \) being alkali metals such as Na and K or halogens such as Cl and Br, \( i= 4, 9, 12, 15, 16 \). These nanoclusters have been chosen due to their high sphericity, which is known to be one of the parameter determining the stability of the endohedral nanoclusters, along with the charge and sizes of the guest atom. In these structures, the atoms are trapped inside previously characterized spheroid hollow structures with positively charged Cd atoms and negatively charged S atoms. Moreover, although the radii of all atoms are similar, Cd atoms are located more inside the structure. For alkali metals, neutral and cationic endohedral compounds have been characterized and, for halogens, neutral and anionic nanoclusters. It is observed that some of these guest atoms are trapped in the center of mass of the cluster, while others are found to be displaced from that center, leading to structures where the guest atom presents a complex dynamical behavior. This fact was confirmed by quantum molecular dynamics calculations, which further confirmed the thermal stability of these endohedral compounds.

2.1 Introduction

Hollow binary nanoclusters of II-VI semiconductor elements have been widely studied in the literature, both theoretically and experimentally [43, 44, 45, 46, 47, 48, 49, 50, 51]. However, studies of the properties of endohedrally doped compounds made of these hollow nanoclusters are scarce [52, 54]. Of particular relevance to the present research is the previous characterization of the \( (X@Zn_{i}S_{i})^{0, \pm 1}_{i=4, 16} \) compounds [53], being \( X \) alkali metals or halogens. In this work it was observed that alkali metals transferred an electron to the cage, while halogen atoms took an electron from the cage, leading to charged ions inside the cage. Moreover, encapsulation of halogen atoms resulted in endohedral nanoclusters with enhanced electron affinity relative to the guest halogen atom (4.5 eV compared to 3.5 eV). These nanoclusters ought, therefore, to be considered as superhalogens in the same vein as the \( Al@Al_{12} \) cluster, for which recent research has confirmed its predicted [55] high electron affinity (EA) of 3.20 eV as well as its ability to ionize spontaneously into \( (Al@Al_{12})^{-}K^{+} \) in the gas phase [56].

Notice that the Cl and Br endohedral nanoclusters studied in this work have electron affinities substantially larger than \( Al@Al_{12} \). Hence, they are expected to have even a stronger superhalogen character. Furthermore, the electron affinities of the halogen endohedral nanoclusters and the ionization energies of the alkali endohedral nanoclusters of \( Zn_{i}S_{i} \) are rather similar, rendering them good candidates to form cluster-assembled materials under mild conditions, since large IE/EA differences would yield substantial heat release during assembling that might destroy the assembled material as it is formed. Such solids, based on \( X@Zn_{12}S_{12} \) structures, have been recently theoretically
characterized [35]. They have fcc crystal lattice structure, and, interestingly, the band-gap is decreased from 3.66 eV found in wurtzite to 2.2 eV in the bare solid, and even further, to 1.8 eV, in the doped solids. These solids may be seen as semiconducting materials, with smaller band-gaps than the solids found in nature, namely, wurtzite and zincblende. Ab initio quantum dynamics calculations further confirmed the thermal stability of the calculated structures. Moreover, the predicted metastability of the fcc structures was supported by the predicted energy barriers towards collapsing into wurtzite, which were found to be larger than 6 eV.

The potential technological applications of these newly designed materials in a large variety of fields, like solar cells, heterogeneous catalysis, molecular transport, optical sensors and so on, makes the searching of new building blocks for such materials worthwhile. Within this context, the theoretical investigations reported herein could help, or guide, experimentalists towards such goal.

Thus, Cd$_i$S$_i$, $i=1$–16 clusters have been synthesized and characterized by BelBruno et al. [50]. Consequently, one could think of using these clusters as building blocks to synthesize new stable molecular solids. However, we propose that using endohedrally doped selected Cd$_i$S$_i$ hollow clusters should represent a wiser choice, because (i) the stability of the cluster structures themselves are not compromised by the endohedral doping and (ii) a larger variety of properties can be tailored by such doping.

Herein, we will describe the physico-chemical properties of (X@Cd$_i$S$_i$)$_j$, $j=4, 9, 12, 15, 16$ clusters, with X = Na, K, Cl, Br, based on our density functional theory and quantum molecular simulation calculations. These clusters were chosen due to their hollow spherical shape, which is one main parameter determining their stability.

Our results, along with the earlier mentioned work by BelBruno et al. and the related experimental work on cadmium chalcogenide stoichiometric hollow clusters by Kasuya et al. [51, 103], and by Riehle et al. [104], suggest that these “hypothetical” cluster-like compounds could be within experimental reach in the near future.

2.2 Methods

All geometries have been fully optimized using the gradient corrected hybrid B3LYP [105, 100, 101] functional within the Kohn–Sham implementation [91] of density functional theory [90]. Harmonic vibrational frequencies are determined by analytical differentiation of gradients, in order to determine whether the structures found are true minima or not, and to extract zero-point energies and Gibbs free energy contributions.

The relativistic compact effective core potentials and shared-exponent basis set [106] of Stevens et al. have been used for Cd and S, as in the study of the isolated clusters [48], and the all-electron 6-311 + G(d) basis set was used for the trapped atom. The 4d electrons of Cd were included in the valence. In order to perform the geometry optimizations and harmonic frequency calculations an extra d function was added on Cd and S, due to its importance for the proper description of the high coordination of the atoms in the three-dimensional cluster structures. Note that pure angular momentum functions were used throughout this study.

To further explore the thermal stability of these compounds, we also undertook ab initio thermal MD simulations at 298K on the calculated local minima structures, controlled by means of the Nose thermostat as implemented in the SIESTA code [107] within DFT approach. Exchange and correlation effects were described using the generalized gradient approximation (GGA), within the revised Perdew-Burke-Ernzerhof (rPBE) functional [108, 109, 110]. Core electrons were replaced by Troullier-Martins norm-conserving pseudopotentials [111] in the Kleinman-Bylander factorized form [112]. In the context of Siesta, the use of pseudopotentials imposes basis orbitals adapted to them. Furthermore, SIESTA employs a localized basis set to represent the Kohn-Sham orbitals for valence electrons. Accordingly, the basis set of atomic orbitals is constructed from numerical solutions of the atomic pseudopotential, and are constrained to be zero beyond a cutoff radius. We used a basis set of double-$\zeta$ plus polarization quality (DZP). A single parameter, orbital energy shift ($\Delta E_{PAO}$), defines the confinement radii of different orbitals. With this basis set, SIESTA calculates the self-consistent potential on a grid in real space. The fineness of this grid is determined in terms of an energy cutoff ($E_{Cutoff}$) in analogy to the energy cutoff when the basis set involves plane waves. We have first checked the influence of the $\Delta E_{PAO}$ and $E_{Cutoff}$ parameters for different endohedral compounds. These values are set to $\Delta E_{PAO} = 50$ meV and $E_{Cutoff} = 200$ Ry in routine calculations, but in addition to this, we have carried out the quantum dynamics simulations for $\Delta E_{PAO} = 50$ meV and $E_{Cutoff} = 200$ Ry, and $\Delta E_{PAO} = 50$ meV and $E_{Cutoff} = 300$ Ry, to check the influence for both parameters on the obtained results. Notice that the smaller the $\Delta E_{PAO}$ value and the larger the $E_{Cutoff}$ value, the more accurate the calculation.

In order to analyze the effect of the orbital energy shift and the mesh cutoff, we have focused on X@Cd$_i$S$_i$ endohedral nanoclusters, being X = Na, K, Cl and Br. The effect of changing $\Delta E_{PAO}$ and $E_{Cutoff}$ appears to
be dramatical for the smallest atom, Na, as can be seen in Figure 2.1. There, the distances of the Na atom with respect to the center of mass of the nanocluster and the total energy along the simulations are depicted, for three different cases mentioned above. One may observe that for $\Delta E_{PAO} = 150$ meV and $E_{Cutoff} = 200$ Ry, the endohedral Na@Cd$_{12}$S$_{12}$ structure is not altered, the Na atom moves near the center of the nanocluster, and the total energy oscillates around the same value. However, more fine calculations, with $\Delta E_{PAO} = 50$ meV and $E_{Cutoff} = 200$ Ry, show that Na atom moves from the center towards the surface of the nanocluster, which leads to a more stable structure, as can be seen in the total energy picture. This is due to the small size of sodium compared to the cavity available in the nanocluster, which allows to move close to the surface, interacting covalently with it. Further increase in $E_{Cutoff}$ has no influence in the final result, and thus calculations using $\Delta E_{PAO} = 50$ meV and $E_{Cutoff} = 300$ Ry does not produce any change in the dynamics. For larger trapped atoms, namely K, Cl and Br, we have observed that changing $\Delta E_{PAO}$ and $E_{Cutoff}$ does not alter the final result (see supplementary material). We therefore conclude that endohedral Na@Cd$_{i}$S$_{i}$ compounds need a higher degree of fineness in the calculations. Therefore, Ab Initio Quantum Dynamics calculations have been carried out with $\Delta E_{PAO} = 50$ meV and $E_{Cutoff} = 200$ Ry for $X = Na$, and $\Delta E_{PAO} = 150$ meV and $E_{Cutoff} = 200$ Ry for the rest, to save computational resources.

All these simulations were carried out for 6 ps with a chosen time step of 1 fs.
Figure 2.1: The distance of the Na atom from the center of mass of the Cd$_{12}$S$_{12}$ nanocluster, in Å, and the total energy of the endohedral Na@Cd$_{12}$S$_{12}$ nanocluster as a function of the simulation time, in fs, for three different choices of the $\Delta E_{PAO}$ and $E_{Cutoff}$ parameters. Top panels: $\Delta E_{PAO} = 150$ meV and $E_{Cutoff} = 200$ Ry. Middle panels: $\Delta E_{PAO} = 50$ meV and $E_{Cutoff} = 200$ Ry. Bottom panels: $\Delta E_{PAO} = 50$ meV and $E_{Cutoff} = 300$ Ry.

2.3 Results

First, the effect of the charge on the geometry of the bare nanoclusters will be analyzed in subsection 2.3.1. We anticipate that the most salient geometrical feature of the charged nanoclusters is that the size of the cavity, as compared to their neutral counterparts, changes noticeably. In this subsection the ionization energies and the
electron affinities of the bare nanoclusters are also discussed. Then, we will focus on the endohedral compounds, in subsection 2.3.2. Both, neutral and cationic nanoclusters has been found to be able to encapsulate alkali metals. Halogen atoms, on the other hand, can be encapsulated by the neutral and anionic nanoclusters.

First the structures of charged and neutral endohedral nanoclusters will be characterized and their properties analyzed. Then, ab initio molecular dynamics simulations will be carried out in order to assess the thermal stability of these compounds.

### 2.3.1 Bare Nanoclusters and Atoms

The structures of the cationic and anionic bare nanoclusters were characterized first. Starting from the neutral nanoclusters, an electron was either, removed (for the cations) or added (for the anions), followed by geometry optimizations and frequency calculations to obtain and characterize the optimized structures of the nanocluster ions. For the structures, the adiabatic ionization energies (IE) and electron affinities (EA) were calculated. The structures of the cationic and anionic nanoclusters followed the well-known square-hexagon rule as do their neutral counterparts.

In Table 2.1, the average radii of the sphere defined by the Cd atoms, \( r_{Cd} \), their standard deviation, and the cavity of the cluster, \( r_{cavity} \), are given along with Ionization Energies (IE) and Electron Affinities (EA) for the neutral clusters. The radius of the cavity inside the spherical nanoclusters is defined by the Cd atoms (see Ref. [53]) and is given by \( r_{cavity} = r_{Cd} - r_{Cd}^{ionic} \), with \( r_{Cd}^{ionic} = 0.97 \) Å. \( r_{cavity} \) is given for all the neutral, cationic and anionic nanoclusters. Notice that, compared with the neutral structures, cationic \( r_{cavity} \) values are slightly affected while anionic ones are significantly increased. Recall that Cd atoms, which are located inner in the structure, have positive partial charges of \( \sim 1e \), while S atoms have negative partial charge of \( \sim 1e \).

<table>
<thead>
<tr>
<th>( i )</th>
<th>IE (eV)</th>
<th>EA (eV)</th>
<th>( \sigma )</th>
<th>( q = 0 )</th>
<th>( q = 1 )</th>
<th>( q = -1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>7.85</td>
<td>2.35</td>
<td>0.00</td>
<td>0.98</td>
<td>0.98</td>
<td>1.04</td>
</tr>
<tr>
<td>9</td>
<td>7.80</td>
<td>2.45</td>
<td>0.18</td>
<td>2.15</td>
<td>2.17</td>
<td>2.20</td>
</tr>
<tr>
<td>12</td>
<td>7.90</td>
<td>2.50</td>
<td>0.00</td>
<td>2.65</td>
<td>2.68</td>
<td>2.71</td>
</tr>
<tr>
<td>15</td>
<td>7.69</td>
<td>2.67</td>
<td>0.37</td>
<td>3.14</td>
<td>3.14</td>
<td>3.17</td>
</tr>
<tr>
<td>16</td>
<td>7.68</td>
<td>2.71</td>
<td>0.09</td>
<td>3.29</td>
<td>3.29</td>
<td>3.30</td>
</tr>
</tbody>
</table>

Comparing \( r_{cavity} \) for the neutral and ionic nanoclusters, we can conclude that \( r_{cavity} \) in general keeps constant in cationic clusters but it increases from neutral to anionic structures. The maximum increase is 0.06 Å.

However, the sphericity of the nanoclusters is not the same. A way of measuring the sphericity of these clusters is the standard deviation (\( \sigma \)) of the distances between the Cd atoms and the center of the nanoclusters. The smaller the \( \sigma \), the more spherical the nanocluster is. It must be pointed out that the structures of the cationic and anionic nanoclusters retain the sphericity of their neutral counterparts. It may be seen that Cd,S nanoclusters with \( i = 4, 12, 16 \) have \( \sigma \approx 0 \) and are almost fully spherical. The \( i = 9 \) nanocluster has only a small sphericity deviation (\( \sigma = 0.15 \)). Hence, all these nanoclusters are highly spherical. However, the case of Cd_{15}S_{15} is particular which, with a \( \sigma = 0.37 \), is far from sphericity. Nevertheless, this structure is highly symmetric. It resembles a rugby ball, which is symmetric but the distances to the center of the ball are not the same. The significance of this particular structure will be clarified later.

The ionization energies of these clusters oscillate around 7.8 eV and the electron affinities around 2.5 eV. These values are indicative of the high stability of the neutral bare nanoclusters.

### 2.3.2 Endohedral Nanoclusters

We have considered all possible \((X@Cd_iS_i)^q\) endohedral compounds, with \( i = 4, 9, 12, 15, 16; q = 0, 1, -1 \) and \( X = Na, K, Cl, Br \). As seen in Section
2.2, ab initio quantum molecular dynamics calculations show that sodium atoms move toward the surface in Cd$_{12}$S$_{12}$. This is indicative of the low thermal stability of these compounds. For other sodium-doped nanocluster similar behavior has been observed, and, consequently, we focus the discussion on the thermally stable K@Cd$_{12}$S$_{12}$, Cl@Cd$_{15}$S$_{15}$ and Br@Cd$_{16}$S$_{16}$ nanoclusters. In the supplementary material information about the thermally unstable Na@Cd$_{15}$S$_{15}$ local minima is available for the interested readers.

The thermodynamic stability of the minima will be assessed by the free energy of encapsulation (Δ$G_{inc}$) defined by the following reaction:

\[
\text{Cd}_i \text{S}_i + X^q \rightarrow (X@\text{Cd}_i \text{S}_i)^q; \quad q = 0, \pm 1
\]

A negative value of Δ$G_{inc}$ indicates that the endohedral nanocluster is thermodynamically more stable than the separated fragments. In Figure 2.2 the characterized X@Cd$_i$S$_i$ endohedral nanoclusters are shown. For the sake of clarity, K and halogen (Cl, Br) endohedral nanoclusters will be discussed separately.

Figure 2.2: Structures of X@Cd$_9$S$_9$, X@Cd$_{12}$S$_{12}$, X@Cd$_{15}$S$_{15}$ and X@Cd$_{16}$S$_{16}$ X = K, Cl, Br. S atoms are drawn in yellow, while Cd atoms are drawn in gray.
2.3.2.1 K@Cd$_{16}$S$_{i}$ endohedral nanoclusters

In Table 2.2 the geometric, electronic and energetic properties of the characterized local minima of K@Cd$_{16}$S$_{i}$ endohedral nanoclusters are given. In addition, the $R^{\text{dyn}}_{\text{range}}$ and $R^{\text{dyn}}_{\text{av}}$ geometrical parameters, representative of the dynamic movement of the trapped potassium atom inside the nanocluster, are given. $R^{\text{dyn}}_{\text{range}}$ denotes the range of the distance between the trapped atom and the center of the nanocluster, while $R^{\text{dyn}}_{\text{av}}$ is the average distance of the trapped atom with respect to the center of the nanocluster along the simulation time.

Table 2.2: Cavity within the Cluster ($r_{\text{cavity}}$), the distance of the guest atom with respect to the center of the cluster ($R^{L\text{M}}_{i}$ for the stationary local minima; $R^{\text{dyn}}_{\text{range}}$ and $R^{\text{dyn}}_{\text{av}}$: the range and average position in the dynamic simulation) in Å. The Free Energy of Complexation, $\Delta G_{\text{inc}}$, in kcal/mol, the Charge of the endohedral Atom, $q_{x}$, and the Ionization Energies, in eV.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$r_{\text{cavity}}$</th>
<th>$R^{L\text{M}}_{i}$</th>
<th>$R^{\text{dyn}}_{\text{range}}$</th>
<th>$R^{\text{dyn}}_{\text{av}}$</th>
<th>$\Delta G_{\text{inc}}$</th>
<th>$q_{x}$</th>
<th>$IE$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K@Cd$<em>{9}$S$</em>{9}$</td>
<td>2.41</td>
<td>0.00</td>
<td>0.00-0.62</td>
<td>0.23 (0.11)</td>
<td>-4.78</td>
<td>0.21</td>
<td>5.74</td>
</tr>
<tr>
<td>K@Cd$<em>{12}$S$</em>{12}$</td>
<td>2.83</td>
<td>0.00</td>
<td>0.00-0.67</td>
<td>0.30 (0.13)</td>
<td>-12.40</td>
<td>0.29</td>
<td>5.50</td>
</tr>
<tr>
<td>K@Cd$<em>{15}$S$</em>{15}$</td>
<td>3.29</td>
<td>0.00</td>
<td>0.00-1.39</td>
<td>0.66 (0.32)</td>
<td>-16.45</td>
<td>0.25</td>
<td>5.24</td>
</tr>
<tr>
<td>K@Cd$<em>{16}$S$</em>{16}$</td>
<td>3.40</td>
<td>1.77</td>
<td>0.05-1.17</td>
<td>0.70 (0.25)</td>
<td>-14.26</td>
<td>0.40</td>
<td>5.50</td>
</tr>
<tr>
<td>($K@Cd_{9}$)$_{9}^{+}$</td>
<td>2.35</td>
<td>0.00</td>
<td>0.00-0.44</td>
<td>0.19 (0.07)</td>
<td>23.80</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>($K@Cd_{12}$)$_{12}^{+}$</td>
<td>2.79</td>
<td>0.00</td>
<td>0.00-0.55</td>
<td>0.27 (0.12)</td>
<td>10.79</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>($K@Cd_{15}$)$_{15}^{+}$</td>
<td>3.26</td>
<td>0.00</td>
<td>0.00-1.15</td>
<td>0.52 (0.25)</td>
<td>0.60</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>($K@Cd_{16}$)$_{16}^{+}$</td>
<td>3.37</td>
<td>1.50</td>
<td>0.00-1.52</td>
<td>0.62 (0.28)</td>
<td>8.85</td>
<td>0.51</td>
<td></td>
</tr>
</tbody>
</table>

Minima structures are found for both neutral and cationic endohedral structures for $i=9, 12, 15, 16$. Observe that in all structures K is positively charged, but a bit more for cationic compounds than in neutral ones. In the former case, the Coulombic repulsion between the trapped K atom and the Cd atoms is larger than in the latter, which dramatically affects the calculated encapsulation free energies, $\Delta G_{\text{inc}}$. Observe that they are negative for neutral compounds and positive for the cationic endohedral nanoclusters. Hence, cationic compounds are predicted to be thermodynamically unstable with respect to their corresponding separated compounds. Nonetheless, the height of the barrier for the evaporation of potassium atoms might render these complexes with long enough lifetimes as to be amenable to experimental detection. In general, in both neutral and cationic compounds, free energy indicates that the compounds are thermodynamically more stable as the size of the nanoclusters increases. This is due to a combination of two factors, namely, the better size fit of the K atom inside the cavity and the smaller Coulombic repulsion between K and Cd atoms. Recall that S atoms are located at longer distance from the center, and therefore locally the K-Cd interaction prevails. These arguments also account for the fact that when the size of the cluster increases, the cavity radii is less affected and consequently remains almost constant. Notice that the largest increase of cavity compared to the bare case occurs for K@Cd$_{9}$S$_{9}$, while the smallest increase occurs for K@Cd$_{16}$S$_{16}$. In these nanoclusters K atom lies at the center of the structure except in neutral and cationic K@Cd$_{16}$S$_{16}$ structures which are too big to keep guest atom in the center of the cluster. In addition to this, endohedral K doping of the Cd$_{16}$S$_{i}$ nanoclusters lowers the ionization energy from $\sim$ 7.8 eV to a value between 5.24 and 5.74 eV, which is similar to that of potassium atom and K@Zn$_{16}$S$_{i}$ nanoclusters.

The Ab Initio Quantum Dynamics simulations of these compounds reveal that the trapped atom moves around the center of the nanocluster, as shown by the values of $R^{\text{dyn}}_{\text{range}}$ and $R^{\text{dyn}}_{\text{av}}$ given in Table 2.2. Since the dynamics of all compounds are similar, for discussion we focus on K@Cd$_{12}$S$_{12}$, and the information about the remaining compounds are given in the Supplementary material. In Figure 2.3, it is observed that the total energy oscillates around the same value during the simulation time, and that the K atom moves around the center of the nanocluster all along the simulation. Therefore, these nanoclusters are predicted to be thermally stable enough to survive long enough time at room temperature as to allow for their experimental detection.
2.3.2.2 Cl@Cd$_{12}$S$_{12}$ and Br@Cd$_{12}$S$_{12}$ Endohedral Nanoclusters

Table 2.3 the geometric, electronic and energetic properties of the characterized local minima of the endohedral neutral and anionic Cl@Cd$_{12}$S$_{12}$ and Br@Cd$_{12}$S$_{12}$ endohedral nanoclusters are given. In addition, the $R_{\text{dyn}}^{\text{range}}$ and $R_{\text{av}}^{\text{dyn}}$ parameters, as representatives of the dynamics of the trapped atoms inside the nanocluster, are also shown.
Table 2.3: Cavity within the Cluster \( r_{cavity} \), the distance of the guest atom with respect to the center of the cluster \( R_{LM} \) for the stationary local minima; \( R_{range}^{dyn} \) and \( R_{av}^{dyn} \): the range and average position in the dynamic simulation in Å. The Free Energy of Complexation, \( \Delta G_{inc} \), in kcal/mol, the Charge of the endohedral Atom, \( q_x \), and the Ionization Energies, in eV.

<table>
<thead>
<tr>
<th>( X )</th>
<th>( r_{cavity} )</th>
<th>( R_{LM} )</th>
<th>( R_{range}^{dyn} )</th>
<th>( R_{av}^{dyn} )</th>
<th>( \Delta G_{inc} )</th>
<th>( q_x )</th>
<th>EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl@Cd_{9}S_{6}</td>
<td>2.12</td>
<td>0.10</td>
<td>0.02-0.31</td>
<td>0.12 (0.03)</td>
<td>-31.53</td>
<td>-0.69</td>
<td>4.66</td>
</tr>
<tr>
<td>Cl@Cd_{12}S_{12}</td>
<td>2.57</td>
<td>0.33</td>
<td>0.03-0.66</td>
<td>0.30 (0.12)</td>
<td>-44.08</td>
<td>-0.60</td>
<td>5.11</td>
</tr>
<tr>
<td>Cl@Cd_{15}S_{15}</td>
<td>3.05</td>
<td>0.81</td>
<td>0.15-1.50</td>
<td>0.69 (0.30)</td>
<td>-47.33</td>
<td>-0.60</td>
<td>5.15</td>
</tr>
<tr>
<td>Cl@Cd_{16}S_{16}</td>
<td>3.18</td>
<td>1.11</td>
<td>0.59-1.59</td>
<td>1.08 (0.21)</td>
<td>-48.87</td>
<td>-0.61</td>
<td>4.96</td>
</tr>
<tr>
<td>(Cl@Cd_{9}S_{9})^-</td>
<td>2.11</td>
<td>0.00</td>
<td>0.00-0.33</td>
<td>0.12 (0.05)</td>
<td>-53.20</td>
<td>-0.79</td>
<td></td>
</tr>
<tr>
<td>(Cl@Cd_{12}S_{12})^-</td>
<td>2.56</td>
<td>0.00</td>
<td>0.00-0.39</td>
<td>0.20 (0.08)</td>
<td>-76.13</td>
<td>-0.75</td>
<td></td>
</tr>
<tr>
<td>(Cl@Cd_{15}S_{15})^-</td>
<td>3.03</td>
<td>0.14</td>
<td>0.03-1.40</td>
<td>0.73 (0.28)</td>
<td>-80.14</td>
<td>-0.72</td>
<td></td>
</tr>
<tr>
<td>(Cl@Cd_{16}S_{16})^-</td>
<td>3.17</td>
<td>1.02</td>
<td>0.52-1.48</td>
<td>1.05 (0.19)</td>
<td>-77.29</td>
<td>-0.70</td>
<td></td>
</tr>
<tr>
<td>Br@Cd_{9}S_{9}</td>
<td>2.16</td>
<td>0.09</td>
<td>0.02-0.29</td>
<td>0.14 (0.06)</td>
<td>-7.42</td>
<td>-0.67</td>
<td>4.68</td>
</tr>
<tr>
<td>Br@Cd_{12}S_{12}</td>
<td>2.59</td>
<td>0.21</td>
<td>0.02-0.53</td>
<td>0.26 (0.10)</td>
<td>-31.64</td>
<td>-0.61</td>
<td>5.13</td>
</tr>
<tr>
<td>Br@Cd_{15}S_{15}</td>
<td>3.04</td>
<td>0.09</td>
<td>0.03-0.97</td>
<td>0.56 (0.21)</td>
<td>-33.76</td>
<td>-0.51</td>
<td>5.31</td>
</tr>
<tr>
<td>Br@Cd_{16}S_{16}</td>
<td>3.18</td>
<td>0.83</td>
<td>0.21-1.31</td>
<td>0.76 (0.21)</td>
<td>-39.17</td>
<td>-0.62</td>
<td>5.10</td>
</tr>
<tr>
<td>(Br@Cd_{9}S_{9})^-</td>
<td>2.14</td>
<td>0.00</td>
<td>0.00-0.31</td>
<td>0.14 (0.06)</td>
<td>-32.45</td>
<td>-0.78</td>
<td></td>
</tr>
<tr>
<td>(Br@Cd_{12}S_{12})^-</td>
<td>2.57</td>
<td>0.00</td>
<td>0.00-0.29</td>
<td>0.18 (0.06)</td>
<td>-67.13</td>
<td>-0.77</td>
<td></td>
</tr>
<tr>
<td>(Br@Cd_{15}S_{15})^-</td>
<td>3.04</td>
<td>0.00</td>
<td>0.00-0.87</td>
<td>0.54 (0.20)</td>
<td>-73.36</td>
<td>-0.73</td>
<td></td>
</tr>
<tr>
<td>(Br@Cd_{16}S_{16})^-</td>
<td>3.17</td>
<td>0.51</td>
<td>0.07-1.38</td>
<td>0.69 (0.22)</td>
<td>-73.80</td>
<td>-0.71</td>
<td></td>
</tr>
</tbody>
</table>

Cl and Br can be trapped by Cd_{9}S_{i} (i=9, 12, 15, 16) nanoclusters, to yield neutral and anionic species. Observe that in all structures Cl and Br are negatively charged. Notice that \( q_x \) is predicted to be more negative for the anionic endohedral compounds. In the latter, the Coulombic attraction between the trapped halogen atom and the Cd atoms increases. This affects noticeably the calculated encapsulation free energies, \( \Delta G_{inc} \), which are found to be negative in all cases, due to the attractive interactions, but are more negative for the anionic species, due to the larger Coulombic interaction. These compounds are predicted to be thermodynamically stable with respect to their corresponding separated compounds. Moreover, in both neutral and anionic compounds, free energy indicates the compounds are thermodynamically more stable as the size of the nanoclusters increases. This is due to a combination of two factors, namely, the better size fit of the halogen atoms inside the cavity and the larger Coulombic attraction between these and Cd atoms. These same arguments explain also why the cavity radii are contracted upon halogen encapsulation, and why this contraction is larger for large clusters. For these nanoclusters the halogen atoms lie at the center or near the center of the nanocluster, except for some of the Cl@Cd_{9}S_{9} nanoclusters and for Br@Cd_{16}S_{16}, which are too big nanoclusters as to keep guest atom at the center of their cavity. The charge of trapped atom decreases as the size of the nanocluster increases. For these elements, the anionic structures are more stable than neutral ones. In case of Cl and Br, the stability increases as the size of the cluster increases.

The Ab Initio Quantum Dynamics simulations of these compounds reveal that the trapped atom moves around the center of the nanocluster, as observed by the inspection of the values of \( R_{range}^{dyn} \) and \( R_{av}^{dyn} \) given in Table 2.3. We focus on Cl@Cd_{12}S_{12} as a representative of the halogen-trapped endohedral compounds. It can be observed in Figure 2.4, that the total energy oscillates slightly around the average value during the whole simulation time. A fact which is very supportive of the thermal stability of the endohedral nanostructures. As seen earlier for the potassium, the Cl atom moves around the center of the cluster. Consequently, these compounds are predicted to be stable enough as to survive long enough time for their experimental detection.
Figure 2.4: Dynamics simulation of Cl@Cd_{12}S_{12}. Top: Dynamical trajectories of the Cl atom inside the nanocluster. This plot was prepared as the K@Cd_{12}S_{12} one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped K atom from the center of mass of the nanocluster as a function of time. S atoms are drawn in yellow, while Cd atoms are drawn in gray.

The calculated electron affinities of the halogen endohedral clusters are substantially larger than those of the corresponding guest atoms; EA(Cl) = 3.62 eV; EA(Br) = 3.36 eV. Hence, these endohedral nanoclusters may be seen as superhalogens (53,54), similarly to those of ZnS nanoclusters. It has been observed for electron affinities that EA(Cd_{i}S_{i}) < EA(X) < EA(X@Cd_{i}S_{i}) and for ionization energies that IE(K) \sim IE(K@Cd_{i}S_{i}) < IE(Cd_{i}S_{i}). The isolated Cd_{i}S_{i} nanoclusters have a closed shell electronic structure. When an alkali is trapped inside the cage, an electron is transferred to the lowest unoccupied molecular orbital (LUMO). This electron can more easily be removed than one from the highest occupied molecular orbital (HOMO) of the isolated cluster, decreasing the ionization potential. Similarly, when a halogen atom is trapped, it takes an electron from the surface, and now the HOMO orbital is singly occupied, therefore increasing the electron affinity with respect to the isolated cluster.

### 2.4 Conclusions

The geometrical structures, electronic and dynamic properties of the endohedral (X@Cd_{i}S_{i})^{0,\pm}_{i=9,12,15,16} nanoclusters, with X standing either for the Na, and K alkali elements or for the Cl and Br halogens, have been characterized by density functional theory and quantum molecular simulation calculations.
The stability of the resulting structures has been rationalized in terms of three parameters. The first is the appropriate matching between the size of the nanocluster, $r_{cavity}$, and the size of the trapped atom. The second is the shape of the nanocluster: the spherical nanoclusters are more prone to incarcerate atoms than the irregular ones. The third is the charge of the trapped atom: negatively charged guest atoms are found to be the thermodynamically most stable ones. Due to the larger cavity size inside Cd$_i$S$_i$ nanoclusters, in comparison to Zn$_i$S$_i$ nanoclusters, Na is too small to lead to stable X@Cd$_i$S$_i$ compounds. This fact has been demonstrated by quantum dynamics calculations.

Encapsulation of halogen atoms results in endohedral nanoclusters with enhanced electron affinity relative to the guest halogen atom. These nanoclusters ought, therefore, to be considered as superhalogens in the same vein as the X@Zn$_i$S$_i$ and the Al@Al$_{12}$ nanoclusters,[55] where recent research has confirmed its predicted high electron affinity of EA=3.20 eV as well as its ability to form salts with electropositive elements like potassium.[56] The Cl and Br endohedral nanoclusters studied in this work have electron affinities substantially larger than Al@Al$_{12}$, namely, EA > 4.5 eV. Hence, they are expected to have a stronger superhalogen character which makes them suitable to form ionic cluster-assembled materials. Furthermore, the electron affinities of the halogen endohedral nanoclusters and the ionization energies of the alkali endohedral nanoclusters of Cd$_i$S$_i$ are rather similar. This is an interesting property, since large IE/EA differences would yield substantial heat release during assembling that might destroy the assembled material as it is formed. Interestingly, X@Zn$_i$S$_i$ compounds were seen to have similar properties, and recently have been shown to be able to build stable cluster-assembled materials [35].

**Supporting Information available**

This information is available in the Appendix A.
CHAPTER 2. STRUCTURE AND STABILITY OF THE ENDOHEDRALLY DOPED (X@C@I) Q = 0, ± 1 I = 4, 9, 12, 15, 16, X = Na, K, Cl, Br, Nano-Clusters
Chapter 3

Thermal Stability of Endohedral first-row Transition-Metal TM@Zn\textsubscript{i}S\textsubscript{i} Structures, \textit{i}=12, 16

Abstract

The thermal stability of the endohedral first-row transition-metal-doped TM@Zn\textsubscript{i}S\textsubscript{i} nanoclusters, where TM stands for the first-row transition-metals (Sc-Zn) and \textit{i}=12,16, has been analyzed for the two lowest-lying spin-states of each metal. These endohedral structures have been seen to be connected with surface structures by the movement of the TM from the inner part of the structure to the surface. We have calculated the relative energies between these two isomers in order to check their relative stabilities. Additionally, we have also characterized the transition states (TS) connecting both isomers. Thus, we have calculated the barriers needed to move from one to the other, and these values are further used to predict their lifetimes of the endohedral compounds. Most of the lifetimes are predicted to be very small, although most of them are large enough to experimental detection. Conversely, the lifetimes of Zn@Zn\textsubscript{12}S\textsubscript{12} and Zn@Zn\textsubscript{16}S\textsubscript{16} have proved to be very large. Finally, ab initio Quantum Dynamics calculations are in agreement with the calculated data.

3.1 Introduction

In this chapter we focus on first-row transition-metal-doped TM@Zn\textsubscript{i}S\textsubscript{i} nanoclusters, where TM stands for the first-row transition-metals (Sc-Zn) and \textit{i}=12, 16. Of particular relevance to the present research is the previous characterization of the endohedral first-row transition-metal-doped TM@Zn\textsubscript{i}S\textsubscript{i} nanoclusters, in which TM stands for the first-row transition-metals from Sc to Zn and \textit{i}=12 and 16 [54]. Zn\textsubscript{12}S\textsubscript{12} and Zn\textsubscript{16}S\textsubscript{16} were chosen because of their high symmetry and highly spheroidal shape, which allow for favored endohedral structures as compared to other nanoclusters [43]. They observed that the encapsulation free energies are negative, suggesting that these compounds are thermodynamically stable. Moreover, there is negligible charge transfer between the dopant transition-metal and its hollow cluster host and, after encapsulation, the spin densities remain localized on the transition-metal atom. This allows for the atomic-like behaviour of the trapped transition-metal atom, which gives rise to their atomic-like magnetic properties. Thus, endohedral transition-metal compounds are interesting, owing to their magnetic properties, which may lead to dimers with (anti)ferromagnetic coupling [38]. In addition, quantum molecular dynamics were carried out for two selected cases, Zn(\textsuperscript{1}S)@Zn\textsubscript{12}S\textsubscript{12} and Ti(\textsuperscript{5}S)@Zn\textsubscript{12}S\textsubscript{12}, as representative of the endohedral nanoclusters with the trapped atom at the center and off-center, respectively. These calculations confirmed the thermal stability of these two compounds.

In this work, and continuing with the previous work of Matxain et al. [54], we have further studied the thermal stability of these previously characterized endohedral clusters, by carrying out quantum molecular dynamics calculations for several TM@Zn\textsubscript{i}S\textsubscript{i} (\textit{i}=12, 16). It has been observed that some of these endohedrally doped nanoclusters are not thermally stable, moving the dopant atom from the inner part of the cluster to the surface. These new structures are called surface structures hereafter. Quantum dynamics calculations are very time consuming, and can not be carried out for all the characterized endohedral structures. Therefore, in order to save computational
resources, we have characterized the surface structures for all compounds, along with the TS connecting both isomers. The energy barriers calculated in such a way will be further used to estimate the lifetimes of the endohedral structures, and will be compared to the performed quantum dynamics calculations.

3.2 Methods

All geometries have been fully optimized using the gradient corrected hybrid B3LYP [105, 113, 101] functional within the Kohn-Sham implementation [91] of density functional theory [90]. Harmonic vibrational frequencies are determined by analytical differentiation of gradients, in order to determine whether the structures found are true minima or transition states, and to extract zero-point energies and enthalpy and entropy contributions to Gibbs free energy, $\Delta G$, which is reported at room temperature. The relativistic compact effective core potentials and shared-exponent basis set [106] of Stevens et. al. (SKBJ) has been used for Zn and S, as described in the study of the isolated clusters [44], and the fully relativistic multielectron fit pseudopotentials, with 10 electrons in the core, developed by Dolg et. al., were used for the trapped atoms [114, 115]. Note that pure angular momentum functions were used throughout this study. All the geometry optimizations and frequency calculations were carried out with the GAUSSIAN03 package [116]. The transition states between the characterized endohedral nano clusters and their corresponding surface structures have been calculated with a IRC calculation.

To further explore the thermal stability of these compounds, we also undertook ab initio molecular dynamics simulations at 300K on some selected cases, using Nose dynamics as implemented in the SIESTA code. These simulations were carried out for 5ps, somewhat larger than standard calculations on dynamics of solids, with a chosen time step of 1fs.

3.3 Results

First of all, in subsection 3.3.1 we present the results for the ab initio molecular dynamics simulations on two selected cases, namely, Mn($^4D$)@Zn$_{12}$S$_{12}$ and Ni($^1D$)@Zn$_{16}$S$_{16}$. Then, in subsections 3.3.2 and 3.3.3 the surface and TS structures are characterized.

3.3.1 Quantum molecular dynamics

In ref. [54], Matxain et. al. carried out quantum molecular dynamics for two selected cases, Zn($^1S$)@Zn$_{12}$S$_{12}$ and Ti($^5S$)@Zn$_{12}$S$_{12}$. These calculations confirmed the thermal stability of these two compounds, since in both cases the dopant atom was kept inside the cage. Here we present two new selected cases, Mn($^4D$)@Zn$_{12}$S$_{12}$ and Ni($^1D$)@Zn$_{16}$S$_{16}$, where the guest transition-metal does not remain confined into the cavity but it moves to the surface of the nanocluster. We have set a simulation time of 5 ps, with a time step of 1 fs, and the trajectories have been calculated at a constant average temperature of 298 K.

Figure 1 shows how the energies vary during the simulation. It can be observed in both cases that, at a given time, the energy decreases dramatically. This fact happens when the transition-metal goes toward the surface of the nanocluster, which leads to a more stable structure. Together with the total energy pictures, the representations of the distance of the Mn and Ni respectively from the center of mass of the nanoclusters during the simulation time, in Figure 2, confirm that the guest atom moves away from the center. Likewise, in Figure 3 the final structures of these two clusters are depicted: in the resulting structures the metals interact covalently with the Zn and S atoms that are around them.

Therefore, quantum dynamics calculations of these selected cases predict that they are not thermally stable and the TM would move towards the surface of the cage through a transition state. In the next subsections we have characterized these surface and transition state structures, in order to rationalize the behaviour and stability of these compounds.
Figure 3.1: Variation of the energy, in eV, of Mn(4D)@Zn\textsubscript{12}S\textsubscript{12} (right) and Ni(3D)@Zn\textsubscript{16}S\textsubscript{16} (left) endohedral nanoclusters as a function of time.

Figure 3.2: The distance of the TM from the center of mass of the nanocluster, in Å, as a function of time, in femtoseconds. On the right Mn(4D)@Zn\textsubscript{12}S\textsubscript{12} and on the left Ni(3D)@Zn\textsubscript{16}S\textsubscript{16}.
Figure 3.3: The resulting compounds from endohedrally doped Mn(\textsuperscript{4}D)@Zn\textsubscript{12}S\textsubscript{12} and Ni(\textsuperscript{1}D)@Zn\textsubscript{16}S\textsubscript{16} respectively are depicted below. S atoms are drawn in yellow, Zn atoms are drawn in red, Mn is drawn in grey, while Ni is drawn in green.

3.3.2 Surface Structures

All transition metals show the existence of a stationary structure with the metal atom integrated into the nanocluster by the formation of several bonds with the neighboring nanoparticle atoms. In this subsection the nanoclusters formed by adding the corresponding transition metal in the surface will be analyzed and their properties will be discussed. For each TM, the two lowest-lying spin states have been considered, like in the endohedrally doped ones \[54\]. In Table 1 the geometrical, electronic and energetic properties of the characterized local minima are given. The spin densities of each metal and the maximum spin density of zink and sulfur atoms in the surface and endohedral compounds are shown in Table 2 and 3. The spin densities of the transition-metals in the endohedral nanoclusters are taken from the work of Matxain and co-workers \[54\]. Hereinafter, a comparison between endohedral nanoclusters and surface structures will be made.

These compounds do not resemble the square-hexagon structure of spheroids, because when the trapped atom bonds with the neighboring S and Zn atoms, the part of the nanocluster where the bonding happens, gets distorted. In Table 1 the number of coordination of the TM is also given. This coordination number corresponds to the number of bonds of the metal in the most stable compound found for each case.
Table 3.1: The charge of transition-metal atom and the coordination number. \( \Delta E \) is the relative energy of the low-spin state and the high-spin state, and \( \Delta G_{\text{surf-end}} \) is the energy difference between the endohedral and the surface structures, both in Kcal/mol. In green the ground spin-state of each metal.

<table>
<thead>
<tr>
<th>( Zn_{12}S_{12} )</th>
<th>( 2S + 1 )</th>
<th>( q_x )</th>
<th>C.N.</th>
<th>( \Delta E )</th>
<th>( \Delta G_{\text{surf-end}} )</th>
<th>( q_x )</th>
<th>C.N.</th>
<th>( \Delta E )</th>
<th>( \Delta G_{\text{surf-end}} )</th>
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<td>0.00</td>
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<td>-</td>
<td>0.70</td>
<td>3</td>
<td>0.00</td>
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<td>-</td>
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<td>-</td>
<td>0.39</td>
<td>3</td>
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<td>-</td>
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<td>-22.62</td>
<td>-</td>
<td>0.77</td>
<td>3</td>
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<td>-15.67</td>
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<td>-20.60</td>
<td>-</td>
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<td>0.00</td>
<td>-</td>
<td>-</td>
<td>-0.26</td>
<td>5</td>
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<td>7.31</td>
<td>-15.58</td>
<td>-</td>
<td>0.32</td>
<td>4</td>
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<tr>
<td>Cu 2</td>
<td>0.23</td>
<td>5</td>
<td>-</td>
<td>-9.97</td>
<td>-</td>
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<td>2</td>
<td>-</td>
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<td>2</td>
<td>-</td>
<td>-4.73</td>
<td>-</td>
<td>0.32</td>
<td>2</td>
<td>-</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Looking at the energy difference between the surface and endohedral nanoclusters, \( \Delta G_{\text{surf-end}} \), it is clear that the surface compounds are thermodynamically more stable than the corresponding endohedral ones, except for \( Zn(1S)Zn_{16}S_{16} \) and \( Cr(7S)Zn_{16}S_{16} \). For this reason, we have researched the transition states between these two structures, in order to analyzed if the endohedral nanoclusters are thermally stable or if they will lead to the more stable surface compounds, depending on how is the energy barrier (see Section 3.3).

The relative high-spin and low-spin energies shown in Table 1 reveal that the earlier and the late transition-metal surface structures favor the low-spin state, unlike the endohedral nanoclusters.

For \( Ti(5F), Mn(4D), Co(2F), Co(4F), \) and \( Zn(1S) \) the coordination number is the same in both \( Zn_{12}S_{12} \) and \( Zn_{16}S_{16} \) compounds. Nonetheless, in most of the nanoclusters, the coordination number is bigger in \( X@Zn_{12}S_{12} \). It is because the volume of the cavity in \( Zn_{12}S_{12} \) is smaller.
Table 3.2: The spin densities of the transition-metals in both endohedral (XZn_{12}S_{12}) and surface (X@Zn_{16}S_{16}) compounds, and the maximum spin densities of the Zn and S atoms in each compound. In green the ground spin-state of each metal.

<table>
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<th>Surface structures</th>
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<th>Endohedral structures</th>
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<td>2S+1</td>
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<td>ρ_{SZn}</td>
<td>ρ_{SZ}</td>
<td>ρ_{STM}</td>
</tr>
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<td>Sc 2</td>
<td>0.74</td>
<td>0.20</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Sc 4</td>
<td>1.45</td>
<td>0.77</td>
<td>0.11</td>
<td>-</td>
</tr>
<tr>
<td>Ti 3</td>
<td>2.00</td>
<td>0.04</td>
<td>-0.03</td>
<td>-</td>
</tr>
<tr>
<td>Ti 5</td>
<td>3.00</td>
<td>0.37</td>
<td>0.14</td>
<td>3.17</td>
</tr>
<tr>
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<td>-0.08</td>
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<td>0.14</td>
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<tr>
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<tr>
<td>Zn 1</td>
<td>-</td>
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In general the charges of the transition-metals (Table 1) in the surface structures are bigger than in the endohedral ones. Moreover, observe in Table 2 and 3 that the maximum spin densities of zink and sulfur atoms are bigger in...
the surface structures. Besides, the maximum values are found in the Zn and S atoms which are bonded to the TM. In some structures, the spin densities of the nanoparticle atoms are negative because they donate electronic density to the metal. Conversely, the positive values of these spin densities are indicative of the donation of electronic density from the metal to the neighboring Zn or S atoms. This is due to the bigger interaction between transition metals and the others atoms forming the cluster in the surface structures than in the endohedral ones. Hence, in these compounds the interaction between the host and the guest atom is bigger which is perfectly understandable considering that in the surface structure the transition metal is directly bonded to S and Zn atoms, while in the endohedrally doped compounds, there is no bond between TM and other atoms.

3.3.3 Transition States

As mentioned before, after observing by quantum molecular dynamics calculations that some first-row transition-metal endohedrally-doped nanoclusters are not thermally stable, we have characterized the transition states between the endohedrally doped nanocluster and their corresponding surface structures in order to conclude if the endohedral compounds are thermally stable or not using their lifetimes, which are shown in Table 4 and 5.

The lifetime of each endohedral nanocluster has been calculated at 298 K from the Gibbs energy of activation \( \Delta G_{TS-end} \) (the difference between the Gibbs free energy of endohedral compounds and the Gibbs free energy of their corresponding transition states), using the Eyring equation:

\[
k = \frac{k_B T}{h} e^{-\frac{\Delta G}{RT}}
\]

where \( k \) is the reaction rate constant, \( T \) is the absolute temperature, \( \Delta G \) is the Gibbs free energy, \( k_B \) the Boltzmann constant, \( h \) is the Planck’s constant and \( R \) is the constant of ideal gas.

Table 3.4: Characterized transition states between endohedral compounds and their respective surface compounds, for TM@Zn\(_{12}\)S\(_{12}\), TM being first-row transition-metal. The imaginary frequency of the transition state, \( \Delta G_{TS-end} \) (kcal/mol) and the calculated reaction rate constant (s\(^{-1}\)) and lifetime (s). In green the ground spin-state of each metal.
Table 3.5: Characterized transition states between endohedral compounds and their respective surface compounds, for TM@Zn\textsubscript{16S\textsubscript{16}}, TM being first-row transition-metal. The imaginary frequency of the transition state, $\Delta G_{TS-end}$ (kcal/mol) and the calculated reaction rate constant ($s^{-1}$) and the lifetime (s). In green the ground spin-state of each metal.

<table>
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<tr>
<th>2S+1</th>
<th>Freq.</th>
<th>$\Delta G_{TS-end}$</th>
<th>$K(s^{-1})$</th>
<th>$\tau(s)$</th>
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<tr>
<td>Sc</td>
<td>2</td>
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<td>4</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>6</td>
<td>63.2i 6.26</td>
<td>1.60$\cdot$10$^8$</td>
<td>6.25$\cdot$10$^{-9}$</td>
</tr>
<tr>
<td>Cr</td>
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<td>68.1i -19.8</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>59.7i 14.95</td>
<td>6.83$\cdot$10$^3$</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>45.8i 15.11</td>
<td>5.21$\cdot$10$^4$</td>
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<td>63.1i 31.66</td>
<td>3.85$\cdot$10$^{-11}$</td>
<td>2.60$\cdot$10$^{10}$</td>
</tr>
</tbody>
</table>

At first glance, it is worth noticing that most of the calculated lifetimes are very small, although most of them are predicted to be large enough to experimental detection. We must emphasize that the lifetimes of Zn(1S)@Zn\textsubscript{12}$S_{12}$ and Zn(1S)@Zn\textsubscript{16}$S_{16}$ are extremely large.

To explain this fact we have to take into account that in the endohedral compounds, the interaction between the guest and the host is very weak, while in the surface structures this interaction is stronger. Moreover, the zink has got all the orbitals full. Hence, Zn is the least reactive of all the first-row transition-metals. This fact also explains why the endohedral Zn@Zn\textsubscript{16}$S_{16}$ is thermodynamically more stable than ZnZn\textsubscript{16}$S_{16}$.

Additionally, lifetimes reveal that endohedral nanoclusters favor high-spin states which coincide with the most stable endohedrally doped nanoclusters.

3.3.4 Confirmation

In addition, we have carried out a molecular dynamic simulation for Zn(1S)@Zn\textsubscript{12}$S_{12}$ whose predicted lifetime is 2.47$\cdot$10$^5$ seconds. The dynamical behaviour of this endohedrally doped nanocluster was analyzed in the previous work by Matxain et al.[54]. They carried out a quantum molecular dynamic simulation of 5 ps and they observed that in the endohedral structure the Zn atom remained confined at the center of the nanocluster. To make sure that this compound is thermally stable, we have increased the simulation time up to 30 ps. In the Figure 4 it is observed that the energy oscillates around the same value during all the simulation time, and that the Zn atom moves around the center of the nanocluster along the simulation up to a maximum radial distance of 0.55 Å. The average radial separation of the caged Zn atom is 0.27$\pm$0.11 Å. In addition, the trajectory of the zink atom along the simulation time is depicted in Figure 5. Therefore, this nanocluster is predicted to be thermally stable enough to survive long time at room temperature as to allow for its experimental detection. It is in agreement with the previously predicted high thermal stability.
3.4 Conclusions

The thermal stability of the first-row transition-metal-doped TM@Zn$_{12}S_{12}$ nanoclusters, in which TM stands for the first-row transition-metals from Sc to Zn and $i=12,16$, has been analyzed by calculating their lifetimes. The two lowest-lying spin-states of each metal have been considered. To calculate these lifetimes we have first characterized the surface structures. Afterwards, we have characterized the transition states between these surface structures and the previously characterized endohedral nanoclusters [54].

Surface compounds do not resemble the square-hexagon structure of spheroids, because when the trapped atom bonds with the neighboring S and Zn atoms, the part of the nanocluster where the bonding happens, gets distorted.
Most of the lifetimes are predicted to be very small, although most of them are large enough to experimental detection. The lifetimes of Zn@Zn$_{12}$S$_{12}$ and Zn@Zn$_{16}$S$_{16}$ have proved to be very large. To explain this fact we have to take into account that in the endohedral compounds, the interaction between the guest and the host is very weak, while in the surface structures this interaction is stronger. Moreover, the zink has got all the orbitals full. Hence, Zn is the least reactive of all the first-row transition-metals.
CHAPTER 3. THERMAL STABILITY OF ENDOHEDRAL FIRST-RWOW TRANSITION-METAL TM@ZN\_I STRUCTURES, I=12, 16
Chapter 4

Concluding Remarks

4.1 General Conclusions

In this work we have dealt with the possibility of designing new building blocks for further assembling new materials. We have focused on II-VI nanoclusters, due to their promising technological applications based on their peculiar optical properties. More concretely, our interest is concentrated on Cd$_i$S$_i$ and Zn$_i$S$_i$ nanoclusters and their capacity to trap alkali metals and halogens, and transition metals, respectively.

One of the major differences between these two kinds of doping is that, while the alkali metals and halogens mostly affect to the optical properties of these nanoclusters, transition metals not only can alter these properties, but also contribute with a new property: magnetism. Another key difference is that, while in X@Cd$_i$S$_i$ nanoclusters (X=Na, K, Cl and Br) there is charge transfer, this does not happen in TM@Zn$_i$S$_i$ (TM being first-row transition-metals) structures. This fact leads to strong coulombic interactions in the former that are not present in the latter.

The thermodynamical stability of X@Cd$_i$S$_i$ endohedral nanoclusters can be rationalized considering three parameters: (i) The appropriate matching between the size of the nanocluster, namely the cavity radii, and the size of the trapped atom. This explains why the sodium-doped CdS nanoclusters are not stable, because sodium is too small to fit into the cavity of the clusters, and therefore, it has too much mobility and reacts with the surface atoms, breaking the endohedral compound. Similarly, if the caged atom is too big, the cluster also breaks. (ii) The second is the shape of the nanocluster: the most spherical ones are more prone to incarcerate atoms than the irregular ones. (iii) And the third parameter is the charge of the guest atom: the thermodynamically most stable compounds are those in which the trapped atom is negatively charged. In the case of the endohedral TM@Zn$_i$S$_i$ structures, the third point is not analyzed in this work, since as mentioned above, charge transfer does not occur for transition-metals. Therefore, the thermodynamic stability of those compounds are between the ones of the halogen trapped structures (recall that halogens are negatively charged and hence there is a favourable interaction with the nanocluster) and of the alkali metal trapped structures (repulsive interactions with the nanocluster).

It must be highlighted that we have tailored the properties of the bare nanoclusters doping them with atoms other than those of the cluster. In the case of Cd$_i$S$_i$ nanoclusters, using alkali metals as dopants lowers the potential ionization. Doping these clusters with halogens, has the effect of a very large increase in the electron affinity. Hence, the electronic properties of these clusters change upon doping them. Likewise, when we dope Zn$_i$S$_i$ nanoclusters with first-row transition-metals, these clusters act as a host protecting the spins of their corresponding dopant atom, where the spin densities remain localized on the transition-metals and the charge transfer is negligible, giving rise to atomic like magnetism.

It has also been observed that it is not only important to characterized the local minimum of this kind of nanoclusters but also to analyze their thermal stability. With this purpose we have used two different methodologies. The first one is to carry out quantum molecular dynamic simulations, in which atoms and molecules are allowed to interact for a period of time, giving a view of the motion of the particles. This technique allowed us to predict the thermal stability of X@Cd$_i$S$_i$, with the exception of Na@Cd$_i$S$_i$ clusters, although they are calculated to be thermodynamically stable. Quantum molecular dynamics calculations of TM@Zn$_i$S$_i$ showed that while few TM keep inside the cage during the simulation time, some others move towards the surface, leading to more stable surface structures. The large amount of TM@Zn$_i$S$_i$ structures along with the high cost of each quantum dynamical
simulation made impossible to carry out these simulations for all structures. Therefore, we have followed another methodology to study the thermal stability of the endohedral compounds. Based on the calculated energy differences between the endohedral compounds and the TS compounds that connect the formers with the surface structures, we have estimated the lifetime of each endohedral structure. Both methodologies are in agreement in predicting Zn@Zn₁₂S₁₂ as the most stable structure with a lifetime of around three days. The other endohedral compounds have much smaller lifetimes, but large enough for experimental detection. Summarizing, endohedral TM@Zn₁₂S₁₂ compounds are less thermally stable than X@Cd₃S₁₄ compounds, although they are thermodynamically more stable than the alkali metal doped structures. The lack of coulombic repulsion, along with the high capacity of the TM to coordinate with more atoms may explain why TM are stabilized in surface structures.

4.2 Future Work

Nowadays, the possibility of synthesizing new solids with clusters as building blocks is gaining momentum due to recent experimental advances that allow the production of clusters of a given size and composition. Cluster-assembled materials are of great interest because they exploit the uniqueness of clusters and situate them among potentially functional materials [4, 117, 119]. These materials serve as a link between the predictable size-invariant properties of solids and the evolution in properties observed at the nanometer scale where every atom counts [119]. In this context the future work could lead with two different areas, namely, the design of new building blocks stable enough to be useful in nanotechnology, and the assembling of these new building blocks in the design of new materials with the desired properties.

Related with the further design of building blocks, among all possibilities two ideas appear to be the most exciting for us. On the one hand, it would be very interesting to estimate the lifetimes of the endohedral X@Cd₃S₁₄ compounds in the same vein as estimated those of the TM@Zn₁₂S₁₂ nanoclusters. In addition to this, the short lifetimes of the characterized TM@Zn₁₂S₁₂ nanoclusters make it impossible to use them in the design of new materials with magnetic properties. One possibility in order to increase the thermal stability of nanoclusters with magnetic properties could be to incarcerate charged transition metals. Of course, the thermodynamical stability of such compounds would decrease, due to the repulsive interactions with the positively charged Zn atoms of the nanocluster. However, this repulsion would also prevent the transition metal to move towards the surface of the nanocluster, increasing in this way the energetical barrier and their lifetimes. It would be very interesting to confirm this hypothesis, and we will work on it.

The building blocks characterized in this work, and those characterized in the future, can be linked together in assembled materials, like fulleranes into fullerites. The properties of these materials would differ from those of the other related solids in the same vein as fullerite properties differ from graphite and diamond properties. Recently, solid structures based on magic X₁₂Y₁₂ compounds, like Mg₁₂O₁₂ and Zn₁₂O₁₂ [32], B₁₂N₁₂ [33, 34] and bare and endohedral X@Zn₁₂S₁₂ [35] structures have been characterized. These X₁₂Y₁₂ compounds are built by six squares and eight hexagons, with pairs of squares located at opposite positions in each cartesian axis. These structural pattern allow these materials to be assembled into different manners, based on edge-edge, square-square, or hexagon-hexagon interactions, respectively.

Considering X@Zn₁₂S₁₂ as the building blocks, Matxain et. al. characterized the solids based on square-square interactions. The bare Zn₁₂S₁₂ assembled solid was predicted to have a band gap of 2.2 eV, much smaller than ZnS zinkblende, which is 3.6 eV. This band gap was further reduced by 0.4 eV upon doping these cages endohedrally with alkali metals and halogens. However, the solids based on hexagon-hexagon and edge-edge interactions are not characterized yet. It would be very interesting to characterize them and compare their predicted properties with other solids. The X@Cd₃S₁₄ nanoclusters presented in this work, doped with alkali metals and halogens, behave qualitatively in a similar way as the related X@Cd₃S₁₄ nanoclusters do. Therefore, they could be assembled in a similar way. Concretely, the assembling of X@Cd₁₂S₁₂ nanoclusters in square-square, hexagon-hexagon and edge-edge solids could be studied.

New materials with spin-transport properties are very promising due to their potentially interesting device applications. Spintronic devices such as spin transistors, spin light-emitting diodes, non-volatile memory, logic devices, optical isolators and ultrafast optical switches are some of the areas of interest for introducing the (anti)ferromagnetic properties in a semiconductor [120, 121], along with their applications in biomedicine. TM doped II-VI materials like vanadium doped ZnO films [122], as well as Mn-doped ZnO films [123] have been recently synthesized. TM@Zn₁₂S₁₂ nanoclusters doped with first-row transition-metals are not useful in principle due to the short lifetime. Nevertheless, if materials with longer lifetimes were characterized by the use of charged transition metals as
in [37], new assembled materials with magnetic properties could be made. Materials whose predicted magnetism could be switched from ferromagnetism to antiferromagnetism, or on the other way around, could be characterized similar to the Mn@Sn\(_{12}\) dimers [38].
Bibliography


Chapter 5

Appendix A

Supplementary Material
5.1 Influence of $\Delta E_{PAO}$ and $E_{Cutoff}$ in X@Cd$_{12}$S$_{12}$ dynamics simulations

Figure 5.1: (Na@Cd$_{12}$S$_{12}$)$^+$, using different $\Delta E_{PAO}$ and $E_{Cutoff}$.

- $\Delta E_{PAO} = 150$ meV $E_{Cutoff} = 200$ Ry
- $\Delta E_{PAO} = 50$ meV $E_{Cutoff} = 300$ Ry
Figure 5.2: \( (K@Cd_{12}S_{12})^+ \), using different \( \Delta E_{PAO} \) and \( E_{Cutoff} \).
\[
\Delta E_{PAO} = 150 \text{ meV} \quad E_{Cutoff} = 200 \text{ Ry}
\]
\[
\Delta E_{PAO} = 50 \text{ meV} \quad E_{Cutoff} = 300 \text{ Ry}
\]
Figure 5.3: \( K@Cd_{12}S_{12} \), using different \( \Delta E_{PAO} \) and \( E_{Cutoff} \).
\( \Delta E_{PAO} = 150 \text{ meV} \ E_{Cutoff} = 200 \text{ Ry} \)
\( \Delta E_{PAO} = 50 \text{ meV} \ E_{Cutoff} = 300 \text{ Ry} \)
Figure 5.4: $(Cl@Cd_{12}S_{12})^-$, using different $\Delta E_{PAO}$ and $E_{Cutoff}$.

$\Delta E_{PAO} = 150$ meV $E_{Cutoff} = 200$ Ry  \hspace{1cm} $\Delta E_{PAO} = 50$ meV $E_{Cutoff} = 300$ Ry

Cl-Center distance

Total Energy
Figure 5.5:  

Cl@Cd_{12}S_{12}, using different $\Delta E_{PAO}$ and $E_{Cutoff}$.  

- $\Delta E_{PAO} = 150$ meV $E_{Cutoff} = 200$ Ry  
- $\Delta E_{PAO} = 50$ meV $E_{Cutoff} = 300$ Ry
Figure 5.6: $(\text{Br@Cd}_{12}\text{S}_{12})^-$, using different $\Delta E_{PAO}$ and $E_{\text{Cutoff}}$.

- $\Delta E_{PAO} = 150 \text{ meV}$, $E_{\text{Cutoff}} = 200 \text{ Ry}$
- $\Delta E_{PAO} = 50 \text{ meV}$, $E_{\text{Cutoff}} = 300 \text{ Ry}$
5.2 Properties of characterized \((Na\overline{C}d_{i}S_{i})\) local minima

Table 5.1: Cavity within the Cluster, the distance of the guest atom with respect to the center of the cluster \((R^{LM})\), \(r_{cavity}\) (Å), the Free Energy of Complexation, \(\Delta G_{inc}\), in Kcal/mol, the Charge of the endohedral Atom, \(q_{x}\), and the Ionization Energies, in eV

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5.3 Dynamics of the calculated \((X\overline{C}d_{i}S_{i})\) clusters, \(X=K, Cl, Br\)
Figure 5.8: $K@Cd_{12}S_{12}$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the $K@Cd_{12}S_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped K atom from the center of mass of the nanocluster as a function of time.
Figure 5.9: $K@Cd_{15}S_{15}$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the $K@Cd_{12}S_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped K atom from the center of mass of the nanocluster as a function of time.
Figure 5.10: $K@Cd_{16}S_{16}$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the $K@Cd_{12}S_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped K atom from the center of mass of the nanocluster as a function of time.
Figure 5.11: Cl@Cd₉S₉. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the K@Cd₁₂S₁₂ one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped Cl atom from the center of mass of the nanocluster as a function of time.
Figure 5.12: Cl@Cd$_{15}$S$_{15}$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the K@Cd$_{12}$S$_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped Cl atom from the center of mass of the nanocluster as a function of time.
Figure 5.13: Cl@Cd_{16}S_{16}. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the K@Cd_{12}S_{12} one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped Cl atom from the center of mass of the nanocluster as a function of time.
Figure 5.14: \((\text{Cl}\text{Cd}S)^-\). Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the \(\text{K}\text{Cd}S\) one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped Cl atom from the center of mass of the nanocluster as a function of time.
Figure 5.15: $(Cl@Cd_{12}S_{12})^-$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the $K@Cd_{12}S_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped Cl atom from the center of mass of the nanocluster as a function of time.
Figure 5.16: \((\text{Cl@Cd}_{16}\text{S}_{16})^-\). Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the \(K\@Cd_{12}\text{S}_{12}\) one. Below, the variation of the energy, in eV (left) and the variation of the distance, \(R\), in Å (right), of the trapped Cl atom from the center of mass of the nanocluster as a function of time.
Figure 5.17: Br@Cd$_9$S$_9$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the K@Cd$_{12}$S$_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped Br atom from the center of mass of the nanocluster as a function of time.
Figure 5.18: $Br_{@Cd_{12}S_{12}}$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the $K_{@Cd_{12}S_{12}}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, $R$, in Å (right), of the trapped Br atom from the center of mass of the nanocluster as a function of time.
Figure 5.19: $Br@Cd_{15}S_{15}$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the $K@Cd_{12}S_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, $R$, in Å (right), of the trapped Br atom from the center of mass of the nanocluster as a function of time.
Figure 5.20: \( Br@Cd_{16}S_{16} \). Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the \( K@Cd_{12}S_{12} \) one. Below, the variation of the energy, in eV (left) and the variation of the distance, \( R \), in Å (right), of the trapped Br atom from the center of mass of the nanocluster as a function of time.
Figure 5.21: \((Br@Cd_9S_9)^-\). Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the \(K@Cd_{12}S_{12}\) one. Below, the variation of the energy, in eV (left) and the variation of the distance, \(R\), in Å (right), of the trapped Br atom from the center of mass of the nanocluster as a function of time.
Figure 5.22: $(Br@Cd_{12}S_{12})^-$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the $K@Cd_{12}S_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, $R$, in Å (right), of the trapped Br atom from the center of mass of the nanocluster as a function of time.
Figure 5.23: $(Br@Cd_{15}S_{15})^-$. Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the $K@Cd_{12}S_{12}$ one. Below, the variation of the energy, in eV (left) and the variation of the distance, R, in Å (right), of the trapped Br atom from the center of mass of the nanocluster as a function of time.
Figure 5.24: \((Br@Cd_{16}S_{16})^-\). Top: Dynamical trajectories of the K atom inside the nanocluster. This plot was prepared as the \(K@Cd_{12}S_{12}\) one. Below, the variation of the energy, in eV (left) and the variation of the distance, \(R\), in Å (right), of the trapped Br atom from the center of mass of the nanocluster as a function of time.