Quantum and Classical Studies of Calcium and Zinc Clusters and of Pyrrole Oligomers

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By

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# Dedication

For my family, who offered me unconditional love and support throughout the course of this dissertation.

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# List of Abbreviations

DFT	Density Functional Theory
B3PW91	Becke-Perdew-Wang 1991
HF	Hartree-Fock
MD	Molecular Dynamics
MC	Monte Carlo
MMC	Metropolis Monte Carlo
ATMC	Adaptive Tempering Monte Carlo
ТВ	Tight-Binding
BE	Binding Energy
EA	Electron Affinity
E	Electronic Energy
CC	Coupled-Clusters
Ру	Pyrrole
PPy	Polypyrrole
INDO	Intermediate Neglect of Differential Overlap
CNDO	Complete Neglect of Differential Overlap
MNDO	Modified Neglect of Diatomic Overlap
НОМО	Highest Occupied Molecular Orbit
LUMO	Lowest Unoccupied Molecular Orbit

#### Abstract

# QUANTUM AND CLASSICAL STUDIES OF CALCIUM AND ZINC CLUSTERS AND OF PYRROLE OLIGOMERS

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An all electron hybrid density functional approach (DFT) with very large basis sets was used for studying Ca<sub>2</sub> through Ca<sub>19</sub> and Zn<sub>3</sub> through Zn<sub>11</sub> neutral clusters and their cluster anions. Energetics, structure and vibrational analysis of all these neutral clusters and cluster anions are reported. The calculated electron affinities (EA) are in excellent agreement with experiment. Additionally, the electron detachment binding energies (BE) up to Ca<sub>6</sub><sup>-</sup> and Zn<sub>6</sub><sup>-</sup> were identified by analyzing the ground and excited states of the cluster anions and of their corresponding neutral clusters. The theoretical BE is in very good agreement with experiment for both calcium and zinc cluster anions.

Polypyrrole (PPy) is a conjugated polymer prototype of conducting polymers. The energetically preferred spatial conformation and charge distribution of n-Py oligomers (n = 1 - 24) in both the reduced and oxidized phases are obtained and analyzed in this work within the hybrid density functional theory. Binding energies, HOMO-LUMO gap energies, radius of gyration, end-to-end distance and vibrational frequencies are reported as a function of oligomer length. The band structure of infinite PPy gives a band gap energy in excellent agreement with experiment for reduced PPy. Evolution of the band gap and the charge-localized states as a function of PPy oxidation level is reported.

Based on the DFT results of n-Py oligomers, a classical potential model to treat dense systems of PPy is developed within a modified rigid-ion polarizable force field. This model potential is then used in the Adaptive Tempering Monte Carlo and the Metropolis Monte Carlo simulations of a 192 4-Py system and 64 12-Py system at different densities. The energy, end to end distance, radius of gyration and order parameter as a function of density are inspected. It is shown that these systems have the structural characteristics of liquids. However, the calculations show that as the density is increased, the system develops regions of stacked chains.

#### Chapter 1: Introduction

#### 1.1 Background

Research associated to mathematical models, numerical techniques and solutions of scientific problems are central to the emerging field of computational sciences. The scientific challenge in this field is to gain understanding through the analysis of mathematical models implemented in high performance computers.

The study of calcium and zinc clusters and their cluster anions, polypyrrole conducting polymers, and the simulation of dense liquids of n-pyrrole oligomers are very computational intensive. Additionally, these subjects are based on fundamental theoretical concepts and possess a high degree of complexity. In order to obtain meaningful predictions in these areas, massive amounts of computations are required. This dissertation addresses all three above mentioned areas of research as summarized in the following sub-sections.

#### 1.1.1 Calcium and Zinc Clusters and Cluster Anions

Metal clusters span the gap between the atomic and the bulk length scales and their study furthers the understanding of the electronic behavior of metals at the nanoscale [1–3] attracting interest of both experimental and theoretical scientists. Today, a wide range of the experimental techniques, such as mass spectrometry [4,5], plasma excitation [6,7], negative ion photoelectron spectroscopy [8], among others, exist to study the structure characterization and electronic properties of nano metal clusters. Numerous experiments have been done for small clusters of metal elements. In 1989, the photoelectron spectra of the alkali metal cluster anions:  $Na_{n=2-5}^{-}$ ,  $K_{n=2-7}^{-}$ ,  $Rb_{n=2-3}^{-}$ , and  $Cs_{n=2-3}^{-}$  were reported by K. M. Mchugh et al [9]. Photoelectron spectra of cold Ti anion clusters containing 1-130 atoms were investigated in 2003, which provided a well-resolved electronic structure of these clusters. Furthermore, the electron affinity versus cluster size was probed experimentally [10]. The electronic structures of V<sup>-</sup> and V<sup>2-</sup> doped Co<sub>n</sub> clusters were compared to those of pure Co<sub>n</sub> clusters and electron affinities and electron detachment energies were measured in 2002 [11]. Calcium and zinc are two elements in the 4th row of the periodic table for which experiments on the electron affinity [12] and the electron detachment spectra [12,13] have been reported recently. It is therefore important and feasible to theoretically study the underlying electronic states involved in the experimental process. Theoretical studies to investigate the geometric and electronic structure of small neutral and charged metal clusters is an active field in cluster science. Density functional theory (DFT) is a widely used first principles method. Hartree-Fock (HF) is another popular theoretical method used to study small nano clusters. For large size clusters, molecular dynamics (MD) and Monte Carlo (MC) might be a better choice when good potential functions exist for representing the system.

The first part of this dissertation focuses on a first principles study of the energetics, structure and electron detachment spectra of calcium and zinc neutral and anion clusters. The theoretical computational research done in this dissertation may be helpful to explain the experimental photoelectron detachment results of calcium and zinc clusters, thus advancing the knowledge on these systems. This part of the dissertation is described in Chapter 2 where the energetics, structure and electron detachment spectra of calcium and zinc neutral and anion clusters are analyzed using a hybrid density functional approach. The results are compared to experimental data and show excellent agreement.

#### 1.1.2 Conducting Polymers: Polypyrrole

All carbon based polymers were believed to be insulators before a novel class of polymers known as "conductive polymers" or "electroactive polymers" were discovered. Well known conjugated polymers that belong to the class of conductive polymers include polyacetylene, polypyrrole, polythiophene, polyaniline, polyfluorene, polytetrathiafulvalenes, polynaphthalene, etc. In general, conducting polymers are semiconductors. However, once the conducting polymer is oxidized, then it becomes a conductor. The conductivity depends on temperature, density of charged carriers and how fast the carriers move in the material. The doped conducting polymers combine mechanical properties of plastics, such as flexibility, toughness, malleability, elasticity with high electrical conductivities. These conducting polymers properties have attracted the attention of many scientists.

Conducting polymers are now being used in a multitude of different applications. For example, the discovery of photoinduced charge transfer between polymers and their environment (either a substrate or solid solvent) has led to efficient heterojunctions of polymer/substrate with important applications in solar cells and chemical detectors. It is confirmed that some of the conducting polymers, such as polyaniline, can be used for corrosion protection of metals [14]. The most highly used material for corrosion protection is zinc. Zinc is proned to loose electrons to oxygen, so zinc coatings do not last long. Polymer coatings prevent the metal underneath from being oxidized such that polyaniline is a better candidate than zinc for effectively preventing rusting. Polyaniline stops corrosion by accepting electrons from the metal, donating them to oxygen and forming a layer of pure metal oxide [15]. Conducting polymers, particularly the soluble type, can be used as an alternative charge dissipator for e-beam lithography because of their easy processability and high conductivity [16]. Conducting polymers can also be used for metallization, especially in printed circuit board technology [17–21]. Electrostatic discharge protection for electronic components is another important application of conducting polymers [22].

Polypyrrole (PPy) is a prototypical conducting polymer. Because of its chemical stability, high conductivity, and easy manufacture, PPy is one of the most studied conducting polymers. PPy is a good candidate for photonic devices [23,24] and chemical sensors [25] due to its strong electrical and optical anisotropies. PPy actuators exhibit large electrochemically induced strains and stresses, which could be exploited for artificial muscles [26,27]. DFT has become a popular method for first principles studies of small molecular systems. Within DFT, the geometry of a system is determined very accurately and spectroscopic observations such as electronic spectrum, atomic vibrations, electronic excitations and multiple ionization energies are well interpreted.

Monte Carlo methods are based on the use of random numbers and statistics to investigate problems related to thermodynamics. These methods can be used to compute the thermal equilibrium properties of classical many-body systems. Because the study of large systems with DFT is computationally intractable, researchers use the MC method to study very large molecular systems. D. Xiao and E. Blaisten-Barojas developed the Adaptive Tempring Monte Carlo (ATMC) method [28], which can be used to optimize the solid and liquid structures at low temperatures.

The conducting polymer part of this dissertation is focused on studies using DFT, MC and ATMC methods, which are described in detail in the next sections of this chapter. Chapter 3 reports the DFT results on n-Py oligomers, including energetics, stucture and charge distribution of reduced and oxidized n-Py oligomers. Chapter 4 contains the development of a new model potential for n-pyrrole, which is afterwards used in ATMC and regular MC studies. This chapter contains the description of the novel model potential and the strategy used for fitting its parameters. Additionally, different n-Py dense systems of many oligomers at different densities are studied and their dynamical and thermodynamics properties are presented in this chapter.

#### 1.2 Methodology

#### **1.2.1** Density Functional Theory

Density functional theory (DFT) is an extremely successful approach for the description of ground state properties of metals, semiconductors, and insulators. The success of density functional theory not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes [29]. Density functional theory is based on Hohenberg-Kohn theorems [30] showing that an interacting system of fermions can be described via its density  $\rho$  instead of its many-body wave function  $\psi$ . For N electrons in a solid, which obey the Pauli principle and repel each other via the Coulomb potential, this means that the basic variable of the system depends only on three spatial coordinates x, y, and z rather than 3N degrees of freedom. A variational principle for finding  $\rho$  exists. The ground state energy  $E_0$  as a function of  $\rho_0(r)$ is

$$E_0 = E[\rho_0(r)]$$
 (1.1)

where

$$\rho_0(r) = \int |\psi_0(r, r_2, \cdots, r_n)|^2 dr_2 \cdots dr_n$$
(1.2)

The ground-state energy is a functional of  $\rho_0$ :

$$E[\rho_0] = \langle \psi_0 | \hat{H} | \psi_0 \rangle = T[\rho_0] + V_{Ne}[\rho_0] + V_{ee}[\rho_0]$$
(1.3)

where  $\langle \psi_0 | \hat{V}_{Ne} | \psi_0 \rangle$  can be written explicitly in terms of the density:

$$V_{Ne} = \int \rho_0(r)v(r)dr \tag{1.4}$$

Where v(r) is the electrostatic interaction between electrons and the nuclei. Assuming one has reliable expressions of T and  $V_{ee}$ , a successful minimization of the energy will yield the ground-state density  $\rho_0$  and thus all other ground-state observables. However, there are two unknowns in Eq. 1.3: T[ $\rho_0$ ] and V<sub>ee</sub>[ $\rho_0$ ].

Kohn-Sham proposed a fictitious reference system of non-interacting electrons. The Hamiltonian of the reference system is:

$$\hat{H}_s = \sum_{i=1}^n \left[ -\frac{1}{2} \nabla_i^2 + V_s(r_i) \right] \equiv \sum_{i=1}^n \hat{h}_i^{KS}$$
(1.5)

By solving the Schrodinger equation of this reference system,

$$\hat{h}_i^{KS} \theta_i^{KS} = \epsilon_i^{KS} \theta_i^{KS} \tag{1.6}$$

the electron density can be calculated:

$$\rho = \rho_s = \sum_{i=1}^{n} |\theta_i^{KS}|^2$$
(1.7)

Kohn and Sham rewrote the Hohenberg-Kohn Eq. 1.3 as follows. Define  $\Delta \overline{T}$  to be the average kinetic energy difference between the real system ground-state kinetic energy and the reference system of non-interacting electrons:

$$\Delta \bar{T}[\rho] \equiv \bar{T}[\rho] - \bar{T}_s[\rho] \tag{1.8}$$

where

$$\bar{T}_s[\rho] = -\frac{1}{2} \sum_{i=1}^n \langle \theta_i^{KS}(l) | \nabla_l^2 | \theta_i^{KS}(l) \rangle$$
(1.9)

Similarly define

$$\Delta \bar{V}_{ee}[\rho] \equiv \bar{V}_{ee}[\rho] - \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2$$
(1.10)

where the quantity  $\frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2$  is the classical expression for the electrostatic interelectronic energy of electrons smeared out in continuous distribution of charge with electron density  $\rho$ . With the definitions above, Eq. 1.3 becomes:

$$E_{v}[\rho] = \int \rho(r)v(r)dr + \bar{T}_{s}[\rho] + \frac{1}{2} \int \int \frac{\rho(r_{1})\rho(r_{2})}{r_{12}}dr_{1}dr_{2} + \Delta \bar{T}[\rho] + \Delta \bar{V}_{ee}[\rho]$$
(1.11)

The functionals  $\Delta \bar{T}$  and  $\Delta \bar{V}_{ee}$  are unknown. Defining the exchange-correlation energy

functional as  $E_{xc}[\rho] \equiv \Delta \overline{T}[\rho] + \Delta \overline{V}_{ee}[\rho]$ , so

$$E_0 = E_v[\rho] = \int \rho(r)v(r)dr + \bar{T}_s[\rho] + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 + E_{xc}[\rho]$$
(1.12)

where,

$$\int \rho(r)v(r)dr = -\sum_{\alpha} Z_{\alpha} \int \frac{\rho(r_1)}{r_{1\alpha}} dr_1$$
(1.13)

Hohenberg and Kohn showed that if  $\rho$  varies extremely slowly with position, then  $E_{xc}[\rho]$  is accurately given with the Local-Density Approximation (LDA),

$$E_{xc}^{LDA}[\rho] = \int \rho(r)\varepsilon_{xc}(\rho)dr \qquad (1.14)$$

$$\varepsilon_{xc}(\rho) = -\frac{3}{4} (\frac{3}{\pi})^{\frac{1}{3}} (\rho(r))^{\frac{1}{3}} + \varepsilon_c^{VWN}(\rho)$$
(1.15)

For open-shell molecules and molecular geometries near dissociation, the Local-Spin-Density Approximation (LSDA) gives better results than the LDA. In LDA, electrons with opposite spins are paired with each other and have the same spatial KS orbital whereas the LSDA allows such electrons to have different spatial KS orbitals  $\theta_{i\alpha}^{KS}$  and  $\theta_{i\beta}^{KS}$ . The LDA and LSDA are based on the uniform-electron-gas model, which is appropriate for a system where  $\rho$  varies slowly with position. The integrand in the expression for  $E_{xc}^{LDA}$  is a function of only  $\rho$ , and the integrand in  $E_{xc}^{LSDA}$  is a function of only  $\rho^{\alpha}$  and  $\rho^{\beta}$ . Functionals that go beyond the LSDA aim to correct the LSDA for the variation of the electron density with position is Generalized-Gradient Approximation (GGA). They do this by including the gradients of  $\rho^{\alpha}$  and  $\rho^{\beta}$  in the integrand. Thus

$$E_{xc}^{GGA}[\rho^{\alpha},\rho^{\beta}] = \int f(\rho^{\alpha}(r),\rho^{\beta}(r),\nabla\rho^{\alpha}(r),\nabla\rho^{\beta}(r))dr$$
(1.16)

Hybrid exchange-correlation functionals are widely used. For example, the B3PW91 (or Becke3PW91) hybrid functional is defined by

$$E_{xc}^{B3PW91} = (1 - a_0 - a_x)E_x^{LSDA} + a_0E_x^{HF} + a_xE_x^{B88} + (1 - a_c)E_c^{VWN} + a_cE_c^{PW91}$$
(1.17)

where

$$E_x^{LSDA} = -\frac{3}{4} (\frac{6}{\pi})^{1/3} \int [(\rho^{\alpha})^{4/3} + (\rho^{\beta})^{4/3}] dr$$
(1.18)

$$E_x^{HF} \equiv -\frac{1}{4} \sum_{i=1}^n \sum_{j=1}^n \langle \theta_i^{KS}(1) \theta_j^{KS}(2) | 1/r_{12} | \theta_j^{KS}(1) \theta_i^{KS}(2) \rangle$$
(1.19)

$$E_x^{B88} = E_x^{LSDA} - b\Sigma_{\sigma=\alpha,\beta} \int \frac{(\rho^{\sigma})^{4/3} \chi_{\sigma}^2}{1 + 6b\chi_{\sigma} sinh^{-1}\chi_{\sigma}} dr$$
(1.20)

 $E_c^{VWN}$  is a very complicated known function of  $\rho$  by Vosko, Wilk, and Nusair.

#### 1.2.2 Metropolis Monte Carlo Methods

The Metropolis Monte Carlo (MMC) method is powerful for calculating averages in the canonical ensemble for systems with constant number of molecules N, constant volume V, and constant temperature T. Assume that A is a property of an N-body system, then its average  $\langle A \rangle$  in the canonical ensemble is:

$$\langle A \rangle = \frac{1}{\mathcal{Z}} \int d\mathbf{r}^N exp[-\beta \mathcal{E}(\mathbf{r}^N)] A(\mathbf{r}^N)$$
 (1.21)

where  $\mathbf{r}^N$  stands for the coordinates of all N particles,  $\beta = 1/k_B T$ ,  $k_B$  is Boltzmann's constant,  $\mathcal{E}$  is the configurational potential energy of the system and  $\mathcal{Z}$  is the partition function given by the following expression:

$$\mathcal{Z} = \int d\mathbf{r}^N exp[-\beta \mathcal{E}(\mathbf{r}^N)] \tag{1.22}$$

The integral in Eq. 1.21 can be calculated by an unrestricted Monte Carlo method. However, accumulating the integrand at randomly generated values of the independent variables is very inefficient because the Boltzmann factor  $exp(-\beta \mathcal{E})$  is very small most of the times at any temperatures. In fact, there are only a restricted number of configurations that may contribute significantly to Eq. 1.21. The Metropolis Monte Carlo method (MMC) is an important sampling scheme that allows for selection of those configurations that contribute the most to Eq. 1.21.

The MMC method is a computational approach for generating a set of m configurations of the system such that only ratios of probability  $P = exp(-\beta \mathcal{E}/E)$  come into play:

$$\frac{P_{i+1}}{P_i} = exp\{-\beta[\mathcal{E}(\mathbf{r}_{i+1}^N) - \mathcal{E}\mathbf{r}_i^N)]\}$$
(1.23)

where  $\mathbf{r}_{i}^{N}$ ,  $\mathbf{r}_{i+1}^{N}$  are two contiguous configurations in a Markov chain. The MMC algorithm can be implemented as follows. First step, generate a configuration  $\mathbf{r}_{old}^{N}$  for the system. Second step, generate a new configuration  $\mathbf{r}_{new}^{N}$  by moving one of the N atoms by a small random displacement. Third step, decide whether the new configuration is to be accepted with probability  $P_{old \rightarrow new} = exp\{-\beta[\mathcal{E}(\mathbf{r}_{new}^{N}) - \mathcal{E}(\mathbf{r}_{old}^{N})]\}$  or rejected with probability (1- $P_{old \rightarrow new}$ ). Formally this is written as:

$$accept = min(1, exp\{-\beta[\mathcal{E}(\mathbf{r}_{new}^N) - \mathcal{E}(\mathbf{r}_{old}^N)]\})$$
(1.24)

If the new configuration is such that  $\mathcal{E}(\mathbf{r}_{new}^N) < \mathcal{E}(\mathbf{r}_{old}^N)$ , this move is accepted because accept = 1. If the new configuration is such that  $\mathcal{E}(\mathbf{r}_{new}^N) \geq \mathcal{E}(\mathbf{r}_{old}^N)$ , this configuration is probabilistically accepted since  $accept = exp\{-\beta[\mathcal{E}(\mathbf{r}_{new}^N) - \mathcal{E}(\mathbf{r}_{old}^N)]\} \leq 1$ . In practice, accept is implemented by calling a random number from a uniform distribution in the interval [0,1] [31]. If  $accept \leq$  the random number, the configuration is accepted; otherwise the configuration is rejected. If the new configuration is rejected, the old configuration is

referred to as "new" and the three-step process is repeated. The average of property, Eq. 1.21, is evaluated as a sum over all new configurations accepted and the old configurations that were re-labled as new:

$$\langle A \rangle = \frac{1}{m} \sum_{i=1}^{m} A(\mathbf{r}_m^N)$$
(1.25)

For MC simulations a few million configurations are generally needed to obtain adequate statistics [32].

#### **1.2.3** Adaptive Tempering Monte Carlo

The Adaptive Tempering Monte Carlo (ATMC) was developed by X. Dong and E. Blaisten-Barojas in 2006 [28]. In the ATMC, the temperature adapts according to changes occurring in a configuration so that a multitude of  $NVT_i$  canonical ensembles are considered along a simulation. Each canonical ensemble  $NVT_i$  is simulated with the Metropolis Monte Carlo with fixed number of steps  $m_{fix}$  and all of the ensembles are connected along the simulation by a super-Markov chain. The ATMC is a method to optimize a system into its most ordered state, which is usually the ground state with lowest possible potential energy at zero temperature. The transition probabilities for temperature changes, either going up (+) or going down (-), are given by:

$$p_{+} = exp[-(E - \langle E \rangle)(\frac{1}{k_{B}(T + \Delta T)} - \frac{1}{k_{B}T})]/Q$$

$$p_{-} = exp[-(E - \langle E \rangle)(\frac{1}{k_{B}(T - \Delta T)} - \frac{1}{k_{B}T})]/Q$$
(1.26)

where E is the MMC one-step configuration energy at  $T, \langle E \rangle$  is the MMC average energy over  $m_{fix}$  steps at T, and Q is a normalization factor which keeps  $p_+ + p_- = 1$ . The  $\Delta T$  is the estimated adaptive local temperature change given by:

$$\Delta T = \frac{T}{1 - \delta E / (\ln(a)k_B T)} \tag{1.27}$$

Here  $\delta E$  is the standard deviation of the energy about the average  $\langle E \rangle$  over  $m_{fix}$  = fixed number of MMC trials at temperature T. Both  $m_{fix}$  and  $\ln(a)$  are parameters.

Within an ATMC simulation, an optimized structure of the system is obtained at low temperature.

#### **1.3** Summary of Dissertation Contents

This dissertation includes three parts: 1) DFT study of calcium and zinc clusters and cluster anions described in Chap. 2. 2) DFT study of pyrrole oligomers and polypyrrole in the reduced and oxidized phases described in Chap. 3. 3) Development of a simulation of dense systems composed of many molecules is described in Chap. 4. Chap. 5 lists details of code implementation for the computational simulations and Chap. 6 summarizes the conclusion.

# Chapter 2: Energetics, Structure and Electron Detachment Spectra of Calcium and Zinc Neutral and Anion Clusters Study with A Density Functional Theory

#### 2.1 Introduction

Calcium is the fifth most abundant element on the earth and plays an essential role for living organisms, compounds and mechanisms. In the past few years much attention was gained to calcium clusters such that energetics, structure, vibrational frequencies and thermodynamic properties have been studied in detail from various perspectives. J. W. Mirick et. al [33] studied the electronic structure of calcium clusters containing up to 13 atoms with DFT. The fission and evaporation of doubly ionized calcium clusters was studied also with DFT method by E. Blaisten-Barojas et. al in 2004 [34]. In the same year, another publication addressed the structural electronic and dynamical properties of calcium nanoclusters up to 84 atoms with a tight-binding method [35]. More recently, calcium clusters containing 15 to 32 atoms were studied by X. Dong with the adaptive tempering Monte Carlo method (ATMC) [28]. Although much research has been done on neutral calcium clusters, the calcium cluster anions have received much less attention. Specifically, their electronic properties are not well known, although their importance for the theoretical description of electron detachment spectroscopy [12].

Zinc is the fourth most common metal in use, trailing only to iron, aluminium, and copper in annual production and it belongs to the IIB column of the periodic table of the elements. Bulk bonding features of group IIB elements are transient from van der Waals to covalent and finally to metallic. For this reason metals in the IIB group are interesting from the perspective of sub-nanometer scale systems. Among these elements, Hg clusters are the most extensively studied [36–42] and clusters of cadmium compounds, such as cadmium sulfide clusters [43–45], cadmium-helium clusters [46], cadmium selenide clusters [47, 48] have received much attention. In 1989, I. Katakuse et al did the experiment to analyze the mass distributions of positive and negative pure cluster ions of zinc and cadmium [49]. To a lesser extent, Zn clusters have been studied both experimentally [12, 13, 49, 50] and theoretically [51–53]. Oleg Kostko [13] presented the photoelectron spectra of zinc anion clusters with photoelectron spectroscopy experiment and Weijun Zheng [12] obtained the same results with the same experiment as Kostko's in his dissertation. Flad et al [51] used the coupled-cluster method including all single and double excitations with a pertubative treatment of the triple excitations to study small clusters of 12 atoms. J. Wang [52] performed the geometry optimizations of zinc clusters with up to 20 atoms using Broyden-Fletcher-Goldfarb-Shanno algorithm, with a convergence criterion of  $10^{-3}$  a.u. Recently K. Iokibe [53] published another paper which used different kind of DFT methods to study the zinc cluster up to 32 atoms. These theoretical studies, however, address neutral zinc clusters only and little is known about the zinc cluster anions.

In this dissertation, I perform an exhaustive all-electron study within hybrid density functional theory of the ground state of neutral clusters and their cluster anions for sizes up to  $Ca_{19}$  and up to  $Zn_{11}$ . Such study gives insight on the energetics, structure, and vibrational analysis and allows for comparison of the electron affinity to the available experimental results. Additionally, the excited states of the smaller neutral clusters and their cluster anions up to n=6 were studied for both calcium and zinc. Knowledge of the excited states of both neutrals and anions allows for molecular identification of the experimental peaks appearing in the electron detachment energy spectrum. The computational task of finding the excited states of larger than 6-atom clusters is beyond the computational power at my hands and is not attempted in this dissertation.

#### 2.2 Energetics of $Ca_n$ (n=2-19) Neutral and Anion Clusters

All-electron calculations on calcium neutral and anion clusters were carried out within the hybrid Becke density functional theory (DFT), B3PW91, which contains the Perdew-Wang local and non-local correlation functionals [54, 55]. The 6-311G(d) triple valence basis set [56, 57] with s, p, d polarization was used throughout this paper. However, for the small Ca clusters up to n = 11 clusters, the basis set was expanded with d-diffuse functions 6-311+G(d). As expected for calcium, diffuse d-functions decrease marginally the energy of the Ca cluster anions because d-orbital momentum symmetry is absent from the occupied states. All self consistent energy results are accurate up to eight decimals and only the first three or four decimals are reported in the tables. The Gaussian 2003 [58] package was used throughout this chapter of my dissertation.

An exhaustive search for the structures of lowest energy was conducted for each cluster size adopting the following strategy. A multitude of cluster structures from previous studies [28,33–35] were used as initial cluster configurations for the geometry optimization with the purpose of finding the energy minima. This optimization was performed with the Berny algorithm and redundant internal coordinates [59]. Additionally, structures in Table 2.1 were verified to be a minimum by the calculation of the vibrational frequencies. Along this study several other cluster structures were identified to be saddles of different orders of the energy landscape. Up to n = 11, the geometry structures of Ca clusters and cluster anions were optimized with both 6-311G(d) and 6-311+G(d) basis sets. It is demonstrated then, that the structure is the same with or without diffuse d-function. The structures of  $Ca_n$ (n = 2-19) are drawn in Fig. 2.1. The structures of neutral Ca<sub>2</sub> through Ca<sub>13</sub> have been reported in previous work [33] within the same DFT approach. Compared to previous  $Ca_{13}$ reported in Mirick's paper [33], the new  $Ca_{13}$  is two twinned pentagonal bipyramids with two decorated faces but the decorated faces are different. The new Ca<sub>13</sub> structure is more stable than the previous one by 0.116 eV. Ca<sub>13</sub> was seeded with one extra atom to yield  $Ca_{14}$ . The structures of neutral  $Ca_{15}$  through  $Ca_{19}$  obtained at the tight-binding (TB) level

[28] were taken as the initial configurations in my optimization. The optimized geometries are shown in Fig. 2.1 also. Those stuctures are the TB structures with minor deformations that break the symmetry. The most stable structure for  $Ca_{15}$  is a pentagonal bipyramid capped by four atoms on the top and four atoms on the bottom. One more atom added to the cap of  $Ca_{15}$  forms  $Ca_{16}$ . The clusters with n = 17-19 are either amorphous structures or symmetric. Most of them have the same structure as obtained from a Morse model potential.  $Ca_{17}$  has two perpendicularly connected pentagonal bipyramids plus four atoms sitting at the bottom.  $Ca_{18}$  is similar to  $Ca_{17}$  with one more atom decorating a face.  $Ca_{19}$ is an icosahedron with a pentagonal pyramid cap and has  $D_{5h}$  symmetry.

The optimized structures of  $\operatorname{Ca}_n^-$  (n = 2-19) are reported in Fig. 2.2. As for the neutral clusters, the d-diffuse functions do not have a strong effect for the optimized cluster anion structure. A commonality of the cluster anions is a slight structural distortion when compared to the neutral counterparts due to the negative charge. For example,  $\operatorname{Ca}_5^-$  and  $\operatorname{Ca}_6^-$  shown in Fig. 2.2 present slightly elongated bond lengths vis-a-vis of the neutral clusters  $\operatorname{Ca}_5 \operatorname{D}_{3h}$  and  $\operatorname{Ca}_6 \operatorname{C}_{2v}$  reported in Ref. [33]. Comparable distortions yield a less symmetric ( $\operatorname{C}_{2v}$ )  $\operatorname{Ca}_7^-$  instead of the D<sub>5h</sub> neutral cluster.  $\operatorname{Ca}_{12}^-$  is an incomplete icosahedron.  $\operatorname{Ca}_{13}^-$  has the same structure as the neutral isomer reported by Mirick's et. al [33] except that the bond lengths are either elongated or shortened.

The symmetries, electronic structures, binding energies (BEs) and the electron affinities (EAs) of Ca<sub>n</sub> (n = 2-19) for both neutral and cluster anions are reported in Table 2.1. The results with d-diffuse functions are also included in this table, where the binding energy is calculated from the energy difference of the total energy for the Ca<sub>n</sub> with respect to the energy of separated neutral calcium atoms. Electron affinity is calculated as the difference between the total energies of the ground state of the neutral and anion clusters taking into account the zero point energy  $\epsilon_0$  of each state:  $(E + \epsilon_0)_{neutral} - (E + \epsilon_0)_{anion}$ . For calcium clusters, the EAs up to n = 11 were calculated with the 6-311G(d) and 6-311+G(d) basis sets. Although binding energies decrease up to 0.1 eV with the larger basis set, it's clear from Table 2.1 that the expanded basis set with diffuse functions adds minor corrections



Figure 2.1: Structures of the neutral calcium clusters. Bond lengths are rounded off and given in  $\mathring{A}$ .



Figure 2.2: Structure of the calcium cluster anions. Bond lengths are rounded off and given in  $\mathring{A}$ .

Ca		l	Neutral							
$\operatorname{Ca}_n$	$\operatorname{Sym}$	State	E (eV)		$\operatorname{Sym}$	State	$E(\epsilon$	eV)	$\mathbf{E}\mathbf{A}$	(eV)
			(d)	+(d)			(d)	+(d)	(d)	+(d)
2	$D_{\infty h}$	$^{1}\Sigma_{q}^{+}$	-0.1468	-0.1478	$D_{\infty h}$	$^{2}\Pi_{u}$	-0.6417		0.4934	
		U				$^{2}\Sigma_{q}^{+}$		-0.6602		0.5121
3	$D_{3h}$	$^{1}\mathrm{A}_{1}^{\prime}$	-0.6612	-0.6647	$D_{3h}$	${}^{2}A_{2}^{''}$	-1.5491	-1.5538	0.8862	0.8873
4	$T_d$	$^{1}A_{1}$	-1.7751	-1.7836	$T_d$	$^{2}A_{1}$	-2.7160	-2.7393	0.9468	0.9613
5	$D_{3h}$	$^{1}A_{1}$	-2.3948	-2.4159	$D_{3h}$	$^{2}\mathrm{A}_{1}^{\prime}$	-3.3957	-3.4244	1.0100	1.0168
6	$C_{2v}$	$^{1}A_{1}$	-3.0826	-3.1112	$C_{2v}$	$^{2}A_{2}$	-4.2415	-4.2667	1.1612	1.1580
7	$D_{5h}$	$^{1}\mathrm{A}_{1}^{\prime}$	-4.3597	-4.4066	$C_{2v}$	$^{2}A_{2}$	-5.4926	-5.5338	1.1441	1.1387
8	$\mathbf{C}_{s}$	$^{1}A'$	-5.1021	-5.1603	$C_s$	$^{2}\mathrm{A}_{2}^{\prime\prime}$	-6.3802	-6.4305	1.2829	1.2753
9	$C_1$	$^{1}A$	-6.1861	-6.2577	$C_1$	$^{2}A$	-7.5249	-7.5583	1.3389	1.3065
10	$D_{3h}$	$^{1}A_{1}^{\prime}$	-7.5126	-7.5995	$C_1$	$^{2}A$	-8.5409	-8.6128	1.0414	1.0263
11	$C_1$	$^{1}A$	-8.2656	-8.3851	$C_1$	$^{2}A$	-9.4992	-9.5996	1.2376	1.2186
12	$C_1$	$^{1}A$	-9.0720		$C_{5v}$	$^{2}A_{2}$	-10.4271		1.3582	
13	$C_1$	$^{1}A$	-10.2689		$C_1$	$^{2}A$	-11.7244		1.4599	
14	$C_1$	$^{1}\mathrm{A}$	-11.3565		$C_1$	$^{2}A$	-12.8522		1.4957	
15	$C_1$	$^{1}\mathrm{A}$	-12.0087		$C_1$	$^{2}A$	-13.5546		1.5497	
16	$C_1$	$^{1}A$	-13.4332		$C_1$	$^{2}A$	-14.8909		1.4563	
17	$C_1$	$^{1}A$	-15.0069		$C_1$	$^{2}A$	-16.5650		1.5581	
18	$C_1$	$^{1}A$	-16.1052		$C_1$	$^{2}A$	-17.6746		1.5662	
19	$D_{5h}$	$^{1}A'$	-17.6005		$D_{5h}$	$^{2}A_{2}$	-19.0646		1.4621	

Table 2.1: Electronic energies (E) with symmetry and ground state identification of  $Ca_2$  through  $Ca_{19}$  anion and neutral clusters and their electron affinity (EA).

of only a couple of hundredths of eV to the EAs. The effect of the diffuse d-function is important only for  $Ca_2^-$  by producing an inversion of the two lower doublet states.

Fig. 2.3 depicts the second difference of the energy E(n-1) + E(n+1) - 2E(n) of neutral and charged calcium clusters. This second-difference is referred to as the energy stability pattern where the peaks correspond to clusters that are relatively more stable than those with nearest sizes. The solid-line in Fig. 2.3 depicts data for the neutral clusters and the dashed-line pertains to the cluster anions. It is readily apparent that neutral calcium clusters containing 4, 7, 10, 13, 17 have high peaks and are therefore very stable. The energy stability pattern of the anion clusters is similar to that of the neutrals except for the peaks at n = 9, 10. The anion  $Ca_{10}^-$  is less stable than  $Ca_9^-$  and  $Ca_{11}^-$ , whereas the neutral  $Ca_{10}$  is very stable when compared to the neighboring size clusters. Fig. 2.4 (dotted-line-triangles)



Figure 2.3: Stability pattern as a function of calcium cluster size. Dotted lines correspond to cluster anions and full lines to neutral culsters.

are plots of the EA of calcium clusters as a function of size showing the comparison with experimental results (full-line-circles) of Ref. [12]. The qualitative agreement for calcium clusters is excellent. The notorious kink at the 10-atom cluster occurs because neutral  $Ca_{10}$ is very stable (peak in Fig. 2.4) whereas the cluster anion  $Ca_{10}^-$  is relatively not stable (valley in Fig. 2.4). There is a second shallow kink at  $Ca_{16}^-$ , which is barely visible in the experimental results and is also apparent in our results.

### **2.3** Excited States and Frequency Analysis of $Ca_n$ (n = 2-6)

For the small Ca clusters containing 2 to 6 atoms, several excited states are identified for both anion and neutral clusters. As mentioned in section 2.2, these calculations were all done with the expanded basis set 6-311+G(d). Energies, symmetry and state identification of the anions are reported in Table 2.2 along with the normal mode vibrational frequencies for all states. Table 2.3 contains similar results for the Ca neutral clusters. For Ca<sub>2</sub><sup>-</sup> the ground state and three excited states are very close in energy. The bond length of this dimer anion in the ground state is 4.342 Å, which shrinks to 3.943 Å in the first excited state (doublet). In addition, two quartet exited states are identified for Ca<sub>2</sub><sup>-</sup>. For larger cluster anions



Figure 2.4: Electron affinity of calcium as a function of cluster size. Dotted lines correspond to this work and full lines to experiments in Ref[33].

 $Ca_3^-$  through  $Ca_6^-$ , most of the excited states of the cluster anion maintain the ground state geometry which figure with distortions responsible for the symmetry reduction.  $Ca_3^- D_{3h}$  has a bond length of 3.784 Å in the ground state and 3.968 Å in the first excited state. The  $Ca_3^$ quartet excited state is an isosceles triangle with bond lengths 3.589/4.177 Å. The anion  $Ca_4^- T_d$  has bond length of 3.775 Å in the ground state and its fist quartet excited state  $D_{2d}$ is a distorted  $T_d$  structure with bond lengths 3.674/4.339 Å. The second quartet state  $C_1$ corresponds to a  $Ca_4^-$  isomer with planar, almost rhomboidal, structure and bond lengths 3.876/3.693 Å. The  $Ca_5^-$  triangular bipyramid structure with bond lengths 3.883/3.787 Å deforms in the excited states to have four different bond lengths: 3.838/3.955/3.747/3.577 Å in the doublet and 3.832/3.693/4.0/3.599 Å in the quartet. Similarly,  $Ca_6^- C_{2v}$  ground state structure is shown in Fig. 2.2 and the first and second excited states maintain the structure with some deformation. The second quartet-excited state of  $Ca_6^-$  is a slightly deformed octahedron ( $C_1$ ) with bond lengths 3.671/3.667/4.215/4.216 Å, which differs from the ground state geometry.

$Ca_n^-$	Sym	State	E (eV)	Frequency (cm $^{-1}$ )
	$D_{\infty h}$	$^{2}\Sigma_{g}^{+}$	0.0	77
$C_{2}^{-}$	$D_{\infty h}$	$^{2}\Pi_{u}$	0.0116	97
$Oa_2$	$D_{\infty h}$	${}^{4}\Sigma_{u}^{+}$	0.6249	159
	$D_{\infty h}$	${}^{4}\Pi_{g}$	0.7184	143
	$D_{3h}$	$^{2}\mathrm{A}_{2}^{\prime\prime}$	0.0	$105(2),\!123$
$Ca_3^-$	$D_{3h}$	$^{2}\mathrm{A}_{1}^{\prime}$	0.1027	73(2),106
	$C_{2v}$	${}^{4}\mathrm{B}_{1}^{-}$	0.7032	56,72,144
	$T_d$	$^{2}A_{1}$	0.0	86(2), 106(3), 134
$Ca_4^-$	$D_{2d}$	$^{4}A_{2}$	0.8914	$51,\!70,\!98,\!100,\!103,\!142$
	$C_1$	$^{4}A$	0.9695	$25,\!61,\!85,\!115,\!127,\!135$
	$D_{3h}$	$^{2}\mathrm{A}_{1}^{\prime}$	0.0	62(2), 84, 85(2), 86, 94, 95, 139
$Ca_5^-$	$C_{2v}$	$^{2}\mathrm{B}_{1}$	0.1439	$53,\!65,\!72,\!79,\!90,\!104,\!132,\!133,\!152$
Ť	$C_{2v}$	${}^{4}\mathrm{B}_{1}$	0.4153	37, 59, 66, 79, 91, 107, 109, 135, 141
	$C_{2v}$	$^{2}A_{2}$	0.0	46,57,61,71,82,96,102,106,112,123,127,146
$C_{0}^{-}$	$C_{2v}$	$^{2}A_{1}$	0.0170	$46,\!58,\!66,\!85,\!86,\!93,\!95,\!98,\!104,\!113,\!116,\!150$
Ua <sub>6</sub>	$C_{2v}$	${}^{4}\mathrm{B}_{1}$	0.3102	$44,\!55,\!56,\!64,\!82,\!87,\!91,\!100,\!118,\!136,\!137,\!146$
	$C_1$	$^{4}A$	0.4762	44, 49, 53, 61, 77, 81, 82, 84, 103, 109, 132, 132

Table 2.2: Ground and excited states of  $Ca_2^-$  through  $Ca_6^-$  and their vibrational frequencies. Energies (E) are relative to the ground state of the cluster anions reported in Table 2.1. The basis set 6-311+G(d) is used.

$Ca_n$	Sym	State	E (eV)	Frequency $(cm^{-1})$
	$D_{\infty h}$	$^{1}\Sigma_{q}^{+}$	0.5124	72
	$D_{\infty h}$	${}^{3}\Pi_{u}$	1.3848	156
$Ca_2$	$D_{\infty h}$	$^{3}\Sigma_{u}^{+}$	1.4321	131
	$D_{\infty h}$	${}^5\Sigma_u^+$	2.9172	156
	$\mathbf{D}_{\infty h}$	${}^{5}\Pi_{u}$	3.0139	109
	$D_{3h}$	$^{1}\mathrm{A}_{1}^{\prime}$	0.8891	99(2),108
$Ca_3$	$C_{2v}$	$^{3}A_{1}^{1}$	1.7620	49,90,136
	$C_{2v}$	${}^{5}A_{1}$	2.7466	57,100,134
	$T_d$	$^{1}A_{1}$	0.9557	104(2), 122(3), 142
C	$D_{2d}$	${}^{3}B_{2}$	1.7895	63,72,92,114(2),147
$Ca_4$	$C_1$	${}^{5}\mathrm{A}$	2.6871	$29,69,71,109,\ 135,\ 156$
	$C_2$	${}^{5}\mathrm{B}$	2.8344	45, 47, 53, 68, 79, 154
	$D_{3h}$	$^{1}A_{1}^{\prime}$	1.0084	70(2),88(2),91,104,133(2),158
C	$C_1$	$^{3}A$	1.4384	32, 59, 79, 91, 106, 117, 124, 144, 156
$Ca_5$	$C_{4v}$	${}^{5}A_{2}$	2.3865	3,58,62,92,105,115(2),119,149
	$C_{2v}$	$^{1}A_{1}$	1.1554	$48,\!69,\!70,\!87,\!93,\!97,\!100,\!101,\!105,\!119,\!124,\!157$
Cae	$C_{2v}$	${}^{3}\mathrm{B}_{1}$	1.4277	51, 56, 77, 79, 87, 96, 102, 121, 125, 138, 144, 153
$\bigcirc a_6$	$C_1$	$^{3}A$	1.6164	29, 30, 53, 73, 89, 90, 107, 111(2), 141(2), 151
	$C_{2v}$	${}^{5}\mathrm{B}_{1}$	1.8498	44,56,84,88,98,100,102,107,115,141,148,152

Table 2.3: Ground and excited states of  $Ca_2$  through  $Ca_6$  and their vibrational frequencies. Energies (E) are relative to the ground state of the cluster anions reported in Table 2.1. The basis set 6-311+G(d) is used.

Additionally, the singlet ground state, triplet and quintet exited states of neutral calcium clusters with n = 2-6 were calculated and energy, symmetry, state identification and vibrational frequencies are reported in Table 2.3. In this table, energies of the neutrals are relative to the ground state energy of the corresponding size anion given in Table 2.1.

# 2.4 Electron Detachment Spectra of Cluster Anions $Ca_n$ (n = 2-6)

Recent experiments on Ca cluster anions photoelectron detachment [12, 13] yields experimental information about the structure of the neutral clusters by recording the kinetic energy of the electron detached from the cluster anions by the light photon. This energy is referred by the experimental community as the "electron binding energy" (BE), which is the energy difference between the ground state of a cluster anion and the ground or excited states of the neutral cluster obtained when the electron is detached. Depending upon the experimental method, electrons might be detached if the anion is either in the ground state or in a low-lying excited state. These low laying excited states could be accessed in the experiment when the cluster anions are formed or light photons are absorbed. Then, the electron detachment spectrum may contain a richer set of BEs, which would contribute to peak broadening or be source of additional peaks. Experiments were carried out at about 3 eV photon energies for Ca . In order to cover the experimental energy range, the ground state of the neutral and anion clusters and their excited states laying within that energy window need to be calculated.

Presumably the electron detachment process is extremely fast, thus the ground state and the excited states of the neutral cluster are accessed experimentally at the same geometry of the anion. This conjecture has been used repeatedly in the literature [60, 61]. However, we found that the energy of the neutral cluster in the geometry of the anion cluster might not belong to a point of the energy surface of any of the stable electronic states of the neutral cluster. This is a fundamental feature of two electronic states that cross in space; the intersection between the two surfaces is associated to only a limited number of geometrical configurations. In this dissertation I only report those cases where the energy surface of the neutral contains the point calculated at the frozen anion configuration, such that the BE is defined as:
$$BE = E_n(neutral \ at \ anion's \ frozen \ geometry) - E_n(anion \ at \ equilibrium)$$
(2.1)

where  $E_n$  is the total electronic energy. This electron detachment mechanism can be viewed as a unimolecular reaction. For example, for calcium clusters:

$$Ca_n^- \to Ca_n (frozen \ at \ anion's \ geometry) + e$$
 (2.2)

The electron has spin  $\frac{1}{2}$  (equivalent to a doublet). The two elements considered in this work, Ca and Zn, have even number of electrons. Thus, the reaction to detach one electron can proceed exclusively according to the spin angular momentum rules in the following combinations of cluster state multiplicities:

$$Doublet \rightarrow \text{singlet} (\text{or triplet or quintet}) + \text{doublet}$$
  
 $Quartet \rightarrow \text{triplet} (\text{or quintet}) + \text{doublet}$ 

Therefore, if the cluster anion is in a state with spin multiplicity 2, in order to detach one electron, the singlet, triplet and quintet states of the neutral cluster need to be taken into consideration. On the other hand, if the electron is detached from the cluster anion in a state with spin multiplicity 4, only triplet and quintet states of the neutral cluster need to be considered.

The predicted theoretical BEs using Eq. 2.1 and energy information in Tables 2.1-2.3 are reported in Table 2.4. These BEs are calculated without considering the zero point energy of the cluster anion states. In fact, zero point energies are very small: 0.006, 0.021, 0.039, 0.049, and 0.07 eV for the ground states of  $Ca_2^-$  through  $Ca_6^-$ . Missing values in Table 2.4 indicate that the frozen configuration of the anion is not a point in the energy surface of the neutral cluster.

Can	State	BE (eV)					
		$2\Sigma^+$	$^{2}\Pi_{\prime\prime}$	$\frac{4\Sigma^+}{4\Sigma^+}$	$4\Pi_a$		
	$^{1}\Sigma^{+}_{a}$	0.5136	0.5286				
	${}^{3}\Pi_{u}^{g}$	1.7335	1.4984	0.7635	0.6954		
$Ca_2$	$^{3}\Sigma_{u}^{+}$	1.5422	1.4251	0.9500	0.7312		
	${}^{5}\Sigma_{u}^{a}$	3.4241	3.1827	2.3319	2.3443		
	${}^{5}\Pi_{u}^{u}$	3.1181	3.0140	2.4505	2.2979		
		$2 \Delta''_{-}$	2 /	A'.	$^{4}\mathrm{B}_{1}$		
	$1 \Delta'$	0.9106	0.7	•1 880	- D1		
Caa	$3\Delta_1$	1.8524	1.7	667	1 0011		
Uag	$5\Delta_1$	2.7503	2.6	602	2.0770		
	111	2.1000	2.0	002	2.0110		
	1.	<sup>2</sup> A <sub>1</sub>	$^{4}A_{2}$		<sup>4</sup> A		
	$^{1}A_{1}$	0.9559	-	-	-		
$Ca_4$	$^{3}B_{2}$	1.9093	0.9	526	0.9872		
1	<sup>5</sup> A	3.0696	2.1	355	1.7449		
	ъВ	3.2322	2.3	559	1.7451		
		$^{2}\mathrm{A}_{1}^{\prime}$	$^{2}$ I	$B_1$	${}^{4}\mathrm{B}_{1}$		
	$^{1}\mathrm{A}_{1}^{\prime}$	1.0315	0.8	964	_		
Ca	$^{3}A$	1.5308	1.4	747	1.0707		
Ca5	${}^{5}A_{2}$	2.5926	2.5	663	2.3292		
		$^{2}A_{2}$	$^{2}A_{1}$	${}^{4}\mathrm{B}_{1}$	$^{4}\mathrm{A}$		
	$^{1}A_{1}$	1.1719	1.1770	_	_		
Cac	${}^{3}\mathrm{B}_{1}$	1.5023	1.5861	1.1697	1.3405		
Vab	$^{3}A$	1.5023	1.5431	1.1691	1.4648		
	${}^{5}\mathrm{B}_{1}$	2.0751	1.9763	1.6500	1.5349		

Table 2.4: Ground and excited states of  $Ca_2$  through  $Ca_6$  and electron binding energies BE. Missing entries correspond to an ion geometries not allowed in the state of the neutral clusters. The basis set 6-311+G(d) is used.

Figs. 2.5 contains comparison between the calculated BEs reported in Table 2.4 for calcium cluster anions (dashed line and spikes) and the experimental results [12] (continuous gray line). Although the experimental peaks are broad, across these cluster sizes there are three main spectral features that can be identified as the electron detaching from the ground state of the cluster anion and accessing the singlet, triplet and quintet states of the neutral cluster of equal size. Peak broadening of the three mayor BEs is expected because the cluster anion may be occupying a band of vibrational states when the electron is detached. Vibrations in the neutral cluster states are also expected to be excited. Therefore a vibrational broadening is added to each of the three major BEs using the vibrational

frequencies reported in Table 2.2 and 2.3. In this work, the Lorentzian line shape function

$$I(\lambda_0) = \sum_{j=1}^{10} \sum_{i=1}^{10} \sum_{k2=1}^{num2} \sum_{k1=1}^{num1} e^{-(i-1)h\nu_{01}(i)} e^{-(j-1)h\nu_{02}(j)} \frac{1}{1 + 4\{h[\nu_1(k1) - \nu_2(k2)] - \lambda_0\}^2/\Gamma^2}$$

$$(2.3)$$

is used as the vibrational broadening function. Where  $\Gamma$  is a constant,  $\nu_{01}$  and  $\nu_{02}$  are the frequencies of neutral clusters and cluster anions respectively reported in Table 2.2 and 2.3. *num1* is the number of frequencies of neutral ground states or excited states and *num2* is the number of frequencies of anion ground states or excited states.  $\nu_1$  and  $\nu_2$ are the frequencies of neutral clusters and cluster anions used in the broadening. Here ten vibrational states are considered.

The dotted line in Figs. 2.5 shows the shape of the peak corresponding to BEs from the anion ground state to the ground and excited states of the neutral clusters when ten vibrational states are used in the broadening. The height of the calculated peaks is scaled such that the calculated and experimental first peak intensity coincide and this scaling factor is used for the rest of the calculated spectrum. Electrons detaching from excited states of the cluster anion are less abundant; BEs from these states contribute to broaden the three main peaks. These secondary BEs are reported in Table 2.4 and shown as delta functions in Figs. 2.5. The tallest spikes correspond to BEs originated from the anion first exited state and spikes with decreasing height correspond to BEs from the second and third excited states of  $\operatorname{Ca}_n^-$ .

The experimental gap between the first and the second peak can then be identified as the energy difference between the ground and first excited states of the neutral cluster. The calculated gaps are 0.95, 0.92, 1.28, 0.47, 0.32 eV for  $Ca_2^-$  through  $Ca_6^-$ , which are in good agreement with the experimental values of 1.13, 0.81, 1.02, 0.55, 0.47 eV, respectively. The major discrepancy is for  $Ca_4^-$  where the experimental second peak shows a clear splitting, which gives rise to two energy gaps of 1.0 and 1.3 eV. Our calculation matches better the



Figure 2.5: Electron binding energy of calcium cluster anions. Dotted lines are vibrationbroaden calculated BEs from the ground state of the anion to the ground and excited states of the neutral. Spikes are calculated BEs from the excited states of the anion. Grey solid line is the experiment in Ref. [12].

higher energy gap. A closer look at the experimental shape of the low energy BE peak shows a systematic shoulder towards low energies for all clusters except  $Ca_4^-$ . This shoulder may be assigned to detachment from the first excited doublet of the anion to the ground state of the neutral cluster. As shown in Table 2.4, cluster anions of all sizes have a first excited state that is very close in energy to the ground state except for  $Ca_4^-$ . Therefore, this characteristic is another agreement between theory and experiment.

Other higher energy excited states of the neutral clusters may exist but their study within the hybrid DFT is not adequate. Therefore, there are still unknowns for the full interpretation of the experimental BEs. Specifically, for  $Ca_5^-$  and  $Ca_6^-$  the experimental spectrum shows features at BEs greater than 2.5 eV, which may correspond to higher energy excited states. In the case of  $Ca_4^-$  there might be additional excited singlet states of neutral  $Ca_4$  that I was unable to locate. Other geometries of  $Ca_4$  were only found to be stable for a quintet excited state at a BE above 3.5 eV.

## 2.5 Energetics of $Zn_n$ (n = 3-11) Neutral and Anion Clusters

For zinc neutral and anion clusters, the same DFT approach was used as that for calcium clusters. However, for the Zn clusters, d-diffuse functions are significantly effective in reducing the energy of the neutrals and anions. For  $Zn_2$ , use of 6-311g(d) yields an unbound cluster. Therefore, the 6-311g(d) basis set was not used for Zn clusters.

The optimized geometries of the Zn clusters are shown in Fig. 2.6. Except for  $Zn_7$  and  $Zn_8$ , the optimized structures of  $Zn_3$  through  $Zn_{11}$  in this work are in agreement with both DFT calculations using smaller basis sets [52] and MP2/LANL2DZ calculations [53].  $Zn_7$  in this work is the same as in Ref. [52] while the structure reported in Ref. [53] is found to be a saddle. In the case of  $Zn_8$ , the structure coincides with the 8b isomer of Ref. [52] and the other reported structures are found to be higher in energy or not stable. As already stated in Ref. [52], the expected comparison of DFT results to coupled-clusters (CC) results [51] is reasonable for Zn clusters with n = 4-6 but may not reproduce well the incipient van del



Figure 2.6: Structure of the zinc neutral clusters. Bond lengths are rounded off and given in  $\mathring{A}$ .

Walls bonding of zinc dimers and trimers.

The geometries of the Zn cluster anions are shown in Fig. 2.7. Not all the optimized Zn anion clusters maintain the exact geometry of the neutrals; in some sizes there are small distortions such as bond and angle small differences. As seen in Fig. 2.7,  $\text{Zn}_6^-$ ,  $\text{Zn}_8^-$  and  $\text{Zn}_{10}^-$  have different geometries than those corresponding to the neutral clusters. Zn<sub>6</sub> has a C<sub>2v</sub> structure while the structure for  $\text{Zn}_6^-$  is C<sub>5v</sub> pentagonal pyramid. Zn<sub>8</sub> has a parallelogram on the left joining a distorted tetrahedron on the right. Zn<sub>8</sub><sup>-</sup> is an anti-cube (planes rotated 45°) and the group symmetry for both of them is C<sub>1</sub>. Zn<sub>11</sub> can be attained by adding one atom to the Zn<sub>10</sub> but Zn<sub>11</sub><sup>-</sup> has a completely different structure (see Fig. 2.7).

Results of the ground state energy E, symmetry group and electronic state identification for neutral and anion zinc clusters containing 2 to 11 atoms are given in Table 2.5, where all



Figure 2.7: Structure of the zinc cluster anions. Bond lengths are rounded off and given in  $\mathring{A}$ .

		Neutral			Anion		
$\Sigma m_n$	$\operatorname{Sym}$	State	E (eV)	$\operatorname{Sym}$	State	E (eV)	EA (eV)
3	$D_{3h}$	$^{1}A_{1}^{\prime}$	-0.1537	$D_{3h}$	$^{2}A_{1}^{\prime}$	-0.6802	0.5173
4	$T_d$	$^{1}A_{1}$	-0.6662	$\mathrm{T}_d$	$^{2}A_{1}$	-1.4739	0.8073
5	$D_{3h}$	$^{1}\mathrm{A}_{1}^{\prime}$	-0.7745	$D_{3h}$	$^{2}\mathrm{A}_{1}^{\prime}$	-1.6688	0.8955
6	$C_{2v}$	$^{1}A_{1}$	-0.9570	$C_{5v}$	$^{2}A_{1}$	-2.1811	1.2114
7	$C_1$	$^{1}\mathrm{A}$	-1.3734	$C_1$	$^{2}A$	-2.8245	1.4429
8	$C_1$	$^{1}\mathrm{A}$	-1.7555	$C_1$	$^{2}A$	-3.4199	1.6515
9	$C_{2v}$	$^{1}A_{1}$	-2.5664	$C_{2v}$	$^{2}A_{1}$	-4.6267	2.0514
10	$C_1$	$^{1}\mathrm{A}$	-3.3758	$C_1$	$^{2}A$	-4.8540	1.4724
11	$C_1$	$^{1}\mathrm{A}$	-3.5998	$C_1$	$^{2}A$	-5.1877	1.5766

Table 2.5: Electronic energies (E) with symmetry and ground state identification of  $Zn_3$  through  $Zn_{11}$  anion and neutral clusters and their electron affinity (EA).

total energies are relative to the energy of separated neutral zinc atoms. The total energies of the neutral and anion zinc atom with 6-311+G(d) are -1779.3068 a.u. and -1779.2719 a.u., respectively.

The energy stability pattern of zinc cluster anions and neutrals is given in Fig. 2.8 (solid line for neutrals and dashed-line for cluster anions). Peaks in Fig. 2.8 indicate that neutral clusters with 4, 7 and possibly 10 atoms are relatively more stable than neighboring sizes and the same behavior is apparent for the cluster anions except for  $Zn_9$  and  $Zn_{10}$ . Therefore in the very small cluster size regime, both Ca and Zn have similar energy stability.

Predictions from CC calculations [51] reported  $Zn_3^-$  as unstable. However, this cluster anion has now been detected experimentally by two groups [12, 13] and confirmed stable by my calculation. In Ref. [51], the reported EAs of Zn<sub>4</sub>, Zn<sub>5</sub> and Zn<sub>6</sub> are lower than the experimental results [12] by 0.22, 0.35, 0.87 eV, respectively. The discrepancies of my results with the same experiment are 0.03, 0.07, 0.35 eV, which are considerably smaller. The excellent qualitative agreement between my calculation and the experimental results of the EA is a validation of the methodology used in this work. For zinc clusters, the calculated EA is comparable to those of the Ca clusters except for  $Zn_2^-$ , which yields a negative EA consistent with not being observed experimentally. The EA kink at Zn<sub>10</sub> is similar to the one observed for the calcium clusters, with the exception that  $Zn_9^-$  is remarkably stable



Figure 2.8: Stability pattern as a function of zinc cluster size. Dotted lines correspond to cluster anions and full lines to neutral culsters.

and therefore the kink seems shallower when compared to the calcium case. As is shown in Fig. 2.4 and Fig. 2.9, the EA results are systematically lower than the experimental values for both Ca and Zn clusters. It is unfortunate that the experimental results do not carry error bars to allow for closer comparison.  $Zn_{10}$  and  $Zn_{11}$  are the two values of the EA with worst comparison to experiment, which might be evidence that other neutral isomers with lower ground state energy exist but have not been found in this work nor in previous works [52, 53].

## **2.6** Excited States and Frequency Analysis of $Zn_n$ (n = 3-6)

For the small Zn clusters containing 2 to 6 atoms, several excited states are identified for both anion and neutral clusters. As for calcium, these calculations were done with the expanded basis set 6-311+G(d). Energies, symmetry and state identification of the anions are reported in Table 2.6 along with the normal mode vibrational frequencies for all states and in Table 2.7 for the Zn neutral clusters. The anion ground state structures are depicted in Fig. 2.7. For Zn<sub>3</sub>, the ground state and the first excited state are equilateral triangles  $D_{3h}$  and the second excited state is a quasi-linear  $C_{2v}$  structure. The bond length in the ground state is 2.695 Å, which elongates in the first excited state to 2.879 Å and shrinks



Figure 2.9: Electron affinity of zinc as a function of cluster size. Dotted lines correspond to this work and full lines to experiments in Ref[12].

to 2.393 Å in the quasi-linear excited state. Tetrahedral  $Zn_4^-$  bond length is 2.718 Å which deforms into a planar square with edge 2.556 Å in the excited state. The triangular bipyramid structure of  $Zn_5^-$  in the ground state has bond lengths 2.895/2.771 Å, which compresses to 2.727/2.696 Å in the excited state.  $Zn_6^-$  is a pentagonal pyramid with edges 2.802/2.705 Å, which deforms considerably in the first excited state (apex atom at 2.616 Å from vertices of an imperfect pentagon). The second excited state structure is composed of two distorted tetrahedra sharing one edge and bond lengths spanning the 2.680-3.065 Å range. The quartet excited state of  $Zn_6^-$  is a deformed square pyramid with one atom decorating one of the triangular faces.

The singlet ground state, triplet and quintet excited states of neutral zinc clusters with n = 3-6 are also studied. Energy, symmetry, state identification and vibrational frequencies are reported in Table 2.7. As in the case of calcium, energies of these states are relative to the ground state energy of the cluster anion of equal size reported in Table 2.5.

$\operatorname{Zn}_n^-$	Sym	State	E (eV)	Frequencies(cm $^{-1}$ )
$Zn_3^-$	$\begin{array}{c} \mathrm{D}_{3h} \\ \mathrm{D}_{3h} \\ \mathrm{C}_{2v} \end{array}$	${}^{2}A'_{1}$ ${}^{2}A'_{1}$ ${}^{4}B_{1}$	$0.0 \\ 0.1670 \\ 1.5854$	$\begin{array}{c} 104(2),\!128\\ 67(2),\!97\\ 21,\!151,\!239\end{array}$
$\mathrm{Zn}_4^-$	$T_d$ $C_1$	$^{2}A_{1}\\ ^{4}A$	$\begin{array}{c} 0.0\\ 1.4654\end{array}$	87(2),100(3),135 43,59,96,126,127,162
$\mathrm{Zn}_5^-$	${ m D}_{3h} { m D}_{3h}$	${}^{2}\mathrm{A}_{1}^{'} \\ {}^{4}\mathrm{A}_{2}^{''}$	$0.0 \\ 1.6792$	52(2), 58(3), 66(2), 90, 119 30(2), 99(2), 120, 131(2), 136, 156
$\operatorname{Zn}_6^-$	$\begin{array}{c} \mathbf{C}_{5v} \\ \mathbf{C}_{2v} \\ \mathbf{C}_i \\ \mathbf{C}_1 \end{array}$	${\rm ^2A_1} \\ {\rm ^2A_1} \\ {\rm ^2A_g} \\ {\rm ^4A}$	$0.0 \\ 0.0124 \\ 0.1094 \\ 1.0435$	27(2), 59(2), 64, 79(2), 111,113(2), 134(2) 18, 33, 36, 37, 91, 94, 105(2), 107, 129, 147, 160 21, 33, 46, 54, 59, 75, 86, 96, 105, 109, 117, 128 18, 21, 45, 47, 66, 83, 103, 108, 126, 143, 147, 179

Table 2.6: Ground and excited states of  $Zn_3^-$  through  $Zn_6^-$  and their vibrational frequencies. Energies (E) are relative to the ground state of the cluster anion given in Table 2.5. The basis set 6-311+G(d) is used.

Table 2.7: Ground and excited states of  $Zn_3$  through  $Zn_6$  and their vibrational frequencies. Energies (E) are relative to the ground state of the cluster anion given in Table 2.5. The basis set 6-311+G(d) is used.

$Zn_n$	Sym	State	E (eV)	Frequencies $(cm_{-1})$
Zn <sub>3</sub>	$egin{array}{c} { m D}_{3h} \ { m C}_s \ { m D}_{3h} \end{array}$	$^{1}A_{1}$ $^{3}A''$ $^{5}A''_{2}$	$\begin{array}{c} 0.5265 \\ 2.3716 \\ 4.7562 \end{array}$	63(2),64 29,137,211 95(2),207
$\mathrm{Zn}_4$	$\begin{array}{c} \mathbf{T}_d \\ \mathbf{C}_1 \\ \mathbf{C}_1 \end{array}$	${}^{1}A_{1}$ ${}^{3}A$ ${}^{5}A$	0.8077 2.6976 4.6593	91(2),103(3),113 3,6,29,121,174,175 47,75,83,134,196,207
$Zn_5$	$\begin{array}{c} \mathrm{D}_{3h} \\ \mathrm{C}_1 \\ \mathrm{C}_1 \end{array}$	$^{1}\mathrm{A}_{1}^{'}\\ ^{3}\mathrm{A}\\ ^{5}\mathrm{A}$	0.8942 2.2065 3.7327	38,43(2),55(2),75,105(2),120 22,66,67,78,86,93,98,127,153 33,48,51,55,110,122,151,217,236
Zn <sub>6</sub>	$\begin{array}{c} \mathbf{C}_{2v} \\ \mathbf{C}_1 \\ \mathbf{C}_1 \\ \mathbf{C}_1 \\ \mathbf{C}_1 \end{array}$	$^{1}A_{1}$ $^{3}A$ $^{3}A$ $^{5}A$	$\begin{array}{c} 1.2242 \\ 2.4626 \\ 2.5204 \\ 3.4881 \end{array}$	$\begin{array}{c} 12,\!44,\!47,\!52,\!62,\!66,\!70,\!72,\!76,\!77,\!87,\!132\\ 16,\!20,\!35,\!47,\!59,\!61,\!81,\!96,\!109,\!143,\!147,\!195\\ 17,\!30,\!32,\!50,\!52,\!69,\!64(3),\!134,\!143,\!156\\ 28,\!51(2),\!78,\!79,\!91,\!93,\!131,\!132,\!138,\!158,\!162\end{array}$

# 2.7 Electron Detachment Spectra of Cluster Anions $Zn_n$ (n = 3-6)

Following the same procedure as for calcium clusters, the electron detachment energy of  $\operatorname{Zn}_n^-$  (n = 3-6) was theoretically predicted by calculating the energy difference between the states of the anions and the states of neutrals at the geometry of the anions. The grey continuous line in Figs. 2.10 depicts the experimental results reported in Ref. [13] and the dashed line corresponds to the calculated BE between the ground state of the anion and the singlet, triplet and quintet states of the neutral cluster. Worth noting is that the experimental results in Ref. [12] are almost identical to those of Ref. [13] and were obtained contemporarily. In our calculation, the BEs have been broaden considering a band of ten vibrational states for each of the two electronic states involved according to frequencies reported in Tables 2.6, 2.7 and equation 2.3. The intensity of the fist peak is scaled to coincide with experiment and the same scaling factor is used throughout the spectrum. Additionally, the delta functions in Figs. 2.10 correspond to BEs from anion ground state to excited states of the neutral and from excited states of the anion to all available states of the neutrals (see Table 2.8). The tallest spikes correspond to energy differences from the anion ground state and lines with decreasing height correspond to the first, second and third excited states of  $\operatorname{Zn}_n^-$ .

The experimental energy gap between the first peak and second peak are 2.25, 2.62, 2.19 and 1.50 eV for  $Zn_3^-$  through  $Zn_6^-$ , respectively. The calculated gap of 2.22, 2.50, 1.93 and 1.22 eV are in excellent agreement with experiment. Experimentally the first peak of  $Zn_3^-$  and  $Zn_6^-$  show a noticeable shoulder at low energies. This shoulder is consistent with BEs from the low excited states of the anion clusters shown as spikes in Figs. 2.10.

7	<u> </u>		DD	( 17)	
$Zn_n$	State		BE	(eV)	
		$^{2}\mathrm{A}_{1}^{\prime}$	$^{2}$	$A'_1$	${}^{4}\mathrm{B}_{1}$
	$^{1}A_{1}$	0.6394	0.3	771	—
$Zn_3$	$^{3}A''$	2.8805	2.8	990	0.8044
	${}^{5}A_{2}^{\prime\prime}$	4.9051	5.0	537	4.3706
		$2 \downarrow$	$A_1$	4	А
	$^{1}A_{1}$	0.8	220	-	_
$Zn_4$	$^{3}A$	3.3	773	1.2	022
	${}^{5}\mathrm{A}$	-	_	3.8	806
		$^{2}$	$\Lambda_1'$	4	$A_2''$
	$^{1}A_{1}^{\prime}$	0.9	684	-	_
$Zn_5$	$^{3}A$	2.8	948	0.9	441
Ū	${}^{5}\mathrm{A}$	5.2	724	3.3	677
		$^{2}A_{1}$	$^{2}A_{1}$	$^{2}A_{a}$	$^{4}A$
	$^{1}A_{1}$	$1.50\overline{30}$	1.3102	1.2725	_
$Zn_6$	$^{3}A$	2.7243	_	_	_
Ŭ	$^{3}A$	_	2.8264	2.9674	1.4862
	$^{5}\mathrm{A}$	4.4567	4.7607	4.8815	3.5895

Table 2.8: Ground and excited states of  $Zn_3$  through  $Zn_6$  and electron binding energies BE. Missing entries correspond to anion geometries not allowed in the state of the neutral clusters. The basis set 6-311+G(d) is used.



Figure 2.10: Electron binding energy of zinc cluster anions. Dotted lines are vibrationbroaden calculated BEs from the ground state of the anion to the ground and excited states of the neutral. Spikes are calculated BEs from the excited states of the anion. Grey solid line is the experiment in Ref. [13].

### 2.8 Conclusion

Based on hybrid DFT calculations, the relaxed configurations of neutral and cluster anions up to  $Ca_{19}^-$  and  $Zn_{11}^-$  are now known. The dissertation provides novel information on the ground state energetics, symmetry and vibrational analysis of neutral and anion calcium clusters up to  $Ca_{19}^-$  and on zinc clusters up to  $Zn_{11}^-$  which allows for calculation of the electron affinity in this cluster size range. Comparison of the electron affinity results with experiment is excellent, reproducing the intriguing kink observed at  $Ca_{10}$  and  $Zn_{10}$ . For calcium this kink occurs because  $Ca_{10}$  is a magic number for the neutral clusters [33] whereas  $Ca_{10}^-$  is a fairly unstable cluster anion as shown in Fig. 2.3. The EA kink in zinc clusters is not as pronounced, pointing to a fairly stable  $Zn_{10}$  [52] that does not qualify as a magic number and an unstable cluster anion as shown in Fig. 2.8.

The DFT method used is limited to only provide precisely the excited states that have different multiplicity than the ground states. Therefore, the calculated electron detachment spectrum is a portion of the experimental observations. The electron detachment spectra of  $Ca_2^-$  through  $Ca_6^-$  and  $Zn_3^-$  through  $Zn_6^-$  were calculated and compared with Zheng's [12] and Kostko's [13] experimental observations. The major spectral characteristics are well calculated for these small clusters, as evidenced by the agreement with experiment. The spectral gap between the first and second experimental features are in excellent agreement with the calculated counterparts. It is predicted that the electron detachment spectra originate from cluster anions in the ground state, but some BEs are broadened when detachment occurs from the first few anion excited states. A good agreement on the broadening is due to the contribution of the excited vibrational states. The work contains the vibrational analysis for the anion states originating the spectral peaks and identifies that spectral peaks in the higher energy region are due to neutral clusters reached in triplet and quintet excited states. Since the reachable states of the neutral clusters have different multiplicities, the electron detachment process may be used as a spin switch if tailored accordingly.

## Chapter 3: Energetics, Structure and Charge Distribution of n-Pyrrole Oligomers

## 3.1 Introduction

Polypyrrole (PPy) is a prototypical conducting polymer. Because of its strong electrical and optical anisotropies, PPy is a good candidate for photonic devices.By electronchemical polymerization PPy is synthesized in two different phases: reduced when the polymer is electrically neutral and oxidized when the polymer is positively charged having transferred electrons to the oxidizing agent [26,62]. By oxidizing a polymer matrix, polarons (localized positive charge due to polarization) are mobile and the solvent carries a stream of negative charges away. When the polymer is reduced with dopants, polarons seem to localize around the dopant neighborhood and the polymer doesn't conduct [62–64]. This property is interesting for environmental and human health applications when high quality chemical sensors are needed. For example, chemical sensors for the detection of analytes such as nitrate anions are feasible by tailoring a PPy film doped with nitrate ions as a sensitive layer. However, the lack of knowledge about the recombination dynamics and polaron mobility is a bottleneck for improving any device efficiency.

Theoretical studies of PPy have used semi-empirical and Hatree-Fock (HF) methods over the past few years. For example, the ultraviolet photoemission and optical absorption spectra for pyrrole (Py) and PPy were analyzed using a spectroscopically parametrized CNDO/S3 method [65]; the vibrational spectra of PPy was studied at the MNDO level [66] and the band structure of PPy within the INDO approximation was reported in ref. [67]. At the HF level, there have been several studies as well: the ground state of Py, 2-Py and PPy [68], the effect of charge-transfer doping on the geometry of PPy [69–71], the energetics of Py dimers as a function of the torsion angle [72], and structure coupled with vibrational spectra [73,74]. More recently, density functional theory (DFT) calculations of PPy have been undertaken for a variety of studies. For example, studies of the band gap of conducting polymers [75], electronic and structural properties of oxidized PPy with chlorine dopants [76], the excited states of the Py monomer and dimer [77] and their vibrational frequencies [78]. Despite these studies, the positive charge localization mechanism that occurs in oxidized PPy has not been given proper description at the quantum level.

The purpose of this study is to investigate the energetics of reduced and oxidized n-Py oligomers and the positive charge localization as a function of oligomer length (n). Results on these areas are pertinent for studies of polaron and bi-polaron formation [79–81]. To that end, the geometrical structures of n-Py (n = 1-9, 12, 15, 18, 20, 24) and infinite PPy chains were studied in their reduced and oxidized phases within the hybrid DFT framework with large basis sets. This chapter is organized as follows: Sec. 3.2 describes the methodology used as well as results for the pyrrole and bipyrrole molecules; Sec. 3.3 describes the geometrical configurations and electronical properties of reduced n-Py; Sec. 3.4 and 3.5 contain the study of oxidized n-Py with and without dopants and results of infinite PPy respectively. This chapter is concluded in Sec. 3.6.

### 3.2 Pyrrole and Bipyrrole

Density functional theory (DFT) and the hybrid Becke-Perdew-Wang 1991 (B3PW91) approach were used throughout this chapter, which includes local and non local correlation functionals [54,82]. A triple valence basis set (6-311G) containing 8s, 7p, 1d gaussians contracted as (62111111, 3311111, 3) was adopted in all calculations [83]. This level of theory reproduces very well the experimental geometry [84] of the neutral Py monomer shown in Fig. 3.1a. Details of this comparison are given in Table 3.1. In this table atoms are labeled with the number scheme given in Fig. 3.1a. The theoretical and experimental bond lengths and bond angles are listed in the second and third columns respectively. The maximum



Figure 3.1: (a) Number scheme for the Py monomer; (b, c) Benzenoid PPy segments in two possible reduced phases; (d) Quinoid PPy segment in the oxidized phase.

error in geometry variables is 0.8%. The Py molecule is a  $C_{2v}$  planar structure with a strong dipole moment of 1.98 D in the direction of the N-H bond and diagonal quadrupole matrix elements of -23.4, -26.5, -34.1 D-Å. The infrared active vibrational frequencies are given in Table 3.2. The agreement of calculated frequencies (first column) with experiment (third column) [85] is excellent as indicated in the fourth column by the ratio of calculated divided by experimental results. This ratio is almost constant with an average of 0.96. This value could be used as a scaling parameter for the spectra of larger oligomers. The second column in this table reports the theoretical intensity of the IR active modes and the theoretical mode-assignments are listed in the fifth column. Assignments are based on the higher coefficients of the vibrational mode eigenvectors.

	Theoretical	Exp. [84]
R(1,2)	1.379	1.382
R(1,5)	1.381	1.370
R(1,6)	1.076	1.076
R(2,3)	1.427	1.417
R(2,7)	1.077	1.077
R(5,10)	1.002	0.996
A(1,5,4)	109.8	109.8
A(2,1,5)	107.5	107.7
A(1,2,3)	107.6	107.4
A(1,5,10)	125.1	125.1
A(2,1,6)	130.9	130.8
A(1,2,7)	125.9	125.5

Table 3.1: Pyrrole calculated bond distances and bond angles compared with experimental values. Distances are in Å and angles in degrees.

The reduced phase of n-Py oligomers and PPy is insulating, charge neutral, and displays the benzenoid alternation of single-double C-C bonds shown in Fig. 3.1b. An alternative realization of the reduced phase is shown in Fig. 3.1c where the benzenoid C-C bond alternation is attained by electric neutralization of trapped anions  $(A^-)$  with solvent cations  $(C^+)$ . Anions or cations that remain in the polymer matrix during polymerization are generically called *dopants*. The oxidized phase of PPy (the polymer is positively charged) is the conducting phase displaying conjugated chains with quinoid single-double C-C bond alternation as depicted in Fig. 3.1d. The change from benzenoid to quinoid structure is promoted by the migration of electrons to the electronegative dopants  $(A^-)$ . In the oxidized state n-Py and PPy chains are cations.

The geometrical structure of bipyrrole, as well as that of larger oligomers, is modulated the most by the rotational degree of freedom around the interring C-C bond. In principle, reduced 2-Py may have four possible isomers: two puckered structures *anti-gauche* and *syngauche*, and two planar structures *anti* and *syn*. The oxidized 2-Py may have only two planar isomers: *anti* and *syn*. The energetics along the rotational path is given in Fig. 3.2a, b for reduced and oxidized bipyrrole, illustrating the stability of rotational isomers as a function of the torsion angle. For neutral 2-Py the global minimum corresponds to the *anti-gauche* 

Frequency	$I_{IR}$	Exp. $[85]$	Factor	Assignment						
	al									
3709	46.5	3527	0.95	$N-H \ str$						
3288	0.37	3148	0.96	C-H str						
3261	8.6	3125	0.96	C-H str						
1505	7.6	1470	0.98	C-N str, C-H ipb						
1432	5.4	1391	0.97	$C=C,C-C \operatorname{str}$						
1176	1.6	1148	0.98	Ring breath						
1111	7.6	1074	0.97	H-C-N,H-C-C-H						
1044	37.9	1018	0.98	C-C str, C-H ipb						
920	0.50	880	0.96	rd						
		b	2							
3278	10.0	3140	0.96	C-H str						
3248	3.9	3116	0.96	C-H str						
1588	6.6	1521	0.96	$C=C \operatorname{str}$						
1465	8.8	1424	0.97	C-N str, N-H ipb						
1339	0.9	1287	0.96	C-N-C,C-H,N-H ipb						
1189	2.9	1134	0.95	C-N-C,C-H,N-H ipb						
1082	31.7	1049	0.97	H-C=C-H ben						
900	1.2	863	0.96	rd						
		a	2							
915	0.0	868	0.95	C-H oopb						
726	0.0	712	0.99	C-H oopb						
640	0.0	618	0.97	$\operatorname{rd}$						
		b	1							
871	4.1	826	0.95	C-H oopb						
749	168.6	720	0.96	C-H oopb						
652	20.8	626	0.96	$\operatorname{rd}$						
619	108.2	474	0.77	N-H oopb						

Table 3.2: Calculated IR-active spectrum of pyrrole. Frequencies are in  $cm^{-1}$ ; str=stretch, rd=ring deform, ipb=in-plane bend, oopb=out-of-plane bend.

 $C_2$  geometry (torsion angle =153°), which is more stable by 0.033 eV than the planar *anti* form (180°), 0.122 eV more stable than the *syn-gauche* form (50°) and 0.18 eV more stable than the *syn* form (0°). Additionally, a normal mode frequency analysis shows that only two neutral isomers are stable, e. g., the *anti-gauche* isomer (C<sub>2</sub> with torsion angle of 153°) and the *syn-gauche* isomer (C<sub>2</sub> with torsion angle of 50°) shown in Figs. 3.3a, b. Once relaxed, the binding energy of the *anti-gauche* isomer becomes -119.32 eV and the *syn-gauche* is 0.07 eV less stable. Therefore, these two neutral isomers can coexist in thermal equilibrium at temperatures of about 700 K. These results are in excellent agreement with MIDI-4 SCF pioneer calculations [73]. For oxidized 2-Py with a +e charge, the two stable isomers are the *anti* ( $C_{2h}$ ) and the *syn* ( $C_{2v}$ ) planar forms shown in Figs. 3.3c, d. The charged *anti*  $C_{2h}$  isomer (6.75 eV above the neutral  $C_2$  *anti-gauche*) is the global minimum, which is lower in energy by 0.144 eV than the charged *syn*  $C_{2v}$  isomer. A high torsional energy barrier of 1.146 eV makes the transition between the two charged isomers not thermally possible.

Tables 3.3 and 3.4 list the calculated normal mode IR-active frequencies for the two neutral bipyrrole isomers and Tables 3.5 and 3.6 contain similar information for the positively charged 2-Py<sup>+</sup> isomers. Results for the neutral isomers are in very good agreement with experiment [73, 86] (see Tables 3.3 and 3.4, 4th and 7th columns). It is to be noted that at the time of the experiments, the symmetry assignment given to neutral bipyrrole was  $D_{2h}$ , which was based on the frequency assignments of infinite chains. My comparison shows that the agreement between experiment and both calculated spectra for *anti-gauche* and *syn-gauche* bipyrrole isomers, is excellent. Therefore, the identification of the molecular symmetry through that IR experiment should be C<sub>2</sub> and not  $D_{2h}$ .



Figure 3.2: Binding energy along the torsion angle. (a) Neutral 2-Py; (b) Oxidized 2-Py<sup>+</sup>.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	This	work	$\operatorname{Exp}^{a}$	Assgm	This '	This work		Assgm
ab $3697$ 9.8N-H str $3697$ 73.2 $3365$ N-H str $3286$ 0.0C-H str $3286$ 10.1C-H str $3262$ 1.3C-H str $3262$ 12.8 $3120$ C-H str $3246$ 0.3C-H str $3247$ 19.0 $3100$ C-H str $1674$ 0.01618C-C i-r str1581 $39.2$ $1527$ C=C str $1523$ 1.21479C-C,C-N str144313.01415H-C-C-H $1477$ 1.61453C-N,C-C str143112.7C-C str $1345$ 1.81303C-C str,N-H ipb12949.81252C-H,N-H ipb $1344$ 0.01263CH ipb11790.21147ring breath $1162$ 1.51118C-N-C-H ipb113855.71105H-C-C-H,H-C-N-H $1132$ 1.81098H-C=C-H109631.9C-H,N-H ipb $1071$ 1.61029H-C-C-H ipb13140.4C-H ipb $990$ 0.2960rd,C-H ipb93112.7894rd $915$ 0.3880rd9052.7rd, C-H oopb $444$ 0.8ripr1302.5Ring ipr $992$ 0.0392ring ip transl $902$ 0.18C-H oopb93511.8795 $77.3$ 789C-H oopb73613.4692C-H,Och oopb $761$	$\rm cm^{-1}$	$I_{IR}$	$\mathrm{cm}^{-1}$		$\mathrm{cm}^{-1}$	$I_{IR}$	$\mathrm{cm}^{-1}$	
36979.8N-H str $3697$ $73.2$ $3365$ N-H str $3286$ 0.0C-H str $3286$ 10.1C-H str $3262$ 1.3C-H str $3262$ 12.8 $3120$ C-H str $3246$ 0.3C-H str $3247$ 19.0 $3100$ C-H str $1674$ 0.01618C-C i-r str1581 $39.2$ $1527$ C=C str $1523$ 1.21479C-C,C-N str14714.61425N-C=C $1477$ 1.61453C-N,C-C str143112.7C-C str $1450$ 0.31410C-N,C-C str143112.7C-C str $1345$ 1.81303C-C str,N-H ipb12949.81252C-H,N-H ipb $1314$ 0.01263CH ipb11790.21147ring breath $1162$ 1.51118C-N-C-H ipb113855.71105H-C-C-H,H-C-N-H $1132$ 1.81098H-C=C-H109631.9C-H,N-H ipb $1071$ 1.61029H-C-C-H ipb106452.91034C-H ipb $900$ 0.2960rd,C-H ipb93112.7894rd $915$ 0.3880rd9052.7rd, C-H oopb $9144$ 0.8ripr1302.5Ring ipr $920$ 0.18C-H oopb93511.8795C-H oopb $919$ 77.3789C-H oopb73613.4692			a				b	)
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15231.21479C-C,C-N str14714.61425N-C=C14771.61453C-N,C-C str144313.01415H-C-C-H14500.31410C-N,C-C str143112.7C-C str13451.81303C-C str,N-H ipb12949.81252C-H,N-H ipb13140.01263CH ipb11790.21147ring breath11621.51118C-N-C-H ipb113855.71105H-C-C-H,H-C-N-H11321.81098H-C=C-H109631.9C-H,N-H ipb10711.61029H-C-C-H ipb106452.91034C-H ipb9900.2960rd,C-H ipb93112.7894rd9150.3880rd9052.7rd, C-H oopb4440.8ripr1302.5Ring ipr3920.0392ring ip transl $ -$ 9020.18C-H oopb9020.2C-H oopb81977.3789C-H oopb73613.4692C-H oopb6111.8669ring def7061.9652C-H,C-C i-r oopb64249.6584ring def6415.6636C-H,N-H oopb623107.2N-H oopb62322.7448C-H,N-H oopb623107.2N-H oopb62322.7448C-H,N-H oopb63 <td>1674</td> <td>0.0</td> <td>1618</td> <td>C-C i-r str</td> <td>1581</td> <td>39.2</td> <td>1527</td> <td>C=C str</td>	1674	0.0	1618	C-C i-r str	1581	39.2	1527	C=C str
14771.61453C-N,C-C str144313.01415H-C-C-H14500.31410C-N,C-C str143112.7C-C str13451.81303C-C str,N-H ipb12949.81252C-H,N-H ipb13140.01263CH ipb11790.21147ring breath11621.51118C-N-C-H ipb113855.71105H-C-C-H,H-C-N-H11321.81098H-C=C-H109631.9C-H,N-H ipb10711.61029H-C-C-H ipb106452.91034C-H ipb9000.2960rd,C-H ipb93112.7894rd9150.3880rd9052.7rd, C-H oopb4440.8ripr1302.5Ring ipr9020.18C-H oopb9020.2C-H oopb81977.3789C-H oopb73613.4692C-H oopb6111.8669ring def7061.9652C-H,C-C i-r oopb64249.6584ring def6415.6636C-H,N-H oopb623107.2N-H oopb62322.7448C-H,N-H oopb6233.6ring oopt3511.7330ring oopb	1523	1.2	1479	$C-C,C-N \operatorname{str}$	1471	4.6	1425	N-C=C
1450 $0.3$ $1410$ C-N,C-C str $1431$ $12.7$ C-C str $1345$ $1.8$ $1303$ C-C str,N-H ipb $1294$ $9.8$ $1252$ C-H,N-H ipb $1314$ $0.0$ $1263$ CH ipb $1179$ $0.2$ $1147$ ring breath $1162$ $1.5$ $1118$ C-N-C-H ipb $1138$ $55.7$ $1105$ H-C-C-H,H-C-N-H $1132$ $1.8$ $1098$ H-C=C-H $1096$ $31.9$ C-H,N-H ipb $1071$ $1.6$ $1029$ H-C-C-H ipb $1064$ $52.9$ $1034$ C-H ipb $990$ $0.2$ $960$ rd,C-H ipb $931$ $12.7$ $894$ rd $915$ $0.3$ $880$ rd $905$ $2.7$ rd, C-H oopb $444$ $0.8$ ripr $130$ $2.5$ Ring ipr $392$ $0.0$ $392$ ring ip transl $902$ $0.2$ C-H oopb $902$ $0.18$ C-H oopb $902$ $0.2$ C-H oopb $819$ $77.3$ $789$ C-H oopb $736$ $13.4$ $692$ C-H oopb $671$ $1.8$ $669$ ring def $706$ $1.9$ $652$ C-H,C-C i-r oopb $642$ $49.6$ $584$ ring def $641$ $5.6$ $636$ C-H,N-H oopb $623$ $107.2$ N-H oopb $623$ $22.7$ $448$ C-H,N-H oopb $121$ $0.6$ ring oopb $351$ $1.7$ $330$ ring oopb $63$ $3.6$ ring oopf $351$ $1.$	1477	1.6	1453	C-N,C-C str	1443	13.0	1415	H-C-C-H
13451.81303C-C str,N-H ipb12949.81252C-H,N-H ipb13140.01263CH ipb11790.21147ring breath11621.51118C-N-C-H ipb113855.71105H-C-C-H,H-C-N-H11321.81098H-C=C-H109631.9C-H,N-H ipb10711.61029H-C-C-H ipb106452.91034C-H ipb9900.2960rd,C-H ipb93112.7894rd9150.3880rd9052.7rd, C-H oopb4440.8ripr1302.5Ring ipr3920.0392ring ip transl $ -$ 9020.18C-H oopb9020.2C-H oopb81977.3789C-H oopb73613.4692C-H oopb6711.8669ring def7061.9652C-H,N-H oopb623107.2N-H oopb62322.7448C-H,N-H oopb623107.2N-H oopb62322.7448C-H,N-H oopb633.6ring oopr3511.7330ring oopb	1450	0.3	1410	C-N,C-C str	1431	12.7		C-C str
1314 $0.0$ $1263$ CH ipb $1179$ $0.2$ $1147$ ring breath $1162$ $1.5$ $1118$ C-N-C-H ipb $1138$ $55.7$ $1105$ H-C-C-H,H-C-N-H $1132$ $1.8$ $1098$ H-C=C-H $1096$ $31.9$ C-H,N-H ipb $1071$ $1.6$ $1029$ H-C-C-H ipb $1064$ $52.9$ $1034$ C-H ipb $990$ $0.2$ $960$ rd,C-H ipb $931$ $12.7$ $894$ rd $915$ $0.3$ $880$ rd $905$ $2.7$ rd, C-H oopb $444$ $0.8$ ripr $130$ $2.5$ Ring ipr $392$ $0.0$ $392$ ring ip transl $-H$ oopb $902$ $0.2$ C-H oopb $902$ $0.18$ C-H oopb $835$ $11.8$ $795$ C-H oopb $819$ $77.3$ $789$ C-H oopb $736$ $13.4$ $692$ C-H oopb $671$ $1.8$ $669$ ring def $706$ $1.9$ $652$ C-H,C-C i-r oopb $642$ $49.6$ $584$ ring def $641$ $5.6$ $636$ C-H,N-H oopb $623$ $107.2$ N-H oopb $623$ $22.7$ $448$ C-H,N-H oopb $121$ $0.6$ ring ooph $351$ $1.7$ $330$ ring ooph $63$ $3.6$ ring oopf $351$ $1.7$ $330$ ring ooph	1345	1.8	1303	C-C str, N-H ipb	1294	9.8	1252	C-H,N-H ipb
11621.51118C-N-C-H ipb113855.71105H-C-C-H,H-C-N-H11321.81098H-C=C-H1096 $31.9$ C-H,N-H ipb10711.61029H-C-C-H ipb1064 $52.9$ 1034C-H ipb9900.2960rd,C-H ipb93112.7 $894$ rd9150.3880rd9052.7rd, C-H oopb4440.8ripr1302.5Ring ipr3920.0392ring ip transl9020.2C-H oopb9020.18C-H oopb9020.2C-H oopb81977.3789C-H oopb73613.4692C-H oopb6711.8669ring def7061.9652C-H,C-C i-r oopb64249.6584ring def6415.6636C-H,N-H oopb623107.2N-H oopb62322.7448C-H,N-H oopb1210.6ring oopb3511.7330ring oopb633.6ring oopr5511.7330ring oopb	1314	0.0	1263	CH ipb	1179	0.2	1147	ring breath
11321.81098H-C=C-H1096 $31.9$ C-H,N-H ipb10711.61029H-C-C-H ipb1064 $52.9$ 1034C-H ipb9900.2960rd,C-H ipb93112.7 $894$ rd9150.3880rd905 $2.7$ rd, C-H oopb4440.8ripr130 $2.5$ Ring ipr3920.0392ring ip transl $$	1162	1.5	1118	C-N-C-H ipb	1138	55.7	1105	H-C-C-H,H-C-N-H
1071 $1.6$ $1029$ H-C-C-H ipb $1064$ $52.9$ $1034$ C-H ipb $990$ $0.2$ $960$ rd, C-H ipb $931$ $12.7$ $894$ rd $915$ $0.3$ $880$ rd $905$ $2.7$ rd, C-H oopb $444$ $0.8$ ripr $130$ $2.5$ Ring ipr $392$ $0.0$ $392$ ring ip transl $$	1132	1.8	1098	H-C=C-H	1096	31.9		C-H,N-H ipb
990 $0.2$ 960rd, C-H ipb931 $12.7$ $894$ rd915 $0.3$ $880$ rd $905$ $2.7$ rd, C-H oopb444 $0.8$ ripr $130$ $2.5$ Ring ipr $392$ $0.0$ $392$ ring ip transl $$	1071	1.6	1029	H-C-C-H ipb	1064	52.9	1034	C-H ipb
915 $0.3$ 880rd905 $2.7$ rd, C-H oopb444 $0.8$ ripr $130$ $2.5$ Ring ipr392 $0.0$ $392$ ring ip transl $$	990	0.2	960	rd,C-H ipb	931	12.7	894	rd
444 $0.8$ ripr $130$ $2.5$ Ring ipr $392$ $0.0$ $392$ ring ip transl $$	915	0.3	880	rd	905	2.7		rd, C-H oopb
392 $0.0$ $392$ ring ip transl $902$ $0.18$ C-H oopb $902$ $0.2$ C-H oopb $819$ $77.3$ $789$ C-H oopb $835$ $11.8$ $795$ C-H oopb $736$ $170.3$ $727$ C-H oopb $736$ $13.4$ $692$ C-H oopb $671$ $1.8$ $669$ ring def $706$ $1.9$ $652$ C-H,C-C i-r oopb $642$ $49.6$ $584$ ring def $641$ $5.6$ $636$ C-H,N-H oopb $623$ $107.2$ N-H oopb $623$ $22.7$ $448$ C-H,N-H oopb $121$ $0.6$ ring oopb $351$ $1.7$ $330$ ring oopb $63$ $3.6$ ring oopr $448$ $748$ $748$ $748$	444	0.8		ripr	130	2.5		Ring ipr
902 $0.18$ C-H oopb $902$ $0.2$ C-H oopb $819$ $77.3$ $789$ C-H oopb $835$ $11.8$ $795$ C-H oopb $736$ $170.3$ $727$ C-H oopb $736$ $13.4$ $692$ C-H oopb $671$ $1.8$ $669$ ring def $706$ $1.9$ $652$ C-H,C-C i-r oopb $642$ $49.6$ $584$ ring def $641$ $5.6$ $636$ C-H,N-H oopb $623$ $107.2$ N-H oopb $623$ $22.7$ $448$ C-H,N-H oopb $121$ $0.6$ ring oopb $351$ $1.7$ $330$ ring oopb $63$ $3.6$ ring oopr $448$ $648$ $107.2$ $107.2$	392	0.0	392	ring ip transl				
819       77.3       789       C-H oopb       835       11.8       795       C-H oopb         736       170.3       727       C-H oopb       736       13.4       692       C-H oopb         671       1.8       669       ring def       706       1.9       652       C-H,C-C i-r oopb         642       49.6       584       ring def       641       5.6       636       C-H,N-H oopb         623       107.2       N-H oopb       623       22.7       448       C-H,N-H oopb         121       0.6       ring oopb       351       1.7       330       ring oopb         63       3.6       ring oopr       351       1.7       330       ring oopb	902	0.18		C-H oopb	902	0.2		C-H oopb
736       170.3       727       C-H oopb       736       13.4       692       C-H oopb         671       1.8       669       ring def       706       1.9       652       C-H,C-C i-r oopb         642       49.6       584       ring def       641       5.6       636       C-H,N-H oopb         623       107.2       N-H oopb       623       22.7       448       C-H,N-H oopb         121       0.6       ring oopb       351       1.7       330       ring oopb         63       3.6       ring oopr       551       1.7       50       1.7	819	77.3	789	C-H oopb	835	11.8	795	C-H oopb
6711.8669ring def7061.9652C-H,C-C i-r oopb64249.6584ring def6415.6636C-H,N-H oopb623107.2N-H oopb62322.7448C-H,N-H oopb1210.6ring oopb3511.7330ring oopb633.6ring oopr5511.7562562	736	170.3	727	C-H oopb	736	13.4	692	C-H oopb
64249.6584ring def6415.6636C-H,N-H oopb623107.2N-H oopb62322.7448C-H,N-H oopb1210.6ring oopb3511.7330ring oopb633.6ring oopr3511.7330ring oopb	671	1.8	669	ring def	706	1.9	652	C-H,C-C i-r oopb
623107.2N-H oopb62322.7448C-H,N-H oopb1210.6ring oopb3511.7330ring oopb633.6ring oopr3511.7330ring oopb	642	49.6	584	ring def	641	5.6	636	C-H,N-H oopb
121         0.6         ring oopb         351         1.7         330         ring oopb           63         3.6         ring oopr         351         1.7         330         1000000000000000000000000000000000000	623	107.2		N-H oopb	623	22.7	448	C-H,N-H oopb
63 3.6 ring oopr	121	0.6		ring oopb	351	1.7	330	ring oopb
<u> </u>	63	3.6		ring oopr				

Table 3.3: Calculated IR-active spectrum of *anti-gauche* bipyrrole (str=stretch, i-r=interring, rd=ring deform, ipb=in-plane bend, oopb=out-of-plane bend, oopr = out-of-plane rotation, ripr = ring in-plane rotation).

<sup>*a*</sup>Ref. [73, 86]

This	work	$\operatorname{Exp}^a$	$\operatorname{Exp}^{a}$ Assgm		This work		Assgm
$\mathrm{cm}^{-1}$	$I_{IR}$	$\mathrm{cm}^{-1}$		$\mathrm{cm}^{-1}$	$\mathrm{cm}^{-1}$	$I_{IR}$	
		a				b	
3692	57.4		N-H str	3691	19.5	3365	N-H str
3285	0.0		C-H str	3284	10.7		C-H str
3268	9.1		C-H str	3268	2.4	3120	C-H str
3252	0.25		C-H str	3251	15.7	3100	C-H str
1671	0.4	1618	C-C i-r str	1589	30.4	1527	C=C str
1522	10.2	1479	C-C,C-N str	1485	7.4	1425	N-C=C
1457	4.9	1453	C-N,C-C str	1454	12.3	1415	H-C-C-H
1430	4.8	1410	C-N,C-C str	1439	1.7		C-C str
1323	7.9	1303	C-C str, N-H ipb	1313	4.9	1252	C-H,N-H ipb
1287	0.8	1263	CH ipb	1173	0.2	1147	ring breath
1158	9.0	1118	C-N-C-H ipb	1146	27.8	1105	H-C-C-H,H-C-N-H
1127	22.4	1098	H-C=C-H	1091	13.8		C-H,N-H ipb
1065	29.0	1029	H-C-C-H ipb	1061	36.1	1034	C-H ipb
986	1.3	960	rd,C-H ipb	924	12.5	894	$\operatorname{rd}$
921	3.4	880	rd	908	0.1		rd, C-H oopb
394	0.2		ripr	117	1.2		Ring ipr
359	3.0	392	ring ip transl				
910	0.1		C-H oopb	903	1.0		C-H oopb
847	16.9	789	C-H oopb	835	59.6	795	C-H oopb
738	22.3	727	C-H oopb	736	155.2	692	C-H oopb
704	0.6	669	ring def	675	0.2	652	C-H,C-C i-r oopb
654	30.5	584	ring def	635	1.1	636	C-H,N-H oopb
624	31.4		N-H oopb	597	135.6	448	C-H,N-H oopb
122	0.2		ring oopb	433	3.7	330	ring oopb
			ring oopr				

Table 3.4: Calculated IR-active spectrum of syn-gauche bipyrrole (str=stretch, i-r=interring, rd=ring deform, ipb=in-plane bend, oopb=out-of-plane bend, oopr = out-of-plane rotation, ripr = ring in-plane rotation).

 $^{a}$ Ref. [73, 86]



Figure 3.3: Stable bipyrrole isomers showing the torsion angles. (a, b) Neutral 2-Py; (c, d) Oxidized 2-Py<sup>+</sup>.

Table 3.5: Calculated vibrational spectrum of *anti* charged bipyrrole (str=stretch, i-r=interring, rd=ring deform, ipb=in-plane bend, oopb=out-of-plane bend, oopr = out-of-plane rotation, ripr = ring in-plane rotation).

			an	$ti 2-Py^+ (C_{2h})$			
$\mathbf{a}_g$	$\mathbf{b}_{g}$		$a_{\iota}$	ι		b <sub>i</sub>	ı
$(cm^{-1})$	$(\mathrm{cm}^{-1})$	$(\mathrm{cm}^{-1})$	$I_{IR}$	Assgm	$(\mathrm{cm}^{-1})$	$I_{IR}$	Assgm
3680	952	952	1.8	C-H oopb	3680	178.8	N-H str
3300	880	884	15.6	C-H oopb	3300	8.3	C-H str
3282	787	787	220.1	C-H oopb	3282	9.8	C-H str
3269	687	675	210.4	N-H oopb	3268	0.0	C-H str
1682	672	632	0.0	C-N oopb	1545	100.9	C-H,N-H ipb
1521	577	587	10.7	C-C=C oopb	1502	56.8	C=C,C-N str
1503	302	122	3.5	ring oopb	1413	369.6	$\operatorname{rd}$
1417		68	4.3	ring oopr	1400	1.4	C-H,N-H ipb
1393					1224	4.8	$\operatorname{rd}$
1308					1181	6.5	Ring breath
1184					1156	107.3	C-H,N-H ipb
1123					1110	94.4	C-H ipb
1113					1062	13.6	C-H,N-H ipb
969					920	44.0	$\operatorname{rd}$
891					880	5.6	$\operatorname{rd}$
459					155	1.4	ripr
406							

syn 2-Py <sup>+</sup> (C <sub>2v</sub> )								
	$a_1$		$a_2$					
$(cm^{-1})$	$I_{IR}$	Assgm	$(cm^{-1})$					
3691	156.2	N-H str	954					
3302	1.8	$C-H \ str$	883					
3286	4.9	$C-H \ str$	785					
3277	0.9	$C-H \ str$	681					
1682	6.5	C=C i-r str	591					
1514	43.8	N-H ipb	583					
1498	1.6	rd	301					
1416	23.9	C-C,N-H ipb	49					
1389	13.4	C-H ipb						
1239	6.2	$C-N \ str$						
1169	38.4	H-C-N-H						
1126	31.7	$\operatorname{H-C-C-C-H}$						
1111	15.5	$C-C \ str$						
966	1.6	$\operatorname{rd}$						
902	1.1	$\mathbf{rd}$						
407	0.0	$\operatorname{ript}$						
160	0.1	$\operatorname{ripr}$						
	$b_1$			b	2			
$((cm^{-1}))$	$I_{IR}$	Assgm	$(\mathrm{cm}^{-1})$	$I_{IR}$	Assgm			
956	1.5	C-H oopb	3682	0.1	N-H str			
885	19.3	C-H oopb	3301	6.7	C-H str			
790	178.7	C-H oopb	3283	5.4	C-H str			
674	241.5	N-H oopb	3275	0.3	C-H str			
627	0.6	C-N-C oopb	1544	65.2	C-H, N-H ipb			
577	26.2	C-C-C oopb	1510	31.8	C=C,C-N str			
119	1.5	ring oopb	1421	317.3	$C-C \operatorname{str}$			
			1386	8.7	C-H, N-H ipb			
			1296	3.9	C-H ipb			
			1173	1.0	Ring breath			
			1156	24.0	H-C-N-H			
			1104	69.0	H-C-C-H			
			1059	14.6	C-H ipb			
			912	49.0	rd			
			875	0.4	$\mathbf{rd}$			
			456	0.1	ripr			

Table 3.6: Vibrational spectrum of *syn* charged bipyrrole (str=stretch, i-r=inter-ring, rd=ring deform, ipb=in-plane bend, oopb=out-of-plane bend, oopr = out-of-plane rotation, ripr = ring in-plane rotation, ript = ring in-plane translation).

A frequency scaling factor, defined as the ratio between the calculated and experimental frequencies, and based on values in Tables 3.3 and 3.4 is on average 0.97. Additionally, this scaling factor could be used to scale the results for bipyrrole in Tables 3.5 and 3.6. Tables 3.5 and 3.6 contain the non-IR active frequencies of the  $a_g$  and  $b_g$  modes in the case of *anti*  $C_{2h}$  charged isomer, and the  $a_2$  mode in the case of the  $syn C_{2v}$  charged isomer. Values of frequencies in the tables have not been scaled.

# 3.3 Geometry, Energetics and Vibrational Analysis of Reduced n-Py Oligomers

A geometry optimization of the larger reduced n-Py was performed for sizes with n up to 24 monomers. The search for the structures of lowest energy was conducted for each oligomer size with the following strategy. A multitude of oligomer structures from molecular dynamics trajectories using the model potential described in chapter 4 were used as initial geometries for the optimization to a minimum of the energy. Minization was performed with the Berny algorithm and redundant internal coordinates [59]. Because the most stable isomer of neutral bipyrrole is the *anti-gauche* form, only repetitions of this form were optimized for larger n-Py oligomers. Combinations of *anti-gauche* with *syn-gauche* forms were not attempted. All geometrical optimizations of the electronic states include the harmonic frequency calculations to ensure finding of minima. Multiple configurations in this study were not minima but rather saddles of different orders. These geometries are not reported in this dissertation. The ground state of the n-Py neutral oligomers are singlet states.

The C-C single-double conjugation in n-Py is believed to result in a stiff backbone reluctant to bend and twist. As a matter of fact, the picture that most experimentalists have of reduced n-Py is that of planar oligomers [86, 87] as shown in Figs. 3.1b,c. This conjecture is a result of semi-empirical quantum mechanical approximations such as INDO that are not computer intensive and can be readily calculated in a PC. My calculations are based on a better quantum approximation that predict a different paradigm displayed in Fig. 3.4. This figure shows the optimized bent configurations of reduced 6, 9, 12, 15, 18, 24-Py. Notice that the torsion angle, as defined for 2-Py, continues to be approximately 153° between neighboring monomers. However, the end-to-end distance and the radius of gyration are substantially different than in planar chains. This chain bending is one of the reasons why PPy, irrespective of the fabrication process [26,62,88] tends to form amorphous rather than crystalline arrays of stacked chains [86]. This effect has also an important role in the volume contraction seen experimentally when an oxidized PPy sample is reduced. These bent conformations are in qualitative agreement with those reported recently within density functional calculations with smaller basis sets [71].

Although the point group of reduced Py is  $C_{2v}$ , larger chains present a loss of symmetry; the even-n-Py reduced oligomers are  $C_2$  (see Fig. 3.4) and odd-n-Py are  $C_s$ . Chains are less symmetric reflecting the bending of the backbone away from a plane. Binding energies of the ground singlet state <sup>1</sup>E<sub>b</sub>, the first excited trimer state <sup>3</sup>E<sub>b</sub> and the HOMO-LUMO energy gap  $\Delta_{HL}$  are reported in Table 3.7. In this table, the binding energy of the triplet state is relative to that of the singlet state. The  $\Delta_{HL}$  for the monomer and dimer are larger than the experimentally reported [89] values of 5.97 eV and 4.49 eV, respectively. This is to be expected for small molecules, as one of the deficiencies of DFT. Fig. 3.5a illustrates the binding energy per monomer of singlet states of n-Py showing a sharp increase for small chains and the slow asymptotic behavior for large chains toward the limiting energy of -57.17 eV/monomer corresponding to an infinite chain. Fig. 3.5b is a plot of the  $\Delta_{HL}$ indicating a rapid decrease as a function of number of monomers and a slow asymptotic trend as oligomers containing 15 or more monomers have almost reached the infinite chain energy gap of 3.17 eV. The latter is in excellent agreement with the experimental value of 3.2 eV [90].

Dependence on the oligomer chain length of both the radius of gyration (average distance squared of monomers from the oligomer center of mass) and the end-to-end distance  $d_{end-end}$ are depicted in Figs. 3.5c, d. As expected, based on the bent conformations shown in Fig. 3.4, the radius of gyration  $R_g$  as a function of chain length (solid line in Fig. 3.5c) increases



Figure 3.4: Optimized structures for reduced n-Py (n = 6, 9, 12, 15, 18, 24).



Figure 3.5: Properties of reduced n-Py oligomers as a function of the number of monomers. (a) Binding energy per monomer; (b) HOMO-LUMO energy gap; (c) Radius of gyration; (d) End-to-end distance.

		Reduced							
n-Py	Single	$\mathbf{et}$	Trij	plet					
	${}^{1}\mathrm{E}_{b}$	$\Delta$	${}^{3}\mathrm{E}_{b}$	$\Delta$					
1	-62.09	6.87	3.87	3.42					
2	-119.32	5.21	2.84	3.24					
3	-176.56	4.46	2.45	2.45					
4	-233.80	4.07	2.30	2.01					
5	-291.04	3.84	2.22	1.83					
6	-348.28	3.69	2.19	1.64					
9	-519.99	3.46	2.15	1.44					
12	-691.71	3.36	2.15	1.33					
15	-863.43	3.31	2.14	1.29					
18	-1035.14	3.29	2.14	1.28					

Table 3.7: Binding energies and HOMO-LUMO energy gap  $\Delta$  for n-Py in the reduced phase. Energies are in eV. Energies of the triplets are relative to the singlet ground state.

less rapidly than  $R_g$  of planar chains (dashed line in Fig. 3.5c). Accordingly, the end-to-end distance is dramatically shorter (solid line Fig. 3.5d) than in planar chains (dashed line in Fig. 3.5d). In the triplet state (triangles in Figs. 3.5c,d), both  $R_g$  and  $d_{end-end}$  are closer to the planar chain values.

The C-C bond length as a function of the C-C position in the 12-Py chain is depicted in the left top panel of Fig. 3.6 as an example of the oligomer benzenoid chains. The numbering of C-C bonds is sequential, starting with the double bond at one of the two chain ends. Arrows point to interring C-C bonds. The Wiberg bond index [91,92] was calculated for the C-C bonds along the n-Py chain with results for 12-Py depicted in Fig. 3.6 (right top panel). There is a clear correlation between bond length and bond order reinforcing that inter-monomer C-C single bonds are longer than the intra-monomer C-C single bonds and have a substantially lower bond order. Additionally, the two end monomers in the oligomers display shorter C-C double bonds with higher bond order.

The vibrational normal mode frequencies of the ground state and their IR-active intensities for n-Py (n = 3-6, 9 and 12) are shown in Fig. 3.7. These spectra correspond to the equilibrium structures shown in Fig. 3.4. IR active frequencies of n-Py are predominantly distributed in two spectral regions: 700-1600 cm<sup>-1</sup> and 3000-4000 cm<sup>-1</sup>. The far IR region



Figure 3.6: Distribution of bond lengths and bond orders along the backbone of reduced and oxidized 12-Py. Arrows mark the position of the C-C interring bonds.



Figure 3.7: IR-active vibrational spectra of reduced n-Py (n = 3, 4, 5, 6, 9, 12).

is associated to motions involving several atoms in each ring whereas most C-H and N-H stretching modes are in the near IR region. These vibrational spectra indicate that the two IR spectral regions are not sensitive to the size of the oligomer. Hence, reduced n-Py with different n have very similar vibrational spectra. As expected, the intensity of modes in these two spectral regions increases as the oligomer size increases.

## 3.4 Geometry, Energetics and Vibrational Analysis of Oxidized n-Py Oligomers

A thorough conformational optimization was implemented for positively charged n-Py oligomers as a function of the sustained positive charge Q. For these charged oligomers, ground states are doublets or singlets depending upon Q being odd or even. The positive charge distribution for different degrees of oxidation are based on the Mulliken analysis of the geometry-optimized ground state wave function of each oligomer. For oxidized n-Py,

the torsion angle is gradually increased from  $153^{\circ}$  as more positive charge Q is added to the backbone until reaching  $180^{\circ}$  (planar chain) when the ratio  $Q/n \ge 1/3$ . For Q/n below 1/3the n-Py oligomers may present kinks where two consecutive monomers have a  $90^{\circ}$  torsion angle between them. Although not systematic, a study was carried out for these kinked oxidized n-Py configurations. Resulting trends indicate that backbones with kinks lead to oxidized n-Py isomers with high binding energies, which in several cases are saddles of the energy landscape.

Findings in this work show that high level oxidized n-Py  $(Q/n \ge 1/3)$  even-membered oligomers display  $C_{2h}$  symmetry and odd-membered oligomers display  $C_{2v}$  symmetry. However, low level oxidized oligomers (Q/n < 1/3) are bent with a smaller curvature than in neutral oligometrian For example 12-Py<sup>6+</sup> and 12-Py<sup>4+</sup> are planar with no puckering between the nearest neighbor rings, whereas in 12-Py<sup>2+</sup> the torsion angle is increased from  $153^{\circ}$  to  $169^{\circ}$  (see Fig. 3.4 and Fig. 3.8). Effects of the increased oxidation level on the binding energy of oxidized oligomers (referred to the neutral) is summarized in Table 3.8. The effect of the increased oxidation level on the single/double C-C bond lengths and bond order structures is illustrated in Fig. 3.6. When n-Py is low level oxidized (Q/n < 1/3) the benzenoid conjugation of reduced n-Py is partly replaced with incipient trends of the quinoid structure. For example, in 12-Py<sup>2+</sup> the benzenoid conjugation is still predominant with interring C-C single bonds being shorter and C-C double bonds being expanded. However, as the ratio Q/n becomes  $Q/n \ge 1/3$ , then regions of quinoid alternation become clear. These quinoid regions span three monomers as shown in Fig. 3.6 for 12-Py<sup>4+</sup> and 12-Py<sup>6+</sup>. Two of quinoid regions are visible in 12-Py<sup>4+</sup> indicating that positive charge localized on each of these regions is +2e. In the case of 12-Py<sup>6+</sup> there are three quinoid regions, and again each region localizes a +2e charge. If the charge is increased further as in 12-Py<sup>8+</sup>, then the extent of the +2e charge localization is shorter barely covering two monomers. The energy of oxidized oligomers increases linearly by 0.92 eV/(+e). The vibrational spectra of oxidized n-Py is similar to the neutral spectra with the exception that frequencies in the



Figure 3.8: Optimized structures of oxidized 12-Py<sup>m+</sup> (m = 2, 3, 4) and 15-Py<sup>m+</sup> (m = 3, 4, 5).

700-1600  $\rm cm^{-1}$  are two orders of magnitude more intense.

The conformational dependence on oxidation level findings are confirmed by analyzing the distribution of charge per monomer along the chain. Based on the Mulliken population analysis, the total charge on each monomer shows an increasing degree of localization in multiple regions of the chain as the oxidation level is increased. This effect is depicted in Fig. 3.9a showing two regions of localization in 12-Py<sup>4+</sup>, three regions in 12-Py<sup>6+</sup>, and four regions in 12-Py<sup>8+</sup>. The charge localization takes place in multiples of +2e, which could be identified with the bipolaron [79–81]. Electron conduction then would take place by charge hoping between these localized regions.

Oxidation is attained experimentally with dopants. Typical oxidizing dopants include iodine, arsenic pentachloride, iron (III) chloride and  $\text{NOPF}_{6+}$ , which are electronegative compounds. A rough simulation of the effects of doping can be obtained within the hybrid DFT methodology used in this work by placing high electron affinity atoms such as fluorine

	Oxidized							
n-Py	$q^{2+}$	$q^{3+}$	$q^{4+}$	$q^{5+}$	$q^{6+}$	$q^{8+}$	$q^{10+}$	$q^{12+}$
					$E_b$			
1	24.03	-	-	-	-	-	-	-
2	18.72	-	-	-	-	-	-	-
3	16.50	-	-	-	-	-	-	-
4	15.20	-	-	-	-	-	-	-
5	14.34	-	-	-	-	-	-	-
6	13.73	24.94	39.24	-	-	-	-	-
9	12.60	21.92	33.73	-	64.78	-	-	-
12	11.93	-	30.67	-	57.26	92.18	-	-
15	11.48	19.08	28.71	39.62	52.41	-	120.95	-
18	11.16	-	-	-	49.02	76.71	-	150.82

Table 3.8: Binding energies and HOMO-LUMO energy gap for n-Py in the m+ oxidized phases (m=2-6, 8, 10, 12). Energies are in eV, all energies are relative to the ground state of the neutral oligomer (reported in Table 3.7).

close to the n-Py chains. The localization of positive charge, then takes place around the positions where these electronegative atoms are located. For example, in 12-Py if several F atoms are located symmetrically above and below the planar chain at three (or four) backbone positions where charge is peaked in Fig. 3.9a, then oxidation takes place yielding  $12-Py^{+6}$  or  $12-Py^{+8}$ . As shown in Fig. 3.9b, charge is transferred from Py atoms at these backbone positions to the fluorine atoms.

The oxidation level influences the HOMO-LUMO energy gap in n-Py. The calculated energy gap for reduced 12-Py is 3.36 eV, in agreement with the experimental [90] value of 3.2eV for bulk PPy. Additionally, for every +2e acquired by the oligomer upon oxidation, there is one localized state created in the gap. As shown in Fig. 3.10 for 12-Py, upon oxidation the HOMO-LUMO gap is reduced from 3.36 eV to 0.29, 0.73, 0.95 or 1.04 eV for every +2e increase in the oxidation level. For oxidation levels where Q/n < 1/3, the positive charge is delocalized along the backbone carbon atoms and the new state created in the energy gap is close in energy to the HOMO. However, as oxidation reaches Q/n =1/3, charge localization occurs and this effect results in level repulsion between the HOMO and the gap-localized states. For infinite PPy these gap-localized states form a band, which may eventually overlap the valence band for the polymer to be conducting.


Figure 3.9: Distribution of charge per monomer along the backbone of oxidized 12-Py. (a) Various oxidation levels; (b) Charge localization due to dopants.



Figure 3.10: Energy levels near the HOMO-LUMO gap of reduced 12-Py, and oxidized 12-Py<sup>m+</sup> (m = 2, 4, 6, 8).

## 3.5 PPy Infinite Chain

The electronic band structure of infinite chains was studied within the same hybrid DFT approach. For reduced PPy, a  $C_{2v}$  planar 4-monomer chain was used in the unit cell of the periodic array. Fig. 3.11 shows 16 bands around the Fermi energy, with all energies relative to the Fermi energy. Each band contains eighty k-points. The Fermi energy was determined as that energy for which the sum of the Fermi-function associated to each of the eigenvalues composing the bands equated the number of electrons (n = 163). The energy band gap of reduced PPy is 3.17eV, which is in excellent agreement with the experimental value of 3.2 eV. Two oxidation levels of PPy were considered. For +1e oxidation, the PPy was obtained by placing two F atoms at 2.2 Å away from the center of a monomer in the unit cell, one above and one below. For +2e oxidation, two F<sub>2</sub> dimers were placed in similar locations. The localized new band due to the charge is mainly an extended p-band formed by the carbon p-orbitals perpendicular to the plane of the monomers. The energy band gap shows a marked dependence with the oxidation level, decreasing from 1.78 eV for +1e to 0.57 eV



Figure 3.11: Electronic band structure of infinite chains of reduced and oxidized PPy.

for +2e. Although fluorine is a strong electronegative element, because the dopants were placed far away from the monomers, a +1e or +2e charge transfer was not fully attained with either two F or two F<sub>2</sub>, but rather +1.08e and +1.48e were obtained. For this reason, as seen in Fig. 3.11 as a function of oxidation level, the Fermi energy is still in the band gap and the valence band does not merge or cross the new localized band as expected in a conductor material. Increasing the size of the basis set size to include diffuse functions does not change significantly the band structure shown in Fig. 3.11.

### 3.6 Conclusion

In summary, this is an exhaustive set of structural and energetic results for n-Py oligomers (n = 1 - 24) in both the reduced and oxidized phases. Outstanding features of the reduced oligomers are their notoriously bent spatial conformation, which result in strong reductions of their radius of gyration and end-to-end distance as compared to planar oligomers. As a result of oxidation (charge Q), these oligomers become increasingly planar until the critical value of  $Q/n \ge 1/3$  yields an oxidation level in which the oligomers are planar. This critical

oxidation level is also accompanied by a spatial localization of positive charge, which is usually referred as polaron. Below the critical value of 1/3 the oxidized oligomers present a delocalized positive charge distributed along the oligomer backbone C atoms. Above the critical value there is charge localization.

Vibrational spectra of n-Py oligomers display two fairly size-insensitive IR spectral regions at 700-1600 cm<sup>-1</sup> and 3000-4000 cm<sup>-1</sup>, which only change slightly with oxidation. As expected, if in the proximity of n-Py several electronegative dopants are included in the calculation, Q localizes in the neighborhood of the dopant and one localized state in the HOMO-LUMO gap appears for every +2e in the oxidation level. The energy band gap of infinite PPy is in excellent agreement with experiment. Additionally, the trend of a decreasing band gap with increasing oxidation level is clearly demonstrated.

All together this work provides a comprehensive and complete study of the effects that reduction-oxidation changes produce in the electronic structure, conformation, energetics and vibrational spectra on n-Py and infinite PPy chains.

## Chapter 4: Monte Carlo Study of PolyPyrrole

### 4.1 PPy Potential Model

The quantum approach of n-Py described in Chapter 3 can be done only for less than 30 monomers, otherwise the computation time becomes intractable. For that reason, this chapter contains the strategy used in the development of a classical potential model to treat larger systems. This model potential can then be used in Monte Carlo simulations with the aim of understanding the experimental observations and being useful in future studies involving thousands to millions of Py monomers.

The PPy potential model is built based on a modified rigid-ion polarizable force field in which the assumptions are to treat each pyrrole ring as a rigid planar body having a dipole centered in each ring's center (see Fig. 4.1). In a pyrrole ring, the dipole represents the negative charge on the N atom counter-balanced by the positive charge on all other atoms. For the neutral (reduced) polymer, the proposed model potential of the system is the sum of interring bond stretching (Morse potential), interring bending angle, torsion, excluded volume (9-6 Mie-Jones) and dipole-dipole interactions:



Figure 4.1: Schematic representation of the atoms, monomer center of mass and dipoles in 4-Py

$$U_{intra} = U_{Morse} + U_{bending} + U_{torsion} + U_{excluded-volume} + U_{dipole-dipole}$$
(4.1)

The Morse potential is used to represent the C-C bond stretching between rings and includes interactions between the center of mass of any two nearest neighboring rings. For a chain with n rings this potential is given by:

$$U_{Morse} = \sum_{i=1}^{n-1} \{ D_e [1 - e^{-\alpha(r_{i,i+1} - r_0)}]^2 - D_e \}$$
(4.2)

where  $D_e$  and  $\alpha$  are parameters,  $r_0 = 3.8579$  Å is the equilibrium distance between two nearest neighboring rings' center of mass and  $r_{i,i+1}$  is the distance between these centers of mass within one oligomer.

The bending potential is used to describe the angular motion between three nearest neighboring rings in the same PPy chain. For a short oligomer, as depicted in Fig. 4.1, bending will occur for two angles  $\angle ABC$  and  $\angle BCD$ , where A, B, C, D are the center of mass coordinates of each ring. Note that these four rings are not coplanar and their centers of mass are not located in a straight line:

$$U_{bending} = \sum_{i=1}^{n-2} K_{\theta} (\cos \theta_i - \cos \theta_0)^2$$
(4.3)

where  $K_{\theta}$  is another parameter and  $\theta_0 = 139.5^{\circ}$ .

The torsion potential has two parts. In the first, two nearest neighboring rings in the same oligomer are linked through their dihedral angle  $\gamma$ . Motion involving this angle is

represented by the first two terms in the following expression:

$$U_{torsion} = \sum_{i=1}^{n-1} \{ K_1 [1 + \cos(\gamma_{i,i+1} + \gamma_0)] + K_2 [1 + \cos 3(\gamma_{i,i+1} + \gamma_0)] + K_3 (\angle 1_i 2_i 2'_{i+1} + \angle 1_i 2_i 3_i + \angle 3_i 2_i 2'_{i+1} - 2\pi)^2 \}$$
(4.4)

where  $K_1$  and  $K_2$  are parameters,  $\gamma_0=26^\circ$  and  $\gamma_{ij}$  is the dihedral angle defined as:

$$\cos\gamma_{ij} = \frac{(\vec{e_j} \times \vec{r_{ij}}) \cdot (\vec{e_i} \times \vec{r_{ij}})}{|\vec{e_j} \times \vec{r_{ij}}||\vec{e_i} \times \vec{r_{ij}}|}$$
(4.5)

Here  $\vec{e_i}$  and  $\vec{e_j}$  are two unit vectors contained in the planes of two contiguous rings as shown in Fig. 4.2. The second part of the torsion potential, represented by the third term in Eq. 4.4, is a constrain that keeps atoms 1,2,3 and 2' in the same plane. Only nearest neighboring rings in one oligomer participate in this term of the torsion potential, where  $K_3$  is a parameter and the angles are visualized in Fig. 4.1. This term is zero when the three involved angles equal  $2\pi$ . Otherwise a repulsion sets in.

The 9-6 Mie-Jones potential is used to describe the excluded volume due to the shape of each ring. With this purpose, the interaction between the center of mass of pyrrole rings that are second-neighbors or further away neighbors are considered, such that

$$U_{excluded-volume} = \sum_{i=1}^{n-2} \sum_{j=i+2}^{n} 2\varepsilon [(\frac{\sigma}{r_{ij}})^9 - \frac{3}{2} (\frac{\sigma}{r_{ij}})^6]$$
(4.6)

where  $\sigma$  and  $\epsilon$  are parameters. Here  $\sigma^3$  is a measure of the excluded volume associated with a ring.

The dipole-dipole potential includes all pairs of interactions:



Figure 4.2: Schematic coordinate system description for the dipole-dipole interaction.

$$U_{dipole-dipole} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{3\mu^2}{r_{ij}^3} [\frac{1}{3}\cos\gamma_{ij} - \cos\phi_i\cos\phi_j]$$
(4.7)

where  $\mu = 1.0121$  D (from DFT) is the magnitude of the dipole moment,  $\gamma_{ij}$  is the dihedral angle given in Eq. 4.5,  $r_{ij}$  is the distance between dipoles placed at the center of each ring (see schematic description in Fig. 4.2),  $\phi_i$  is the angle between the dipole  $\vec{\mu}_i$  (along  $\vec{e}_i$ ) and  $\vec{r}_{ij}$  and  $\phi_j$  is the angle between  $\vec{\mu}_j$  (along  $\vec{e}_j$ ) and  $\vec{r}_{ij}$ .

The eight parameters that appear in Eqs. 4.1 - 4.7 were fitted to energies calculated with DFT. The idea is to match as best as possible both the binding energy and the geometry of the n-Py oligomers (n = 2-10, 12, 15, 18, 24) described in Chap. 3. The parameters of the Morse potential,  $D_e$  and  $\alpha$ , are fitted first. For 2-Py, only the Morse, torsion angle and dipole potentials exist in Eq. 4.1 since the dipole-dipole potential from Eq. 4.7 gives a constant. In order to generate the target points in DFT, the 2-Py oligomer's interring C-C bond length is changed while keeping the torsion angle  $\gamma = 154^{\circ}$  with carbons 1, 2, 3, 2' and 1', 2', 3', 2 maintained in the same plane ( $U_{torsion} = 0$ ). Twenty five target points were calculated with DFT and a nonlinear regression algorithm minimizing the least square error was used to fit the two parameters  $D_e$  and  $\alpha$  entering in Eq. 4.2. The best values are



Figure 4.3: Comparison of 2-Py energy surface of the Morse potential calculated with DFT and the model potential.

 $D_e = 7.0196 \text{ eV}, \alpha = 1.9197 \text{ }^{A^{-1}}$  with an error of 0.0363. Fig. 4.3 shows that in regions close to the minimum the fit is excellent. It is expected that only small vibrations of the C-C interring bond (~ 0.2 Å) may occur along a simulation.

In order to fit parameters in the first and second terms of the torsion potential Eq. 4.4, 11 values of the DFT binding energy were obtained by keeping the C-C interring bond length of 2-Py fixed with carbons 1, 2, 3, 2' and 1', 2', 3', 2 in the same plane and changing the torsion angle  $\gamma$ . The target data is visualized in Fig. 4.4 (circles). The best parameters are  $K_1 = 0.081 \text{ eV}$ ,  $K_2 = 0.0322 \text{ eV}$  and the error is  $3.81 \times 10^{-4}$ . A visualization of the fit is given in Fig. 4.4.

The remaining four parameters are fitted on a database of 22 target points containing the equilibrium binding energies for n-Py (n = 2-7, 9, 12, 15, 18, 24) plus 10 target points from the energy surface of 4-Py. The best values of these parameters are  $\epsilon = 0.0069$  eV;  $\sigma$ = 9.6801 Å; K<sub> $\theta$ </sub> = 1.2517 eV; K<sub>3</sub> = 5.1808 eV and the error is 0.0365. A calculation of the



Figure 4.4: Comparison of 2-Py energy surface of the torsion potential calculated with DFT and the model potential.

binding energy of n-Py at their equilibrium configurations using all parameters is compared with the target DFT values in Fig. 4.5. As clearly seen, the agreement is excellent.

The interaction between N chains is modeled by

$$U_{inter} = 2\varepsilon_{inter} \sum_{i=1}^{N} \sum_{j\neq i=1}^{N} \left[ \left( \frac{\sigma_{inter}}{r_{ij}} \right)^9 - \frac{3}{2} \left( \frac{\sigma_{inter}}{r_{ij}} \right)^6 \right]$$
(4.8)

where  $\varepsilon_{inter} = 0.066$  eV and  $\sigma_{inter} = 5.8686$  Å were fitted to 10 target points of two 12-Py chains at different distances. The full potential for a system of N oligomers is

$$U_{total} = \sum_{i=1}^{N} [U_{intra}(i) + U_{inter}]$$

The implementation of this fit was done using subroutine RLIN of the IMSL library



Figure 4.5: Comparison between the binding energy of n-Py (n = 2-7, 9, 12, 15, 18, 20, 24) calculated with DFT and with the model potential.

[93].

# 4.2 Simulation of n-Py (n = 3 - 24, 36) with the ATMC

### 4.2.1 Strategy for the MC Step

In both the ATMC and the regular MMC, the model potential entering in the calculation of the potential energy E is described in Sec. 4.1. Two operators  $\hat{t}$  and  $\hat{R}$  are needed to locate a rigid body in space, where  $\hat{t}$  describes the translation of the rigid body and  $\hat{R}$  describes the rotation of the rigid body.

The orientation of a rigid body specifies the relation between two reference systems: one axes system is fixed in space  $(e^s)$ , the other axes system is fixed on the body  $(e^b)$  and they are related through the rotation matrix  $\mathbb{R}$ :

$$e^b = \mathbb{R} \cdot e^s; \quad e^s = \mathbb{R}^{-1} \cdot e^b \tag{4.9}$$

One way to relate one system of axes  $(x, y, z)^s$  to another fixed in the body  $(x, y, z)^b$  is through the Euler angles  $\theta$ ,  $\psi$ ,  $\phi$ , in which case the rotation matrix  $\mathbb{R}$  is defined as:

$$\mathbb{R} = \begin{pmatrix} \cos\phi\cos\psi - \sin\phi\cos\theta\sin\psi & \sin\phi\cos\psi + \cos\phi\cos\theta\sin\psi & \sin\theta\sin\psi \\ -\cos\phi\sin\psi - \sin\phi\cos\theta\cos\psi & -\sin\phi\sin\psi + \cos\phi\cos\theta\cos\psi & \sin\theta\cos\psi \\ \sin\phi\sin\theta & -\cos\phi\sin\theta & \cos\theta \end{pmatrix}$$
(4.10)

This matrix is unitary, thus  $\mathbb{R}^* = \mathbb{R}^{-1}$ , where  $\mathbb{R}^*$  is the conjugate transpose.

Evans introduced the use of a quaternion [94] as generalized coordinate for dealing with rigid body system transformations. A quaternion Q is a set of four scalar quantities,  $Q = (q_0, q_1, q_2, q_3)$  given in terms of the Euler angles:

$$q_{0} = \cos \frac{1}{2}\theta \cos \frac{1}{2}(\phi + \psi); \qquad q_{1} = \sin \frac{1}{2}\theta \cos \frac{1}{2}(\phi - \psi) q_{2} = \sin \frac{1}{2}\theta \sin \frac{1}{2}(\phi - \psi); \qquad q_{3} = \cos \frac{1}{2}\theta \sin \frac{1}{2}(\phi + \psi)$$
(4.11)

The quaternion of interest here satisfy the constrain:

$$q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1 (4.12)$$

The rotation matrix in terms of the quaternion becomes

$$\mathbb{R} = \begin{pmatrix} q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(q_1q_2 + q_0q_3) & 2(q_1q_3 - q_0q_2) \\ 2(q_1q_2 - q_0q_3) & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2(q_2q_3 + q_0q_1) \\ 2(q_1q_3 + q_0q_2) & 2(q_2q_3 - q_0q_1) & q_0^2 - q_1^2 - q_2^2 + q_3^2 \end{pmatrix}$$
(4.13)

The positions of atoms in one ring in the laboratory, fixed space system, are obtained from those in the body system using Eq. 4.9. For one ring:

$$x^{s}(i,\nu) = x^{s}_{CM}(i) + \mathbb{R}_{11}(i)x^{b}(\nu) + \mathbb{R}_{21}(i)y^{b}(\nu) + \mathbb{R}_{31}(i)z^{b}(\nu)$$
  

$$y^{s}(i,\nu) = y^{s}_{CM}(i) + \mathbb{R}_{12}(i)x^{b}(\nu) + \mathbb{R}_{22}(i)y^{b}(\nu) + \mathbb{R}_{32}(i)z^{b}(\nu)$$
  

$$z^{s}(i,\nu) = z^{s}_{CM}(i) + \mathbb{R}_{13}(i)x^{b}(\nu) + \mathbb{R}_{23}(i)y^{b}(\nu) + \mathbb{R}_{33}(i)z^{b}(\nu)$$
  
(4.14)

where *i* identifies each ring in one n-Py and runs from 1 to n. The index  $\nu$  identifies each atom in one ring and runs between 1 and 8, except for end rings where it goes up to 10. The  $x_{CM}^s$ ,  $y_{CM}^s$ ,  $z_{CM}^s$  are the coordinates of the center of mass of the ring in question in the laboratory frame.

In the model potential described in Sec. 4.1, movement of a monomer as a whole can be done with the regular translation operator  $\hat{t}$ . This involves MC moves that are contained in  $U_{Morse}$ ,  $U_{bending}$  and  $U_{excluded-volume}$ , Eqs. 4.2, 4.3 and 4.6. However, in order to represent the planar aspect of each ring, these rings should be treated as rigid bodies. Therefore in order to generate motions of the dihedral angle  $\gamma$  and the dipoles (Eqs. 4.4 and 4.7), the rotation operator  $\hat{R}$  needs to be considered in the MMC and ATMC. The quaternion approach was adopted, in which each ring is treated as a rigid body and it may rotate in space.

The implementation of the rigid body rotations require several steps. Step one involves setting the coordinates of all atoms in a ring in the body system. As shown in Fig. 3.1a, these coordinates are  $\{x_{\nu}^{b}\}, \{y_{\nu}^{b}\}, \{z_{\nu}^{b}\}$ , where  $\nu = 1$  - 10 if the ring is an end-monomer and  $\nu = 1$ -8 if the ring is not at the end of the polymer chain. These body-system coordinates were optimized with DFT. Step two involves defining an initial position of the oligomer in the laboratory, fixed space system. This is accomplished by giving an initial position to the center of mass for each ring of the oligomer,  $\{x_{CM}^{s}(i)\}, \{y_{CM}^{s}(i)\}, \{z_{CM}^{s}(i)\}$ , where i = 1, 2, ..., n, in the laboratory frame. Step three defines the initial orientation of the rings in each oligomer. This is achieved by giving an initial quaternion to each ring in the oligomer,  $q_0(i)$ ,  $q_1(i)$ ,  $q_2(i)$ ,  $q_3(i)$ , where i = 1, 2, ..., n. Therefore the full chain is described in the laboratory frame. The fourth step involves obtaining the coordinates of all atoms in the laboratory frame using Eq. 4.14. This step ensures an initial position for all atoms in the oligomer, such that rings' torsion angle  $\gamma$  and dipole moment can be uniquely obtained in the laboratory frame. Then, the orientation contribution to the energy from Eq. 4.4 and 4.7 can be calculated.

With the above in mind, moving one ring in a MC step implies to move its center of mass and to rotate it. Therefore, one MC step involves a new configuration from the previous by  $\{\vec{r}_{CM}^s(i)\} = \{\vec{r}_{CM}^s(i)\} + d\vec{r}$  and Q(i) = Q(i) + dQ for the *i*th monomer. Both dr and dQchange dynamically in the simulation in such a manner that the percentage of acceptances and rejections fluctuate between 40% and 60%.

With the positions of all atoms of one n-Py oligomer, the potential of the system can be calculated through Eqs. 4.1 - 4.7. As described in Sec. 1.2.2, in each MMC step, the new configuration is generated by adding random displacements to the original center of mass  $\{x_{CM}^s(i)\}, \{y_{CM}^s(i)\}, \{z_{CM}^s(i)\}, \{z_{CM}^s(i)\}\}$ . For one monomer, the new translation is obtained as  $x_{CM}^s(i) + dx, y_{CM}^s(i) + dy, z_{CM}^s(i) + dz$ , where dx, dy, dz are calculated by multiplying dr (dr = 0.01 - 0.05 Å) with the sign of a random number between [-1, 1]. Then, the potential energy is calculated for this new configuration, which is accepted or rejected using Metropolis acceptance criterion. After that, the quaternion of the monomer previously selected is changed to  $q_0(i) + dq_0, q_1(i) + dq_1, q_2(i) + dq_2, q_3(i) + dq_3$ , where  $dq_0, dq_1, dq_2$  and  $dq_3$ are the product of dq (dq = 0.007 - 0.01) and the sign of a random number in the interval [-1, 1]. Additionally, dr and dq are adjusted to keep a 50/50 percent acceptance/rejection rate. This configuration, where the orientation of monomer is changed, is accepted or not with the MMC criterion.

#### 4.2.2 Isolated n-Py Oligomers

The ATMC geometry optimization of single chains of n-Py (n = 3-12, 15, 18, 24, 36) was done in order to ensure that the proposed model potential is appropriate for the PPy system. Several different initial configurations of n-Py are selected. The simulation is started by running one thousand steps of the MMC at the temperature 1000 K to relax the configuration. Then the ATMC simulation is started from 1000 K and the ATMC drives the system to very low temperature near 0 K. The fixed number of configuration trials  $(m_{fix})$  at temperature T was chosen to be 100 and the parameter a in Eq. 1.27 is 1.5. The temperature evolution as the ATMC progresses is given in Fig 4.6 for 24-Py and 36-Py. For each n-Py, the ATMC gives several local minimum structures, which are quasi degenerate. The geometries in Fig. 4.7 illustrate structures for n-Py (n = 6, 9, 12, 18, 24, 36) of the lowest local minimum energy found at very low temperature. Most small Py oligomers with n < 18 have several bending chains which are very similar to the DFT results. For the longer chains  $(n \ge 18)$ , the oligometric become wavy. The lowest local minimum energy of n-Py (n = 3-12, 15, 18, 24, 36) from ATMC is compared to the binding energy of n-Py calculated by DFT. Here the binding energy of n-Py is calculated with the total DFT energy minus the sum of DFT energy of each ring. The comparing results are shown in Fig. 4.8. The red line with circle corresponds to be DFT results and the black line with triangle are the ATMC calculations. From the figure, it is evident that the two results match very well.

#### 4.2.3 Molecular systems of many oligomers

Three different molecular systems are considered, each of them containing a large number of n-Py molecules. One system contains 192 chains of 4-Py, the second and third are composed of 64 chains of 12-Py and 42 chains of 12-Py. The initial configuration of the 192 4-Py system is shown in Figs. 4.9(a) and (b). Fig. 4.9(a) is the structure of the rings center of mass and (b) contains the ring structure with all atoms. Periodic boundary conditions are used throughout these simulations. The oligomers are initially arranged inside a computational box with center of mass of each chain located in face-centered cubic (FCC) positions. Initially all chains are considered to be flat. The size of the computational box changes if a different system density is to be considered. Several densities were considered for this molecular system, and lattice sizes  $L_a$ ,  $L_b$  and  $L_c$  associated with them are reported



Figure 4.6: Temperature evolution along the ATMC tempering process for 24-Py and 36-Py.



Figure 4.7: The structures of lowest local minimum energy of n-Py (n=6,9,12,18,24,36) obtained with the ATMC



Figure 4.8: The lowest local minimum energy of n-Py (n=3-12,15,18,24,36) compared to the binding energy of n-Py calculated with DFT.

in Table 4.1 along with the number of unit-cell- repetitions in each direction.

The general simulation process is as follows. As a first step each system is relaxed from the initial configuration by a warm-up mechanism in which the MMC is run between 1,000-10,000 steps at high temperatures of either 1000K or 1200K. In a second step the ATMC is run starting from the last configuration of the relaxing step with parameters a = 1.5 and  $m_{fix} = 100$ . During this step the system is drove from high temperature to low temperature. The expectation is that the global minimum of the system has been reached. However, for non-crystalline systems, there might be a collection of preferred minima states. Therefore the ATMC was repeated 10 times, each time starting from the last configuration of the previous run. The third step consists of running an MMC, starting from the configuration obtained in the second step, to equilibrate the system at T = 300 K and then collect results over 500,000 to 1,000,000.

For these systems of many oligomers, a quasi-order parameter was defined along the lines of Ref. [95]. The order parameter is intended to identify regions of stacked chains versus regions of fully disordered chains. For this purpose, a chain axis is defined by a vector  $\vec{a} = \vec{r}_1 - \vec{r}_n$  joining the centers of mass of the first and last ring of each oligomer.



Figure 4.9: Initial configurations of the molecular systems. (a) 192 4-Py molecules at  $\rho = 0.88g/cm^3$  (chain centers of mass located in FCC positions); (b) same as (a) with all atoms; (c) 64 12-Py molecules at  $\rho = 0.66g/cm^3$  (chain centers of mass located in FCC positions); (d) same as (c) with all atoms.

n-Py	$ ho~({ m g/cm^3})$	$L_a$ (Å)	$\mathcal{L}_b(\mathring{A})$	$L_c$ (Å)	$n_a$	$n_b$	$n_c$	Lattice
4-Py	0.88	17.40	10.66	10.66	3	4	4	FCC
	0.94	17.00	10.44	10.44	3	4	4	FCC
	1.15	15.50	9.90	9.90	3	4	4	FCC
	1.50	14.83	9.33	9.33	3	4	4	FCC
	2.00	11.57	8.68	8.68	3	4	4	FCC
12-ру	0.43	58.00	14.50	14.50	1	4	4	FCC
	0.50	55.01	13.75	13.75	1	4	4	FCC
	0.66	50.15	12.54	12.54	1	4	4	FCC
	0.82	46.65	11.66	11.66	1	4	4	FCC
	0.98	44.00	11.00	11.00	1	4	4	FCC
	1.03	40.00	5.14	12.33	1	7	3	$\mathbf{SC}$
	1.13	38.00	5.00	12.00	1	7	3	$\mathbf{SC}$

Table 4.1: Description of molecular systems

Next, the system orientation is defined by  $\vec{n}$ , which is the average direction of alignment of all chains. The angle between  $\vec{n}$  and  $\vec{a}$  is called  $\theta$ , such that the order parameter is defined as

$$S = \frac{1}{2} \langle (3\cos^2\theta - 1) \rangle \tag{4.15}$$

If  $\theta$  is around 0 or  $\pi$  (parallel alignment),  $\cos\theta = \pm 1$  and S = 1. On the other hand, if the chains orientation are entirely random, then  $\langle \cos^2\theta \rangle = \frac{1}{3}$  and S = 0. Thus, S is a measure of the chain alignment.

An illustration of the ATMC process of the 192 4-Py system at  $\rho = 0.88 \ g/cm^3$  is provided in Fig. 4.10 and at  $\rho = 2.00 \ g/cm^3$  is given in Fig. 4.11. Both figures show the temperature evolution as the tempering progresses and the changes that various quantities undergo along this process. For low density, the radius of gyration and the end to end distance are shorter at high temperature than those at low temperature, and the order parameter changes in a wide range from 0.0 - 1.0. For high density, Fig. 4.11, the order parameter changes between 1.0 - 0.8, which means the system displays chain stacking.

When the ATMC is completed, the regular MMC simulation is performed to obtain the thermodynamics properties of the system at 300 K. Five densities were considered, as indicated in Table 4.1. Table 4.2 contains the average and standard deviation of several properties. Comparison of the MMC results of energy per chain, end-to-end distance, radius of gyration at different densities show that these properties are fairly insensitive to density changes for  $\rho < 1.50 \ g/cm^3$ . However, the order parameter has an obvious change and keeps increasing with increasing density. At higher density  $\rho = 2.00 \ g/cm^3$ , the order parameter is close to 1, meaning that the molecules cannot rotate or translate freely. It appears that this system undergoes an order-disorder transition in the proximity of  $\rho = 1.5 \ g/cm^3$ .



Figure 4.10: Temperature evolution as the ATMC progress for 192 4-Py molecules system at  $\rho_3 = 0.88 \text{ g/cm}^3$ . All plots are a collection of 10 ATMC runs except the top right plot, which corresponds to one run.

4-Py	$ ho~({ m g/cm^3})$	$E_b/N$ (eV)	$d_{end-end}$ (Å)	$\mathbf{R}_g(\mathbf{A})$	S
DFT $(0 \text{ K})$	Iso. mono.	-19.9176	12.85	4.10	_
	0.88	$-20.904{\pm}0.04$	$12.83 {\pm} 0.02$	$4.02{\pm}0.01$	$0.09{\pm}0.03$
	0.94	$-20.904 \pm 0.04$	$12.83 {\pm} 0.02$	$4.02{\pm}0.01$	$0.05{\pm}0.02$
MC (300k)	1.15	$-20.875 {\pm} 0.04$	$12.82{\pm}0.02$	$4.02{\pm}0.01$	$0.11{\pm}0.01$
	1.50	$-20.765 {\pm} 0.05$	$12.84{\pm}0.02$	$4.02{\pm}0.01$	$0.77{\pm}0.01$
	2.00	$-18.867 {\pm} 0.04$	$12.60 {\pm} 0.02$	$3.98{\pm}0.04$	$0.86{\pm}0.00$

Table 4.2: MMC simulation results compare to DFT results for 192 4-Py molicular systems at T = 300 K.

Fig. 4.12 shows the final configuration of the 192 4-Py system with  $\rho = 0.88$  g/cm<sup>3</sup> and  $\rho = 2.0$  g/cm<sup>3</sup> at T = 300 K. Fig. 4.13 illustrates the radial distribution function of this system at these densities. Plots on the left take into account only intra-chain distances and plots to the right show the distribution for inter-chain distances. All distances are between centers of mass. Three peaks appearing in the intra-chain g(r) represent bond lengths between the nearest neighbor rings, second neighbor rings and third nearest rings, respectively. The distribution function of the inter-chain distances display characteristics of a liquid. As density increases, the g(r) becomes more structured showing an increased local order; which may characterize a system of stacked chains. Angle distributions are described in Fig. 4.14. Fig. 4.14(a) is the torsion angle (dihedral angle) distribution of all chains in the system. From the figure, it is clear that the torsion angle is around 154° and does not change with density. Fig. 4.14(b) and (c) are the angle distributions between the second and third nearest neighbor is around 154° or 110°.

Another two molecular systems are 64 12-Py chains and 42 12-Py chains. The initial configurations of of 64 12-Py chains are arranged in the box with their center of mass in FCC positions (Figs 4.9(c) and (d)) and the initial chains are flat. The initial configurations of 42 12-Py chains are arranged in the box with center of mass of each chain in simple cubic (SC) positions and the initial chains are bending. The lattice constants are listed in Table 4.1. Periodic boundary conditions are used throughout the simulations. Before starting the ATMC, 1000 steps are run to relax the initial configuration at temperature of 1000 K.



Figure 4.11: Temperature evolution as the ATMC progress for 192 4-Py molecules system at  $\rho_3 = 2.00 \text{ g/cm}^3$ . All plots are a collection of 10 ATMC runs except the top right plot, which corresponds to one run.



Figure 4.12: Final configuration of 192 4-Py system with  $\rho = 0.88 \text{ g/cm}^3$  in (a) and (b) and  $\rho = 2.00 \text{ g/cm}^3$  in (c) and (d) at T = 300 K.



Figure 4.13: Radial distribution of the ring centers of mass for the 192 4-Py system at T = 300 K for  $\rho_1 = 0.88 \text{ g/cm}^3$ ,  $\rho_2 = 1.15 \text{ g/cm}^3$  and  $\rho_3 = 2.00 \text{ g/cm}^3$ . Left plots contain only intra-chain distances; Right plots contain only intra-chain distances.



Figure 4.14: Torsion angle distribution for the 192 4-Py system at T = 300 K and  $\rho_1 = 0.88 \text{ g/cm}^3$ ,  $\rho_2 = 1.15 \text{ g/cm}^3$  and  $\rho_3 = 2.00 \text{ g/cm}^3$ . (a) torsion angle (b) angle between the second nearest neighbors (c) angle between the third nearest neighbors

12-Py	$ ho ~({ m g/cm^3})$	$E_b/N$ (eV)	$d_{end-end}$ (Å)	$\mathbf{R}_g$ (Å)	S
DFT $(0 \text{ K})$	Iso. mono.	-75.8604	36.97	11.67	_
	0.43	$-76.106 \pm 0.041$	$39.49 {\pm} 0.12$	$12.00 {\pm} 0.04$	$0.41{\pm}0.02$
	0.50	$-76.150 {\pm} 0.042$	$39.76 {\pm} 0.09$	$12.04{\pm}0.03$	$0.58{\pm}0.02$
MC (300k)	0.66	$-76.277 {\pm} 0.041$	$40.14 {\pm} 0.14$	$12.11 {\pm} 0.02$	$0.86{\pm}0.01$
	0.82	$-76.370 {\pm} 0.042$	$40.63 {\pm} 0.06$	$12.18{\pm}0.02$	$0.96{\pm}0.02$
	0.98	$-76.418 {\pm} 0.044$	$40.32 {\pm} 0.09$	$12.13 {\pm} 0.01$	$0.95{\pm}0.02$
	1.03	$-76.465 {\pm} 0.212$	$40.33 {\pm} 0.07$	$12.15 {\pm} 0.02$	$0.98{\pm}0.01$
	1.13	$-76.418 {\pm} 0.187$	$38.39 {\pm} 0.05$	$11.80{\pm}0.04$	$0.98{\pm}0.01$

Table 4.3: MMC simulation results compare to DFT results for 42 and 64 12-Py molecular systems at T = 300 K.

The parameters in the ATMC are  $T_{max} = 1200$  K,  $T_{min} = 0$  K, a = 1.5 and  $m_{fix} = 100$ . Fig. 4.15 and 4.16 illustrate the temperature evolution as the ATMC progresses at  $\rho = 0.43$  g/cm<sup>3</sup> and 0.98 g/cm<sup>3</sup> respectively. After the ATMC simulation, the regular MMC simulation is performed to obtain the thermodynamic properties of the system at T = 300 K.

Average values of energy per chain, radius of gyration and end-to-end distance are provided in Table 4.3. The energy is decreasing as density increases, while the end-to-end distance and the radius of gyration tend to increase with increasing density. It is evident that stacking occurs at high density, because the order parameter is very close to 1. Possibly the system is nematic at densities above  $\rho = 0.8 \text{ g/cm}^3$ .



Figure 4.15: Temperature evolution as the ATMC progress for 64 12-Py molecules system at T = 300 K and  $\rho_1 = 0.43$  g/cm<sup>3</sup>.

Fig. 4.17 shows the radial distribution of this system. (a) plots correspond to intra-chain distances; The (b) and (c) plots show the distribution for inter-chain distances for systems at various densities. All distances are between centers of mass.



Figure 4.16: Temperature evolution as the ATMC progress for 64 12-Py molecules system at T = 300 K and  $\rho_1 = 0.98$  g/cm<sup>3</sup>.

### 4.3 Conclusion

Based on the DFT results of n-Py oligomers, a classical potential model of PPy is developed to treat dense molecular systems containing many oligomers. This model potential is then used in the ATMC and the MMC simulations of single chains 6, 9, 12, 18, 24 and 36-Py. For short chains with less than 18 monomers, the configurations are comparable to the DFT results. For longer n-Py chains, the configurations are wavy. This potential model is used to simulate a 192 4-Py system and a 64 12-Py system at different densities. The energy, end to end distance, radius of gyration and order parameter as a function of density are inspected. The energy increases as the density increases for 4-Py but the energy decreases for increasing density of the 12-Py system. End to end distance and radius of gyration are insensitive to the change of density for 192 4-Py system but keep increasing with increasing the density for 64 12-Py. The order parameters for both 4-Py and 12-Py tend to increase from low density to high density which means the system is in a disorder state at low density but acquires a chain stacking at high density. The radial distribution functions for these systems are also analyzed, showing that these systems have characteristics of liquids.



Figure 4.17: Radial distribution of the ring centers of mass for 64 12-Py molecule system at T = 300 K where  $\rho_1 = 0.43$  g/cm<sup>3</sup>,  $\rho_2 = 0.82$  g/cm<sup>3</sup>,  $\rho_3 = 0.98$  g/cm<sup>3</sup>,  $\rho_4 = 1.03$  g/cm<sup>3</sup>,  $\rho_5 = 1.13$  g/cm<sup>3</sup> (a) considering only intra-ring distances; (b) considering only inter-ring distances.

### Chapter 5: Implementation of Simulation

## 5.1 Computer Platforms

Several computer platforms were used for the calculations in this work. Most optimizations and frequency calculations of Calcium and Zinc clusters, specially for clusters with more than 8 atoms, were performed on the super computers in the Pittsburgh Supercomputer Center (PSC). One of these computers used was "Lemieux", an HP MPP machine with 3000 Opteron processors. There were 4 processors on a node and each node had 4 Gb of memory. Lemieux was decommissioned on December 22, 2006. A second super computer used in this dissertation was "Rachel", also at PSC. Rachel is an IBM SMP machine with Alpha processors and 256 Gb of main memory. It was decommissioned on July 1, 2008. Rachel's replacement is "Pople", an SGI Altix 4700, shared-memory NUMA system with 192 blades. Each blade holds 2 Itanium2 Montvale 9130 M dual-core processors, for a total of 768 cores. The four cores on each blade share 8 Gb of local memory. The processors are connected by a NUMA link interconnect. that allows the local memory on each processor to be accessible to all the other processors. Pople runs an enhanced version of the SuSE Linux operating system. There are multiple frontend processors, which are also Itanium2 processors and which run the same version of SuSE Linux as the compute processors. Most calculation with Gaussian 2003 were done on four nodes in parallel for geometry optimizations.

The small clusters and short Py oligomers optimization, frequency calculations and MC simulations for PPy were performed on local computers "CMaSC1", "CMaSC4" and "Cluster3" in the Computational Materials Science Center (CMaSC) of George Mason University (GMU). CMaSC1 is a Dell server with dual Intel Xeon 3 GHz processors, hyperthreading and 3 Gb memory. This is a 32-bit machine with the SuSE Linux operating system. CMaSC4 has an Intel quad core 2.4 GHz,4 Gb with an openSuSE Linux operating system.

Cluster3 is an IBM workstation computer with dual AMD opteron 2 GHz processors and 2 Gb memory. This is a 64-bit machine running the SuSE Linux operating system. Some DFT calculations were performed on supercomputer "Bach" of College of Science of GMU. This is an Altix 370 with 64 Itanium2 processors. The processor speed is 1.5 GHz and the main memory is 128 Gb. The operating system is SuSE Linux Enterprise Server for SGI (R) Altix (R) Systems.

One of the scripts used to submit the Gaussian03 jobs to the supercomputers is given in Appendix A.

The IMSL library was used for parameter fitting in the PPy model potential. This fitting was done on the computers in the computer labratory of the College of Science of GMU. This cluster is composed of 20 computers. Each computer has two Intel(R) Pentium(R) 4 CPU 3.80 GHz processors. The operating Linux system is SL release 4.4.

### 5.2 Software Packages

All DFT calculations in this dissertation work were done using the Gaussian03 package (G03) [58]. This is the latest version in the Gaussian series of electronic structure programs and contains progressive developments of the Gaussian 70, 76, 80, 82, 86, 88, 90, 92, 94, and 98 systems. Gaussian is generally referred to as an ab-initio quantum mechanical computational package, which can be used to study molecules and chemical reactions under a wide range of conditions. This package can also provide invaluable information on stable species and compounds which are difficult or impossible to observe experimentally, such as short-lived intermediates and transition structures in the gas phase and in solution. Typical calculations provide energies, molecular structure, vibrational frequencies of molecular systems and other chemical information using a variety of methodologies ranging from semi-empirical methods to Hartree-Fock calculations, higher order correlation corrections such as Moller-Plesset methods coupled cluster methodologies among others. A variety of finite basis sets is included on a very practical database. Density Functional Theory methods are also available, including about ten different functions and corrections.

In this work, geometry optimization (OPT) of G03 is the most used keyword for both Ca and Zn clusters and PPy. This keyword requests that a geometry optimization be performed. The geometry of the system is adjusted until a stationary point on the potential energy surface is found. For all DFT calculation the algorithm used for minimizations (optimizations to a local minimum) and optimizations to transition states and higher-order saddle points is the Berny algorithm using redundant internal coordinates. The Berny algorithm using internal coordinates (Opt = Z-matrix) is also used when needed. For Ca and Zn clusters and n-Py and PPy, only the redundant internal coordinates is used to relax the coordinates of all atoms of that cluster. For n-Py with dopants, the internal coordinates is used since the distance between the dopants and Py rings should be fixed.

Vibrational frequencies calculation (Freq) is another keyword used extensively in this work because it allows for checking whether the optimized structure is a minimum or a saddle point. All the optimization calculations in this work are followed by the frequency calculations. The keyword Freq computes force constants (gradients of the potential energy in the 3N space, N = number of atoms) and the resulting vibrational frequencies from diagonal of the Hessian matrix. Intensities are also computed. Vibrational frequencies are computed by determining the second derivatives of the energy with respect to the cartesian nuclear coordinates and then transforming to mass-weighted coordinates. This transformation is only valid at a stationary point. Thus, it is meaningless to compute frequencies at any geometry other than a stationary point for the method used for frequency determination.

The other important keyword is Population analysis (Pop) which controls printing of molecular orbitals and several types of population analysis and atomic charge assignments. Generally the Mulliken population analysis is adopted in this work which gives total atomic charges and orbital energies. Since the bond order of the backbone of PPy is important for analyzing the bonding properties of the polymer, the NBO option is adopted in which a full Natural Bond Orbital analysis gives precise bond orders.



Figure 5.1: Sketch for calling the G03 program.

The keyword PBC of G03 allows users to specify options for Periodic Boundary Condition jobs. It is used for PPy in this work. Periodic systems repeat periodically any molecular geometry provided in the unit cell. The additional required input one, two or three translation vectors indicating the replication direction(s). In this work a one-dimensional PBC energy calculation for PPy yielded its band structure. A sketch for calling the G03 options is described in Fig. 5.1.

The IMSL library is a comprehensive set of mathematical and statistical functions that programmers can embed into their software applications. The IMSL libraries provide highperformance computing software and extensive documentation to develop and execute sophisticated numerical analysis applications. These libraries free users from developing their own internal code by providing pre-written mathematical and statistical algorithms. It is regarded as the most sophisticated, flexible, scalable and highly accessible technology available for numerical analysis in the most important mainstream programming environments in use today. The IMSL numerical libraries have been the cornerstone of high-performance and desktop computing as well as predictive analytic applications in science, technical and
business environments for well over three decades. Programmers at major corporations, research laboratories and academic institutions have used the IMSL library tools to build software applications in fields including engineering, research and development, financial engineering, physics, business analysis, data mining, biotechnology, plus many more.

Fitting the parameters of PPy potential was done by calling the RNLIN subroutine of IMSL library. Routine RNLIN is a nonlinear regression model using the least squares method for fitting. The routine allows the user to specify the functional form of the model, which has substantial flexibility over linear regression [93]. The nonlinear regression model is

$$y_i = f(x_i, \theta) + \varepsilon_i, i = 1, 2, \dots, n \tag{5.1}$$

where the observed values of the  $y'_i s$  constitute the responses or values of the dependent variable, the known  $x'_i s$  are the vectors of the values of the independent variables,  $\theta$  is the vector of regression parameters, and the  $\varepsilon'_i s$  are independently distributed normal errors with mean zero and variance  $\sigma^2$ . In the implementation used in this work, the vector  $\theta$ is the parameters of the PPy potential model to be fitted.  $y_i$  in Eq. 5.2 are the binding energies of n-Py from G03 optimizations and  $f(x_i, \theta)$  are the energies calculated with the PPy model potential. For this model, a least squares estimate of  $\theta$  is also a maximum likelihood estimate of  $\theta$ . The residuals for the model are

$$e_i(\theta) = y_i - f(x_i, \theta), i = 1, 2, ..., n$$
(5.2)

A value of  $\theta$  that minimizes  $|s_c|^2 = \sum_{i=1}^n [e_i(\theta)]^2$  is a least squares estimate of  $\theta$ . Routine RNLIN is designed so that these residuals are input one at a time from a user-supplied subroutine. The routine RNLIN uses a modified Levenberg-Marquardt method to generate a sequence of approximations to a minimum point. Let  $\hat{\theta}_c$  be the current estimate of  $\theta$ . A new estimate is given by  $\hat{\theta}_c + s_c$ , where  $s_c$  is a solution to

$$(J(\hat{\theta}_c)^T J(\hat{\theta}_c) + \mu_c I) s_c = J(\hat{\theta}_c)^T e(\hat{\theta}_c)$$
(5.3)

Here  $J(\hat{\theta}_c)$  is the Jacobian evaluated at  $\hat{\theta}_c$ . A solution of the equations is obtained when  $\mu_c = 0$ . If  $|s_c|^2 < \delta_c$ , this update is accepted. Otherwise,  $\mu_c$  is set to a positive value and another solution is obtained.

## 5.3 MC Simulation of PPy

The flow chart of the MC simulation for PPy is given in Fig. 5.2. In the flow chart, i means the *ith* chain and j means the *jth* monomer in that oligomer. The total number of oligomers in the system is *nmol* and in each oligomer there are *nchain* monomers. The total number of monomers is *nmol* × *nchain*. The initial coordinates of center of mass (cm) for each monomer and the initial quaternion are generated in a given box positioning the cm at FCC locations. In order to get the positions of each atom in the monomer ring, the subroutine *atomcoor* is called (See Appendix B). Each MC step involves two eventual moves: the cm (translation) and the quaternion (monomer orientation). Each translation step is followed by a quaternion step but they do not affect each other.

Fig. 5.3 is the flow chart of the PPy model potential implementation. In the flowchart, n is the *nth* monomer in the system. For example, if the *jth* monomer of the *ith* oligomer chain is being considered, then n = (i - 1) \* nchain + j. If the position of center of mass is changed, then all the potentials, Eq. 4.2, 4.3, 4.4, 4.6 and 4.7 are included. The detail information is described in Fig. 5.3. If the position of center of mass for the first monomer in that chain is changed,  $U_{morse}(n)$ ,  $U_{torsion}(n)$ ,  $U_{bending}(n)$ ,  $U_{excluded-volume}(n)$  and  $U_{dipole-dipole}(n, n')$   $(n \neq n')$  are considered; if the center of mass of the monomer at the end of the oligomer chain is involved, then  $U_{morse}(n-1)$ ,  $U_{torsion}(n-1)$ ,  $U_{bending}(n-2)$ ,  $U_{bending}(n-1)$ ,  $U_{excluded-volume}(n-2)$ ,  $U_{excluded-volume}(n)$  and  $U_{dipole-dipole}(n, n')$   $(n \neq n')$  will be considered. If the monomer between the chain is changed, then  $U_{morse}(n-1)$ ,  $U_{bending}(n-1)$ ,  $U_{torsion}(n-1)$ ,  $U_{torsion}(n)$ ,  $U_{bending}(n-1)$ ,  $U_{bending}(n)$ ,  $U_{excluded-volume}(n)$  and  $U_{dipole-dipole}(n, n')$   $(n \neq n')$  will be considered. If the monomer between the chain is changed, then  $U_{morse}(n-1)$ ,  $U_{bending}(n)$ ,  $U_{excluded-volume}(n)$  and  $U_{dipole-dipole}(n, n')$  ( $n \neq n'$ ) need to be included. If quaternion of the monomer (orientation of the monomer ring) is changed then only  $U_{torsion}$  and  $U_{dipole-dipole}$  (Eq. 4.4 and 4.7) are considered.



Figure 5.2: Flow chart of PPy MC Simulation.



Figure 5.3: Flow chart of PPy MC Simulation.

### Chapter 6: Concluding Remarks

This chapter is a brief summarize of the work achieved in this dissertation.

The optimized configurations of neutral and anion clusters up to  $Ca_{19}^-$  and  $Zn_{11}^-$  were studied based on hybrid DFT calculations. The ground state energetics, symmetry and vibrational analysis of neutral and anion calcium clusters up to  $Ca_{19}^-$  and on zinc clusters up to  $Zn_{11}^-$  were reported. The electron affinity for these clusters was calculated by computing the energy difference between the ground state energy of neutral clusters and the ground state energy of the corresponding cluster anions. Comparison of the electron affinity theoretical results with experiment is excellent, reproducing the intriguing kink observed at  $Ca_{10}$ and  $Zn_{10}$ . The excited states of  $Ca_2^-$  through  $Ca_6^-$  and  $Zn_3^-$  through  $Zn_6^-$ , cluster anions having different multiplicity than the ground states were studied with DFT. The excited states energy allowed for calculation of the electron detachment spectrum. Comparison of these results with experimental observations is excellent. Although the DFT method only can provide precisely the excited states with different multiplicity, the major spectral characteristics are well calculated for these small clusters, as evidenced by the agreement with experiment. Particularly important is the agreement theory-experiment on the energy gap between the first and second observed experiment peaks.

An exhaustive study of the structural and energetic results for n-Py oligomers (n = 1 - 24) in both the reduced and oxidized phases was completed within a hybrid DFT method. It was found that the reduced oligomers have notoriously bent spatial conformations while oxidized oligomers are flat planar chains. The degree of oxidation controls the bending. Oxidized oligomers with charge  $Q/n \ge 1/3$  display the planar structure while for Q/n < 1/3 the oligomer structures become increasingly bent. The value Q/n = 1/3 is a critical oxidation value. Below the critical value the oxidized oligomers present a delocalized positive

charge distributed along the oligomer backbone carbon atoms. Above the critical value there is charge localization. When dopants were included in the proximity of n-Py, Q localizes in the neighborhood of the dopant and one localized state in the HOMO-LUMO gap appears for every +2e in the oxidation level. The energy band gap of infinite PPy is in excellent agreement with experiment. Additionally, the trend of a decreasing band gap with increasing oxidation level was clearly demonstrated. Vibrational spectra of n-Py oligomers was calculated and proves to be quite insensitive to oxidation. Both reduced and oxidized oligomers display two IR spectral regions at 700-1600 cm<sup>-1</sup> and 3000-4000 cm<sup>-1</sup>.

A novel PPy model potential was proposed based on the results obtained with DFT. With this potential model, ATMC and MMC simulations were used to study single oligomers of various lengths: 24-Py, 36-Py, 48-Py. Energies were compared to DFT results and they matched very well. Both the ATMC and MMC simulations were used to study PPy systems with many oligomers: 192 4-Py, 42 12-Py, and 64 12-Py at different densities. This study shows that at high density,  $\rho > 1$ , both 4-Py and 12-Py systems are nematic. At lower density,  $\rho < 0.9$ , the short chain system of 4-Py is isotropic and disordered while the system with 12-Py systems shows a high degree of chain stacking. The energy, end-to-end distance and radius of gyration are insensitive to density increases for short chain systems. For longer chain systems, the end-to-end distance and radius of gyration decrease with increasing density.

Chapter 5 provides a description of the computer platforms and the computational software packages used in this work. Some small scripts for submitting the jobs to supercomputers were listed. The flow chart of the MMC simulation for PPy was given and several subroutines were listed in the appendix.

# Appendix A: Script for submitting the job to supercomputer

```
#!/bin/csh
#PBS -1 walltime=167:10:00
#PBS -1 nodes=1:ppn=4
#PBS -1 vmem=6gb
#PBS -1 pvmem=1500mb
#PBS -m aeb
#PBS -joe
```

# Define the directory where the input file resides, and into which # the output and checkpoint files should be placed.

set base = \$HOME/ppy

# Define and set up the scratch directory. The scratch directory
# should offer large capacity and high performance, and it may be
# removed automatically when the job terminates.

set scr = \$HOME/12py\_scr

```
rm -rf $scr
mkdir -m 700 $scr
```

# Copy the input file to the scratch directory.

cp \$base/12py.gjf \$scr

# Execute Gaussian 03, writing the output to the specified base directory.

cd \$scr g03 < 12py.gjf >& \$base/12py.log

# Copy the checkpoint file to the specified permanent base directory # so that it can be reused.

 $mv \ \$scr/12py.chk \ \$base$ 

# Clean up the scratch directory on job completion.

cd \$base

 $\rm rm - rf \ \$scr$ 

# Appendix B: Subroutine atomcoor

```
Subroutine coor (x, y, z, q1, q2, q3, q4, XBODY, YBODY, ZBODY, xc, yc, zc )
implicit none
integer :: i,k
double precision, dimension(natom) :: A11,A12,A13,A21,A22,A23,A31,A32,A33
```

 $\mathbf{do} \quad i \,{=}\, 1, natom$ 

$$\begin{array}{l} A11(i) = -q1(i)*q1(i)+q2(i)*q2(i)-q3(i)*q3(i)+q4(i)*q4(i) \\ A12(i) = 2.0*(q3(i)*q4(i)-q1(i)*q2(i)) \\ A13(i) = 2.0*(q2(i)*q3(i)+q1(i)*q4(i)) \\ A21(i) = -2.0*(q1(i)*q2(i)+q3(i)*q4(i)) \\ A22(i) = q1(i)*q1(i)-q2(i)*q2(i)-q3(i)*q3(i)+q4(i)*q4(i) \\ A23(i) = 2.0*(q2(i)*q4(i)-q1(i)*q3(i)) \\ A31(i) = 2.0*(q2(i)*q3(i)-q1(i)*q4(i)) \\ A32(i) = -2.0*(q1(i)*q3(i)+q2(i)*q4(i)) \\ A33(i) = -q1(i)*q1(i)-q2(i)*q2(i)+q3(i)*q3(i)+q4(i)*q4(i) \\ \end{array}$$

end do

 $\mathbf{end} \ \mathbf{subroutine} \ \mathbf{coor}$ 

Appendix C: List of Publications

#### Energetics, Structure, and Electron Detachment Spectra of Calcium and Zinc Neutral and Anion Clusters: A Density Functional Theory Study

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A hybrid density functional approach with very large basis sets was used for studying  $Ca_2$  through  $Ca_{19}$  and  $Zn_3$  through  $Zn_{11}$  neutral clusters and their cluster anions. Energetics, structure, and vibrational analysis of all these neutral clusters and cluster anions are reported. The calculated electron affinities are in excellent agreement with experiment displaying a characteristic kink at  $Ca_{10}$  and  $Zn_{10}$ . This kink occurs because the 10-atom neutral cluster is very stable whereas the cluster anion is not. Additionally, the electron detachment binding energies (BEs) up to  $Ca_6^-$  and  $Zn_6^-$  were identified by analyzing the ground and excited states of the cluster anions and of their corresponding size neutral clusters. The theoretical BE is in very good agreement with experiment for both calcium and zinc cluster anions. The three main peaks in the spectrum correspond to BEs from the ground state of the cluster anion (doublet) to the ground state of the neutral cluster (singlet) and to the first triplet and quintet excited states of the neutral cluster. The calculated energy gap from the lowest BE peak to the second peak is in excellent agreement with experiment. The calculation reproduces very well the energy gap observed in  $Ca_4^-$  and  $Zn_4^-$ , which is larger than those for other sizes and is indicative of the strong stability of the anion and neutral tetramers.

#### 1. Introduction

Calcium is the fifth most abundant element on the earth and plays an essential role for living organisms, compounds, and mechanisms. Metal clusters span the gap between the atomic and the bulk length scales, and their study furthers the understanding of the electronic behavior of metals at the nanoscale.<sup>1–3</sup> Calcium clusters have attracted the interest of scientists in the past few years such that energetics, structure, vibrational frequencies, and thermodynamic properties have been studied in detail from various perspectives.<sup>4–7</sup> On the other hand, calcium cluster anions have received much less attention, especially concerning their electronic properties, which are fundamental for the theoretical description of photoelectron detachment spectroscopy.<sup>8</sup>

Zinc is the fourth most common metal in use, trailing only to iron, aluminum, and copper in annual production. Bulk bonding features of group IIB elements are transient from van der Waals to covalent and finally to metallic, which make these metals interesting from the perspective of subnanometer scale systems. Among these elements Hg clusters are the most extensively studied.<sup>9–15</sup> To a lesser extent, Zn clusters have also been studied, both experimentally<sup>8,16,17</sup> and theoretically.<sup>18–20</sup> However, the theoretical studies address neutral zinc clusters only, and little is known about the zinc cluster anions.

Older experimental photoelectron spectroscopy results for small clusters of elements in the fourth row of the periodic table comprise K,<sup>21</sup> Ti,<sup>22</sup> and Co.<sup>23</sup> Calcium and zinc are two elements in the fourth row of the periodic table for which experiments on the electron affinity<sup>8</sup> and the electron detachment spectra<sup>8,17</sup> have been reported more recently. It is therefore important and feasible to theoretically study the underlying electronic states involved in the experimental process. In this work we perform an exhaustive all-electron study within hybrid density functional

theory (DFT) of the ground state of neutral clusters and cluster anions for sizes up to  $Ca_{19}$  and up to  $Zn_{11}$ . Such study gives insight on the energetics, structure, and vibrational analysis and allows for comparison of the electron affinity to the available experimental results. Additionally, the excited states of the smaller neutral clusters and their cluster anions up to n = 6were studied for both calcium and zinc. Knowledge of the excited states of both neutrals and anions allows for molecular identification of the experimental peaks appearing in the electron detachment energy spectrum. The computational task of finding the excited states of larger than 6-atom clusters is beyond our current computational power and is not attempted in this paper.

This paper is organized as follows. Section 2 contains the theoretical methodology, the energetics of the calcium and zinc neutral and anion clusters, and provides a comparison of experimental and theoretical results of the electron affinities up to Ca<sub>19</sub> and Zn<sub>11</sub>. Sections 3 and 4 give details on the excited states of the neutral and negatively charged clusters up to Ca<sub>6</sub> and Zn<sub>6</sub> that enter in the identification of the electron detachment spectra and provide comparison with experimental results. This paper is concluded with closing remarks in section 5.

#### 2. Energetics of Ca<sub>n</sub> (n = 2-19) and Zn<sub>n</sub> (n = 3-11)Neutral and Anion Clusters

All-electron calculations on calcium and zinc neutral and anion clusters were carried out within the hybrid Becke density functional theory (DFT), B3PW91, which contains the Perdew– Wang local and nonlocal correlation functionals.<sup>24,25</sup> The 6-311G(d) triple valence basis set<sup>27,28</sup> with s, p, d polarization was used throughout this paper. However, for the small Ca clusters up to n = 11 and for all Zn clusters, the basis set was expanded with d-diffuse functions 6-311+G(d). As expected for calcium, diffuse d-functions decrease marginally the energy of the Ca cluster anions because d-orbital momentum symmetry

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Calcium and Zinc Neutral and Anion Clusters

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TABLE 1: Electronic Energies (E) with Symmetry and Ground-State Identification of  $Ca_2$  through  $Ca_{19}$  Anion and Neutral Clusters and Their Electron Affinity (EA)

			neutral				anion			
		E (eV)				E (eV)		EA (eV)		
Ca <sub>n</sub>	sym	state	6-311 g(d)	6-311+g(d)	sym	state	6-311 g(d)	6-311+g(d)	6-311 g(d)	6-311+g(d)
2	$D_{\infty h}$	${}^{1}\Sigma_{g}^{+}$	-0.1468	-0.1478	$D_{\infty h}$	$^{2}\Pi_{\mu}$	-0.6417		0.4934	
		0				$2\Sigma_{g}^{+}$		-0.6602		0.5121
3	$D_{3h}$	$^{1}A_{1}'$	-0.6612	-0.6647	$D_{3h}$	${}^{2}A_{2}''$	-1.5491	-1.5538	0.8862	0.8873
4	$T_d$	${}^{1}A_{1}$	-1.7751	-1.7836	$T_d$	${}^{2}A_{1}$	-2.7160	-2.7393	0.9468	0.9613
5	$D_{3h}$	$^{1}A_{1}$	-2.3948	-2.4159	$D_{3h}$	${}^{2}A_{1}'$	-3.3957	-3.4244	1.0100	1.0168
6	$C_{2v}$	${}^{1}A_{1}$	-3.0826	-3.1112	$C_{2v}$	${}^{2}A_{2}$	-4.2415	-4.2667	1.1612	1.1580
7	$D_{5h}$	$^{1}A_{1}'$	-4.3597	-4.4066	$C_{2v}$	${}^{2}A_{2}$	-5.4926	-5.5338	1.1441	1.1387
8	$C_s$	$^{1}A'$	-5.1021	-5.1603	$C_s$	${}^{2}A_{2}''$	-6.3802	-6.4305	1.2829	1.2753
9	$C_1$	$^{1}A$	-6.1861	-6.2577	$C_1$	$^{2}A$	-7.5249	-7.5583	1.3389	1.3065
10	$D_{3h}$	$^{1}A_{1}'$	-7.5126	-7.5995	$C_1$	$^{2}A$	-8.5409	-8.6128	1.0414	1.0263
11	$C_1$	$^{1}A$	-8.2656	-8.3851	$C_1$	$^{2}A$	-9.4992	-9.5996	1.2376	1.2186
12	$C_1$	<sup>1</sup> A	-9.0720		$C_{5v}$	${}^{2}A_{2}$	-10.4271		1.3582	
13	$C_1$	$^{1}A$	-10.2689		$C_1$	$^{2}A$	-11.7244		1.4599	
14	$C_1$	$^{1}A$	-11.3565		$C_{1}$	$^{2}A$	-12.8522		1.4957	
15	$C_1$	$^{1}A$	-12.0087		$C_1$	$^{2}A$	-13.5546		1.5497	
16	$C_1$	$^{1}A$	-13.4332		$C_1$	$^{2}A$	-14.8909		1.4563	
17	$C_1$	$^{1}A$	-15.0069		$C_1$	$^{2}A$	-16.5650		1.5581	
18	$C_1$	$^{1}A$	-16.1052		$C_1$	$^{2}A$	-17.6746		1.5662	
19	$D_{5h}$	$^{1}A'$	-17.6005		$D_{5h}$	$^{2}A_{2}$	-19.0646		1.4621	

is absent from the occupied states. On the other hand for Zn clusters, d-diffuse functions are significantly effective in reducing the energy of the neutrals and anions. All self-consistent energy results are accurate up to eight decimals and only the first three or four decimals are reported in the tables. The Gaussian  $2003^{29}$  package was used throughout this paper.

For studying theoretically the electron affinity (EA) and comparing with EA experiments,<sup>8</sup> the ground state of the cluster anions Ca<sub>2</sub><sup>-</sup> through Ca<sub>19</sub><sup>-</sup> and the ground state of the corresponding neutral clusters Ca<sub>2</sub> through Ca<sub>19</sub> are studied in this section. A similar study is performed for Zn<sub>3</sub><sup>-</sup> through Zn<sub>11</sub><sup>-</sup>. On the basis of this information, the EA is calculated as the difference between the total energies of the ground state of the neutral and anion clusters taking into account the zero point energy  $\varepsilon_0$  of each state: ( $E_{\text{TOTAL}} + \epsilon_0$ ) neutral – ( $E_{\text{TOTAL}} + \epsilon_0$ )anion.

Results of the ground-state energy E, symmetry group, and electronic state identification for neutral and anion calcium clusters containing 2-19 atoms are given in Table 1, where all total energies are relative to the energy of separated neutral calcium atoms. The total energies of the neutral calcium atom and its anion are -677.50978286 au, -677.50976233 au with 6-311G(d), and -677.50981264 au, -677.51303514 au with 6-311+G(d), respectively. The total energies of the neutral and anion zinc atoms with 6-311+G(d) are -1779.30681367 au and -1779.27185139 au, respectively. An exhaustive search for the structures of lowest energy was conducted for each cluster size adopting the following strategy. A multitude of cluster structures from previous studies<sup>4-7</sup> were used as initial geometries of the geometry optimization with the purpose of finding the energy minima. This optimization was performed with the Berny algorithm and redundant internal coordinates.<sup>26</sup> Additionally, structures in Table 1 were verified to be a minimum by the calculation of the vibrational frequencies. The Berny algorithm is based on steepest descents. Therefore, in configuration space the algorithm drives the system to the minimum closest to the initial geometry. It is known that a cluster of atoms has many minima, each minimum corresponding to a stable isomer of that cluster size. Along this study, several stable isomers were identified for each cluster size, although Table 1 reports only those isomers corresponding to the minimum of lowest energy found up-to-date. Several saddles of different orders of the energy landscape were also discovered and are not reported in this paper either. Up to n = 11, Table 1 shows results employing the 6-311G(d) and 6-311+G(d) basis sets. Although energies decrease up to 0.1 eV with the larger basis set, our results show that energy differences such as the EA are marginally affected by the added diffuse d-function. The effect of the diffuse d-function is important only for  $Ca_2^-$  by producing an inversion of the two lower doublet states.

Figure 1a depicts the second difference of the energy E(n - 1) + E(n + 1) - 2E(n) for calcium clusters. In upcoming paragraphs this second difference is referred to as the energy stability pattern. In this energy pattern, peaks correspond to clusters that are relatively more stable than those with nearest sizes. The solid line in Figure 1a depicts data for the neutral clusters and the dashed line pertains to the cluster anions. It is readily apparent that neutral calcium clusters containing 4, 7, 10, 13, and 17 have high peaks and are therefore very stable. The energy stability pattern of the anion clusters is similar to that of the neutrals except for the peaks at n = 9 and 10. The anion  $Ca_{10}^{-1}$  is less stable than  $Ca_{9}^{-1}$  or  $Ca_{11}^{-1}$  whereas the neutral  $Ca_{10}$  is very stable when compared to the neighboring size clusters.

Zinc cluster anions and neutrals containing 3-11 atoms are reported in Table 2, and their energy stability pattern is given in Figure 1b (solid line for neutrals and dashed line for cluster anions). The table summarizes the ground-state energy, symmetry, and electronic state. Energies are relative to the energy of the separated neutral atoms. Peaks in Figure 1b indicate that neutral clusters with 4, 7, and possibly 10 atoms are relatively more stable than neighboring sizes, and the same behavior is apparent for the cluster anions except for Zn<sub>9</sub> and Zn<sub>10</sub>. Therefore in the very small cluster size regime, both Ca and Zn have similar energy stability.

The geometries of the Ca cluster anions are shown in Figure 2. The structures of neutral Ca<sub>2</sub> through Ca<sub>12</sub> have been reported in previous work<sup>4</sup> within the same DFT approach. Ca<sub>13</sub> is a twinned pentagonal pyramid with one decorated face, which is 0.1163 eV more stable than the lowest of three previously reported isomers.<sup>4</sup> With this new structure, the number of known



Figure 1. Stability pattern as a function of cluster size: (a) calcium; (b) zinc. Dotted lines correspond to cluster anions and full lines to neutral clusters.

TABLE 2: Electronic Energies (*E*) with Symmetry and Ground-State Identification of Zn<sub>3</sub> through Zn<sub>9</sub> Anion and Neutral Clusters and Their Electron Affinity (EA)

		neutr	al		anio		
$Zn_n$	sym	state	E(eV)	sym	state	E(eV)	EA (eV)
3	$D_{3h}$	${}^{1}A_{1}'$	-0.1537	$D_{3h}$	$^{2}A_{1}^{\prime}$	-0.6802	0.5173
4	$T_d$	$^{1}A_{1}$	-0.6662	$T_d$	$^{2}A_{1}$	-1.4739	0.8073
5	$D_{3h}$	$^{1}A_{1}'$	-0.7745	$D_{3h}$	${}^{2}A_{1}'$	-1.6688	0.8955
6	$C_{2v}$	$^{1}A_{1}$	-0.9570	$C_{5v}$	$^{2}A_{1}$	-2.1811	1.2114
7	$C_1$	$^{1}A$	-1.3734	$C_1$	$^{2}A$	-2.8245	1.4429
8	$C_1$	$^{1}A$	-1.7555	$C_1$	$^{2}A$	-3.4199	1.6515
9	$C_{2v}$	$^{1}A_{1}$	-2.5664	$C_{2v}$	$^{2}A_{1}$	-4.6267	2.0514
10	$C_1$	$^{1}A$	-3.3758	$C_1$	$^{2}A$	-4.8540	1.4724
11	$C_1$	$^{1}A$	-3.5998	$C_1$	$^{2}A$	-5.1877	1.5766

stable isomers of Ca<sub>13</sub> is increased to four. This new Ca<sub>13</sub> was seeded with one extra atom to yield Ca<sub>14</sub>. Neutral Ca<sub>15</sub> through Ca<sub>19</sub> are slightly distorted structures predicted at the tightbinding (TB) level.<sup>7</sup> Geometry optimizations of the n = 15-19clusters were started from a variety of initial configurations, including the published structures.<sup>7</sup> Results reported in Table 1 indicate that the TB structures with minor deformations that break the symmetry are the lowest in energy found to date. A commonality of the cluster anions is a slight structural distortion when compared to the neutral counterparts due to the negative charge. For example, Ca<sub>5</sub><sup>-</sup> and Ca<sub>6</sub><sup>-</sup> shown in Figure 2 present slightly elongated bond lengths vis-a-vis of the neutral clusters Ca<sub>5</sub> D<sub>3h</sub> and Ca<sub>6</sub> C<sub>2v</sub> reported in ref 4. Comparable distortions yield a less symmetric (C<sub>2v</sub>) Ca<sub>7</sub><sup>-</sup> instead of the D<sub>5h</sub> neutral cluster.

The geometries of the Zn cluster anions are shown in Figure 3. Except for  $Zn_7$  and  $Zn_8$ , our optimized structures of  $Zn_3$ through  $Zn_{11}$  are in agreement with both DFT calculations using basis sets without diffuse d-functions<sup>19</sup> and MP2/LANL2DZ calculations.<sup>20</sup> Our Zn<sub>7</sub> is the same as that given in ref 19 while the structure reported in ref 20 is found to be a saddle. In the case of Zn<sub>8</sub>, our structure coincides with the 8b isomer of ref 19 and the other reported structures are found to be higher in energy or not stable. As already stated in ref 19, the expected comparison of DFT results to coupled-clusters (CC) results18 is reasonable for Zn clusters with n = 4-6 but may not reproduce well the incipient van der Waals bonding of zinc dimers and trimers. Not all the Zn anion clusters maintain the structure of the neutrals with small distortions. As seen in Figure 3,  $Zn_6^-$ ,  $Zn_8^-$ , and  $Zn_{10}^-$  have different geometries than those corresponding to the neutral clusters.

The EAs of the Ca and Zn clusters are reported in the last column of Tables 1 and 2. For calcium clusters, the EAs up to n = 11 were calculated with the 6-311G(d) and 6-311+G(d)

basis sets. As is clear from Table 1, the expanded basis set with diffuse functions adds minor corrections of only a couple of hundredths of an electronvolt to the EA. Figures 4a and 4b (dotted lines with triangles) are plots of the EA of calcium and zinc clusters as a function of size showing the comparison with experimental results (solid line with circles) of ref 8. The qualitative agreement for both calcium and zinc clusters is excellent. For calcium, the notorious kink at the 10-atom cluster occurs because neutral  $Ca_{10}$  is very stable (peak in Figure 1a) whereas the cluster anion Ca10<sup>-</sup> is relatively not stable (valley in Figure 1a). There is a second shallow kink at Ca<sub>16</sub><sup>-</sup>, which is barely visible in the experimental results and is also apparent in our results. For zinc clusters, the calculated EA is comparable to those of the Ca clusters except for Zn2-, which yields a negative EA consistent with not being observed experimentally. The EA kink at  $Zn_{10}$  is similar to the one observed for the calcium clusters, with the exception that Zn9<sup>-</sup> is remarkably stable and therefore the kink seems shallower when compared to the calcium case. As is shown in Figure 4, the EA results are systematically lower than the experimental values for both Ca and Zn clusters. It is unfortunate that the experimental results do not carry error bars to allow for closer comparison. Zn<sub>10</sub> and Zn<sub>11</sub> are the two values of the EA with worst comparison to experiment, which might be evidence that other neutral isomers with lower ground-state energy exist but have not been found in this work nor in previous work.19,20

Predictions from CC calculations<sup>18</sup> reported  $Zn_3^-$  as unstable. However, this cluster anion has now been detected experimentally by two groups,<sup>8,17</sup> and confirmed by our calculation. In ref 18 the reported EAs of Zn<sub>4</sub>, Zn<sub>5</sub>, and Zn<sub>6</sub> are lower than the experimental results<sup>8</sup> by 0.22, 0.35, and 0.87 eV, respectively. The discrepancies of our results with the same experiment are 0.03, 0.07, and 0.35 eV, which are considerably smaller. The excellent qualitative agreement between our calculation and the experimental results of the EA is a validation of the methodology used in this work.

# 3. Excited States and Frequency Analysis of $Ca_n$ (n = 2-6) and $Zn_n$ (n = 3-6) Neutral and Anion Clusters

For the small Ca clusters containing two to six atoms, several excited states are identified for both anion and neutral clusters. As mentioned in section 2, these calculations were all done with the expanded basis set 6-311+G(d). Energies, symmetry, and state identification of the anions are reported in Table 3 along with the normal mode vibrational frequencies for all states. Table 4 contains results for the Ca neutral clusters. For Ca<sub>2</sub><sup>-</sup> the ground state and three excited states are very close in energy.



Figure 2. Structure of the calcium cluster anions. Bond lengths are rounded off and given in angstroms.

The bond length of this dimer anion in the ground state is 4.342 Å, which shrinks to 3.943 Å in the first excited state (doublet). In addition, two quartet exited states are identified for Ca2-For larger cluster anions Ca3- through Ca6-, most of the excited states of the cluster anion maintain the ground-state geometry (Figure 2) with distortions responsible for the symmetry reduction. Ca<sub>3</sub><sup>-</sup>  $D_{3h}$  has a bond length of 3.784 Å in the ground state and 3.968 Å in the first excited state. The Ca3- quartet excited state is an isosceles triangle with bond lengths 3.589/ 4.177 Å. The anion Ca<sub>4</sub><sup>-</sup>  $T_d$  has bond length of 3.775 Å in the ground state, and its first quartet excited state D<sub>2d</sub> is a distorted  $T_d$  structure with bond lengths 3.674/4.339 Å. The second quartet state C1 corresponds to a Ca4- isomer with planar, almost rhomboidal, structure and bond lengths 3.876/3.693 Å. The Ca5triangular bipyramid structure with bond lengths 3.883/3.787 Å deforms in the excited states to have four different bond lengths: 3.838/3.955/3.747/3.577 Å in the doublet and 3.832/ 3.693/4.0/3.599 Å in the quartet. Similarly, Ca6- C2v groundstate structure is shown in Figure 2 and the first and second excited states maintain the structure with some deformation. The second quartet excited state of Ca6- is a slightly deformed octahedron  $(C_1)$  with bond lengths 3.671/3.667/4.215/4.216 Å, which differs from the ground-state geometry.

Additionally, the singlet ground state, triple, and quintet exited states of neutral calcium clusters with n = 2-6 were calculated

and energy, symmetry, and state identification are reported in Table 4 (second through fourth columns). In this table, energies of the neutrals are relative to the ground-state energy of the corresponding size anion given in Table 1.

Similarly, for the small Zn clusters containing two to six atoms, several excited states are identified for both anion and neutral clusters. As for calcium, these calculations were done with the expanded basis set 6-311+G(d). Energies, symmetry, and state identification of the anions are reported in Table 5 along with the normal mode vibrational frequencies for all states and in Table 6 for the Zn neutral clusters. The anion groundstate structures are depicted in Figure 3. For Zn<sub>3</sub>, the ground state and the first excited state are equilateral triangles  $D_{3h}$  and the second excited state is a quasi-linear  $C_{2\nu}$  structure. The bond length in the ground state is 2.695 Å, which elongates in the first excited state to 2.879 Å and shrinks to 2.393 Å in the quasilinear excited state. Tetrahedral Zn4<sup>-</sup> bond length is 2.718 Å, which deforms into a planar square with edge 2.556 Å in the excited state. The triangular bipyramid structure of Zn5- in the ground state has bond lengths 2.895/2.771 Å, which compresses to 2.727/2.696 Å in the excited state.  $Zn_6^-$  is a pentagonal pyramid with edges 2.802/2.705 Å, which deforms considerably in the first excited state (apex atom at 2.616 Å from vertices of an imperfect pentagon). The second excited state structure is composed of two distorted tetrahedra sharing one edge and bond

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Figure 3. Structure of the zinc cluster anions. Bond lengths are rounded off and given in angstroms.



Figure 4. Electron affinity as a function of cluster size: (a) calcium; (b) zinc. Dotted lines correspond to this work and full lines to experiments in ref 8.

lengths spanning 2.680–3.065 Å. The quartet excited state of  $Zn_6^-$  is a deformed square pyramid with one atom decorating one of the triangular faces.

The singlet ground state, triplet, and quintet excited states of neutral zinc clusters with n = 3-6 are also studied. Energy, symmetry, and state identification are reported in Table 6 (second through fourth columns). As in the case of calcium, energies of these states are relative to the ground-state energy of the cluster anion of equal size reported in Table 2.

# 4. Electron Detachment Spectra of Cluster Anions $Ca_n$ (n = 2-6) and $Zn_n$ (n = 2-6)

Recent experiments on Ca and Zn cluster anions photoelectron detachment<sup>8,17</sup> may yield experimental information about the structure of the neutral clusters by recording the kinetic energy

of the electron detached from the cluster anions. This energy is referred to by the experimental community as the electron binding energy (BE), which is the energy difference between the ground state of a cluster anion and the ground or excited states of the neutral cluster obtained when the electron is detached. Depending upon the experimental method, electrons might be detached if the anion is in a low-laying excited state. These low-laying excited states could be accessed in the experiment when the cluster anions are formed or the photophotons are absorbed. Then, the electron detachment spectrum would contain a richer set of BEs, which would contribute to peak broadening or be a source of additional peaks. Experiments were carried out at about 3 eV photon energies for Ca and  $Zn^8$  and close to 5 eV for Zn.<sup>17</sup> In order to cover the experimental energy range, the ground state of the neutral and anion clusters

TABLE 3: Excited States of Ca<sub>2</sub><sup>-</sup> through Ca<sub>6</sub><sup>-</sup> and Their Vibrational Frequencies<sup>a</sup>

	-	0 0		-
$Ca_n^-$	sym	state	<i>E</i> (eV)	frequency (cm <sup>-1</sup> )
$Ca_2^-$	$D_{\infty h}$	$2\Sigma_{g}^{+}$	0.0	77
	$D_{\circ\circ h}$	${}^{2}\Pi_{u}$	0.0116	97
	$D_{\circ\circ h}$	$4\Sigma_u^+$	0.6249	159
	$D_{\circ\circ h}$	${}^{4}\Pi_{g}$	0.7184	143
Ca <sub>3</sub> -	$D_{3h}$	${}^{2}A_{2}''$	0.0	105(2), 123
	$D_{3h}$	${}^{2}A_{1}'$	0.1027	73(2), 106
	$C_{2v}$	${}^{4}B_{1}$	0.7032	56, 72, 144
$Ca_4^-$	$T_{d}$	${}^{2}A_{1}$	0.0	86(2), 106(3), 134
	$D_{2d}$	<sup>4</sup> A <sub>2</sub>	0.8914	51, 70, 98, 100, 103, 142
	$C_1$	<sup>4</sup> A	0.9695	25, 61, 85, 115, 127, 135
Ca <sub>5</sub> -	$D_{3h}$	${}^{2}A_{1}'$	0.0	62(2), 84, 85(2), 86, 94, 95, 139
	$C_{2v}$	${}^{2}B_{1}$	0.1439	53, 65, 72, 79, 90, 104, 132, 133, 152
	$C_{2v}$	${}^{4}B_{1}$	0.4153	37, 59, 66, 79, 91, 107, 109, 135, 141
$Ca_6^-$	$C_{2v}$	${}^{2}A_{2}$	0.0	46, 57, 61, 71, 82, 96, 102, 106, 112, 123, 127, 146
	$C_{2v}$	${}^{2}A_{1}$	0.0170	46, 58, 66, 85, 86, 93, 95, 98, 104, 113, 116, 150
	$C_{2v}$	${}^{4}B_{1}$	0.3102	44, 55, 56, 64, 82, 87, 91, 100, 118, 136, 137, 146
	$C_1$	<sup>4</sup> A	0.4762	44, 49, 53, 61, 77, 81, 82, 84, 103, 109, 132, 132

"Energies (E) are relative to the ground state of the cluster anions reported in Table 1. The basis set 6-311+G(d) is used.

TABLE 4: Ground and Excited States of  $Ca_2$  through  $Ca_6$  and Electron Binding Energies  $BE^{\alpha}$ 

						BE	(eV)	
$Ca_n$	sym	state	$E(\mathrm{eV})$	$^{2}\Sigma_{g}$ +	$^{2}I$	$I_u$	${}^{4}\Sigma_{u} +$	${}^{4}\Pi_{g}$
Ca <sub>2</sub>	$D_{\infty h}$	${}^{1}\Sigma_{o}^{+}$	0.5124	0.513	6 0.5	286		
-	$D_{\infty h}$	${}^{3}\Pi_{u}^{\circ}$	1.3848	1.733	5 1.49	984	0.7635	0.6954
	$D_{\infty h}$	${}^{3}\Sigma_{u}^{+}$	1.4321	1.542	2 1.42	251	0.9500	0.7312
	$D_{\infty h}$	$5\Sigma_u^+$	2.9172	3.424	1 3.1	827	2.3319	2.3443
	$D_{\infty h}$	${}^{5}\Pi_{u}$	3.0139	3.118	1 3.0	140	2.4505	2.2979
						В	E (eV)	
$Ca_n$	sym	stat	e <i>E</i> (	eV)	$^2A_2^{\prime\prime}$		$^{2}A_{1}^{\prime}$	${}^{4}\mathrm{B}_{1}$
Ca <sub>3</sub>	$D_{3h}$	$^{1}A_{1}$	· 0.8	891	0.9106	(	0.7880	
	$C_{2v}$	${}^{3}A_{1}$	1.7	620	1.8524		1.7667	1.0911
	$C_{2v}$	<sup>5</sup> A <sub>1</sub>	2.7	466	2.7593	4	2.6692	2.0770
						В	E (eV)	
$Ca_n$	sym	stat	e <i>E</i> (	eV)	$^{2}A_{1}$		<sup>4</sup> A <sub>2</sub>	<sup>4</sup> A
Ca <sub>4</sub>	$T_d$	$^{1}A_{1}$	0.9	557	0.9559			
	$D_{2d}$	${}^{3}B_{2}$	1.7	895	1.9093	(	).9526	0.9872
	$C_1$	<sup>5</sup> A	2.6	871	3.0696	2	2.1355	1.7449
	$C_2$	۶B	2.8	344	3.2322	2	2.3559	1.7451
						В	E (eV)	
$Ca_n$	sym	stat	e <i>E</i> (	eV)	$^{2}A_{1}^{\prime } \\$		${}^{2}\mathbf{B}_{1}$	${}^{4}\mathrm{B}_{1}$
Ca <sub>5</sub>	$D_{3h}$	$^{1}A_{1}$	′ 1.0	084	1.0315	(	).8964	
	$C_1$	<sup>3</sup> A	1.4	384	1.5308		1.4747	1.0707
	$C_{4v}$	<sup>5</sup> A <sub>2</sub>	2.3	865	2.5926	2	2.5663	2.3292
						BE	(eV)	
$Ca_n$	sym	state	$E(\mathrm{eV})$	$^{2}A_{2}$	24	A1	${}^{4}\mathrm{B}_{1}$	<sup>4</sup> A
Ca <sub>6</sub>	$C_{2v}$	$^{1}A_{1}$	1.1554	1.171	9 1.1	770		
	$C_{2v}$	${}^{3}B_{1}$	1.4277	1.502	3 1.5	861	1.1697	1.3405
	$C_1$	<sup>3</sup> A	1.6164	1.502	3 1.54	431	1.1691	1.4648
	$C_{2n}$	<sup>5</sup> B1	1.8498	2.075	1 1.9	763	1.6500	1.5349

"Neutral clusters' energies (*E*) are relative to the ground state of the cluster anion in Table 1. Missing entries correspond to anion geometries not allowed in the state of the neutral clusters. The basis set 6-311+G(d) is used.

and their excited states laying within that energy window need to be calculated.

Presumably the electron detachment process is extremely fast, thus the ground state and the excited states of the neutral cluster are accessed experimentally at the same geometry of the anion. This conjecture has been used repeatedly in the literature.<sup>30,31</sup> However, we found that the energy of the neutral cluster in the geometry of the anion cluster might not belong to a point of the energy surface of any of the stable electronic states of the neutral cluster. This is a fundamental feature of two electronic states that cross in space; the intersection between the two surfaces is associated to only a few geometrical configurations. In this paper we report those cases where the energy surface of the neutral contains the point calculated at the frozen anion configuration, such that the BE is defined as:

 $BE = E_n$ (neutral at anion's frozen geometry) –

 $E_n$ (anion at equilibrium) (1)

This electron detachment mechanism can be viewed as a unimolecular reaction. For example, for calcium clusters:

#### $\operatorname{Ca}_n^{-} \to \operatorname{Ca}_n(\text{frozen at anion's geometry}) + e$ (2)

The electron has spin  $\frac{1}{2}$  (equivalent to a doublet), and the two elements considered in this work, Ca and Zn, have an even number of electrons. Thus, the reaction to detach an electron can proceed exclusively according to the spin angular momentum rules in the following combinations of state multiplicities:

#### doublet $\rightarrow$ singlet (or triplet or quintet) + doublet

quartet  $\rightarrow$  triplet (or quintet) + doublet

Therefore, if the cluster anion is in a state with spin multiplicity 2, in order to detach one electron the singlet, triplet, and quintet states of the neutral cluster need to be taken into consideration. On the other hand, if the electron is detached from the cluster anion in a state with spin multiplicity 4, only triplet and quintet states of the neutral cluster need to be considered.

The predicted theoretical BEs using eq 1 and energy information in Tables 3–6 are reported in Tables 4 and 6. These BEs are calculated without considering the zero point energy of the cluster anion states. In fact, zero point energies are very small: 0.006, 0.021, 0.039, 0.049, and 0.07 eV for the ground states of  $Ca_2^-$  through  $Ca_6^-$  and 0.021, 0.038, 0.038, 0.062 eV for Zn<sub>3</sub><sup>-</sup> through Zn<sub>6</sub><sup>-</sup>. Missing values in Tables 4 and 6 indicate that the frozen configuration of the anion is not a point in the energy surface of the neutral cluster.

Figure 5 contains comparison between the calculated BEs reported in Table 4 for calcium cluster anions (dashed line and spikes) and the experimental results<sup>8</sup> (continuous gray line).

TABLE 5: Excited States of Zn<sub>3</sub><sup>-</sup> through Zn<sub>6</sub><sup>-</sup> and Their Vibrational Frequencies<sup>a</sup>

	5	0 0		•
$Zn_n^-$	sym	state	<i>E</i> (eV)	frequencies (cm <sup>-1</sup> )
$Zn_3^-$	$D_{3h}$	${}^{2}A_{1}'$	0.0	104(2), 128
	$D_{3h}$	${}^{2}A_{1}'$	0.1670	67(2), 97
	$C_{2v}$	${}^{4}B_{1}$	1.5854	21, 151, 239
$Zn_4^-$	$T_{d}$	${}^{2}A_{1}$	0.0	87(2), 100(3), 135
	$C_1$	<sup>4</sup> A	1.4654	43, 59, 96, 126, 127, 162
$Zn_5^-$	$D_{3h}$	${}^{2}A_{1}'$	0.0	52(2), 58(3), 66(2), 90, 119
	$D_{3h}$	${}^{4}A_{2}''$	1.6792	30(2), 99(2), 120, 131(2), 136, 156
$Zn_6^-$	$C_{5v}$	${}^{2}A_{1}$	0.0	27(2), 59(2), 64, 79(2), 111, 113(2), 134(2)
	$C_{2v}$	${}^{2}A_{1}$	0.0124	18, 33, 36, 37, 91, 94, 105(2), 107, 129, 147, 160
	$C_i$	$^{2}A_{g}$	0.1094	21, 33, 46, 54, 59, 75, 86, 96, 105, 109, 117, 128
	$C_1$	<sup>4</sup> A	1.0435	18, 21, 45, 47, 66, 83, 103, 108, 126, 143, 147, 179

"Energies (E) are relative to the ground state of the cluster anion given in Table 2. The basis set 6-311+G(d) is used.

TABLE 6: Ground and Excited States of  $Zn_3$  through  $Zn_6$  and Electron Binding Energies  $(BE)^a$ 

						BE (eV)	
$Zn_n$	syn	n s	state	$E(\mathrm{eV})$	$^{2}A_{1}^{\prime}$	${}^{2}A_{1}'$	${}^{4}B_{1}$
Zn <sub>3</sub>	$D_{3h}$ $C_s$ $D_{3h}$	1 3 5	A <sub>1</sub> A" A <sub>2</sub> "	0.5265 2.3716 4.7562	0.6394 2.8805 4.9051	0.3771 2.8990 5.0537	0.8044 4.3706
						BE (e	eV)
$Zn_n$	s	ym	stat	e E(	(eV)	$^{2}A_{1}$	<sup>4</sup> A
Zn <sub>4</sub>	1 ( (	Cd C1 C1	<sup>1</sup> A <sub>1</sub> <sup>3</sup> A <sup>5</sup> A	0.8 2.6 4.6	8077 6976 6593	0.8220 3.3773	1.2022 3.8806
						BE (e	eV)
$Zn_n$	s	ym	stat	e E(	(eV)	${}^{2}A_{1}'$	${}^{4}A_{2}''$
7n.							
2115		$D_{3h}$ $C_1$ $C_1$	<sup>1</sup> A <sub>1</sub> <sup>3</sup> A <sup>5</sup> A	, 0.8 2.2 3.7	8942 2065 7327	0.9684 2.8948 5.2724	0.9441 3.3677
	I ( (	$\sum_{1}^{3h}$	<sup>1</sup> A <sub>1</sub> <sup>3</sup> A <sup>5</sup> A	, 0.8 2.2 3.7	8942 2065 7327	0.9684 2.8948 5.2724 BE (eV)	0.9441 3.3677
Zn <sub>n</sub>	sym	$\sum_{1}^{3h}$	$E = E(e^{1A_1}$	$^{\prime}$ 0.8 2.2 3.7 2.2 3.7	8942 2065 7327 1 <sup>2</sup> A	$\begin{array}{c} 0.9684 \\ 2.8948 \\ 5.2724 \end{array}$ BE (eV) $\begin{array}{c} \\ BE \\ a_1 \end{array}  {}^2A_g \end{array}$	0.9441 3.3677 4A
$\frac{Zn_n}{Zn_6}$	$\frac{I}{C_{2\nu}}$ $C_{2\nu}$ $C_{1}$	$ \frac{D_{3h}}{C_1} $ state $ \frac{1}{A_1} $ 3A	$^{1}A_{1}$ $^{3}A$ $^{5}A$ $^{5}A$ $^{2}E = E (e)$ $1.22$ $2.46$ $2.56$	$\begin{array}{c} 0.8 \\ 2.2 \\ 3.7 \\ \hline \\ 0.8 \\ \hline \\ 0.8 \\ \hline \\ 0.8 0$	$   \begin{array}{r}     3942 \\     2065 \\     7327 \\     \hline     1                          $	$\begin{array}{c} 0.9684 \\ 2.8948 \\ 5.2724 \\ \hline BE (eV) \\ \hline \\ \hline \\ \hline \\ 02 \\ 1.2725 \\ \hline \\ \hline \\ 02 \\ 1.2725 \\ \hline \\ \hline \\ 04 \\ 1.2725 \\ 1.2725 \\ \hline \\ 04 \\ 1.2725 \\ 1.2725 \\ 1.2725 \\ 1.2725 \\ 1.27$	0.9441 3.3677 4A 5

<sup>*e*</sup>Neutral cluster energies (*E*) are relative to the cluster anions' ground state in Table 2. Missing entries correspond to anion geometries not allowed in the state of the neutral clusters. The basis set 6-311+G(d) is used.

Although the experimental peaks are broad, across these cluster sizes there are three features that we identify as the electron detaching from the ground state of the cluster anion and accessing the singlet, triplet, and quintet states of the neutral cluster of equal size. Peak broadening of the three major BEs is expected because the cluster anion may be occupying a band of vibrational states when the electron is detached. Vibrations in the neutral cluster states are also expected to be excited. Therefore a vibrational broadening is added to each of the three major BEs using the vibrational frequencies reported in Table 3. Multiple excitations of vibrational states shift the BEs also reported in Table 4 by about 0.1 eV and give substantial broadening. The dotted line in Figure 5 shows the shape of the peak corresponding to BEs from the anion ground state to the ground and excited states of the neutral clusters when 10 vibrational states are used in the broadening. The height of the calculated peaks is scaled such that the calculated and experimental first peak intensity coincide and this scaling factor is used for the rest of the calculated spectrum. Electrons detaching from excited states of the cluster anion are less abundant; BEs from these states contribute to broaden the three main peaks. These secondary BEs are reported in Table 4 and shown as delta functions in Figure 5. The tallest spikes correspond to BEs originated from the anion first exited state and spikes with decreasing height correspond to BEs from the second and third excited states of Ca  $n^{-}$ .

The experimental gap between the first and the second peak can then be identified as the energy difference between the ground and first excited states of the neutral cluster. The calculated gaps are 0.95, 0.92, 1.28, 0.47, 0.32 eV for Ca2through Ca6-, which are in very good agreement with the experimental values of 1.13, 0.81, 1.02, 0.55, and 0.47 eV, respectively. The major discrepancy is for Ca<sub>4</sub><sup>-</sup>, where the experimental second peak shows a clear splitting, which gives rise to two energy gaps of 1.0 and 1.3 eV. Our calculation matches better the higher energy gap. A closer look at the experimental shape of the low-energy BE peak shows a systematic shoulder toward low energies for all clusters except Ca4<sup>-</sup>. This shoulder may be assigned to detachment from the first excited doublet of the anion to the ground state of the neutral cluster. As shown in Table 3, cluster anions of all sizes have a first excited state that is very close in energy to the ground state except for Ca4-. Therefore, this characteristic is another agreement between theory and experiment.

Other higher energy excited states of the neutral clusters may exist, but their study within the hybrid DFT is not adequate. Therefore, there are still unknowns for the full interpretation of the experimental BEs. Specifically, for  $Ca_5^-$  and  $Ca_6^-$  the experimental spectrum shows features at BEs greater than 2.5 eV, which may correspond to higher energy excited states. In the case of  $Ca_4^-$  there might be additional excited singlet states of neutral  $Ca_4$  that we were unable to locate. Other geometries of  $Ca_4$  were only found to be stable for a quintet excited state at a BE above 3.5 eV.

Following the same procedure as for calcium clusters, the electron detachment energy of  $Zn_n^-$  (n = 3-6) was theoretically predicted by calculating the energy difference between the states of the anions and the states of neutrals at the geometry of the anions. The gray continuous line in Figure 6 depicts the experimental results reported in ref 17 and the dashed line corresponds to the calculated BE between the ground state of the anion and the singlet, triplet, and quintet states of the neutral cluster. Worth noting is that the experimental results in ref 8 are almost identical to those of ref 17 and were obtained considering a band of 10 vibrational states for each of the two electronic states involved according to frequencies reported in

![](_page_126_Figure_2.jpeg)

Figure 5. Electron binding energy of calcium cluster anions. Dotted lines are vibration-broaden calculated BEs from the ground state of the anion to the ground and excited states of the neutral. Spikes are calculated BEs from the excited states of the anion. The gray solid line is the experiment in ref 8.

Table 5. The intensity of the first peak is scaled to coincide with the experiment, and the same scaling factor is used throughout the spectrum. Additionally, the delta functions in Figure 6 correspond to BEs from anion ground state to excited states of the neutral and from excited states of the anion to all available states of the neutrals (see Table 6). The tallest spikes correspond to energy differences from the anion ground state and lines with decreasing height correspond to the first, second, and third excited states of  $Zn_n^-$ .

The experimental energy gaps between the first peak and second peak are 2.25, 2.62, 2.19, and 1.50 eV for  $Zn_3^-$  through  $Zn_6^-$ , respectively. The calculated gaps of 2.22, 2.50, 1.93, and 1.22 eV are in excellent agreement with experiment. Experimentally the first peak of  $Zn_3^-$  and  $Zn_6^-$  shows a noticeable shoulder at low energies, which is consistent with BEs from the low excited states of the anion clusters shown as spikes in Figure 6.

#### 5. Conclusion

On the basis of the hybrid DFT calculations, this paper provides novel information on the ground-state energetics, symmetry, and vibrational analysis of anion calcium clusters up to  $Ca_{19}^{-}$  and on anion zinc clusters up to  $Zn_{11}^{-}$  which allows for calculation of the electron affinity in this cluster size range. Comparison of the electron affinity results with experiment is excellent, reproducing the intriguing kink observed at  $Ca_{10}$  and  $Zn_{10}$ . For calcium, this kink occurs because  $Ca_{10}$  is a magic number for the neutral clusters<sup>4</sup> whereas  $Ca_{10}^{-}$  is a fairly unstable cluster anion as shown in Figure 1a. The EA kink in zinc clusters is not as pronounced, pointing to a fairly stable  $Zn_{10}^{19}$  that does not qualify as a magic number and a fairly unstable cluster anion as shown in Figure 1b.

The DFT method used is limited to only provide precisely the excited states that have different multiplicity than the ground states. Therefore, the calculated electron detachment spectrum is a portion of the experimental observations. The electron detachment spectra of  $\mathrm{Ca_2^-}$  through  $\mathrm{Ca_6^-}$  and  $\mathrm{Zn_3^-}$  through Zn6- were calculated and compared with Zheng's8 and Kostko's17 experimental observations. The major spectral characteristics are well calculated for these small clusters, as evidenced by the agreement with experiment. The spectral gaps between the first and second experimental features are in excellent agreement with the calculated counterparts. It is predicted that the electron detachment spectra originate from cluster anions in the ground state, but some BEs are broadened when detachment occurs from the first few anion excited states. A good agreement on the broadening is due to the contribution of the excited vibrational states. The paper contains the vibrational analysis for the anion states originating the spectral peaks and identifies that spectral peaks in the higher energy region are due to neutral clusters reached in triplet and quintet excited states. Since the reachable states of the neutral clusters have different multiplicities, the electron detachment process may be used as a spin switch if tailored accordingly.

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![](_page_127_Figure_1.jpeg)

Figure 6. Electron binding energy of zinc cluster anions. Dotted lines are vibration-broaden calculated BEs from the ground state of the anion to the ground and excited states of the neutral. Spikes are calculated BEs from the excited states of the anion. The gray solid line is the experiment in ref 17.

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# Energetics, structure, and charge distribution of reduced and oxidized *n*-pyrrole oligomers: A density functional approach

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Polypyrrole is a conjugated polymer prototype of conducting polymers. The energetically preferred spatial conformation of *n*-pyrrole oligomers (n=1-24) in both the reduced and oxidized phases is obtained and analyzed in this paper within the hybrid density functional theory. Binding energies, gap energies, radius of gyration, end-to-end distance, and vibrational frequencies are reported as functions of oligomer length. Reduced *n*-pyrrole are bent chains for all sizes showing a dramatic departure from planarity. Vibrational spectra of n-pyrrole oligomers indicate the presence of two fairly size-insensitive frequency regions, which increase in intensity with increasing oligomer size. Several oxidation levels were analyzed for n-pyrrole through the distribution of the carbon-carbon bond orders and single/double bond lengths. It is shown that the oxidation level is directly related to the way positive charge localizes along the *n*-pyrrole oligomer chain. If charge/n < 1/3, the oligomers are bent and charge is delocalized; if charge/ $n \ge 1/3$ , the oligomers are planar and charge notoriously localizes in n/charge regions along the backbone. Calculations with electronegative dopants show that charge localizes in the neighborhood of the dopant. It is demonstrated that one localized state in the gap between the highest occupied and lowest-unoccupied states appears for every +2e in the oxidation level. The band structure of infinite reduced polypyrrole gives a band gap energy in excellent agreement with experiment. The evolution of the band gap and the charge-localized band as a function of polypyrrole oxidation level is reported. © 2008 American Institute of Physics. [DOI: 10.1063/1.2996297]

#### I. INTRODUCTION

Polypyrrole (PPy) is a prototypical conducting polymer. Because of its strong electrical and optical anisotropies, PPy is a good candidate for photonic devices. The discovery of photoinduced charge transfer between polymers and their environment (either a substrate or a solid solvent) has led to efficient heterojunctions of polymer/substrate with important applications in solar cells and chemical detectors. However, the lack of knowledge about the recombination dynamics and polaron mobility is a bottleneck to improve any device efficiency. By electrochemical polymerization, PPy is synthesized in two different phases: reduced when the polymer is electrically neutral and oxidized when the polymer is positively charged, having transferred electrons to the oxidizing agent.<sup>1,2</sup>

Theoretical studies of PPy have extensively used semiempirical and Hartree–Fock (HF) methods. For example, the ultraviolet photoemission and optical absorption spectra for pyrrole (Py) and PPy were analyzed using a spectroscopically parametrized complete neglect of differential overlap method;<sup>3</sup> the vibrational spectra of PPy was studied at the modified neglect of differential overlap level,<sup>4</sup> and the band structure of PPy within the intermediate neglect of differential overlap approximation was published.<sup>5</sup> At the Hartree Fock level, there have been several studies as well: the ground states of Py, 2-Py, and PPy,<sup>6</sup> the effect of charge-transfer doping on the geometry of PPy,<sup>7–9</sup> the energetics of Py dimers as a function of the torsion angle,<sup>10</sup> and structure coupled with vibrational spectra.<sup>11,12</sup> More recently, density functional theory (DFT) calculations of PPy have been undertaken for a variety of studies, for example, studies on the band gap of conducting polymers,<sup>13</sup> electronic and structural properties of oxidized PPy with chlorine dopants,<sup>14</sup> the excited states of the Py monomer and dimer,<sup>15</sup> and their vibrational frequencies.<sup>16</sup> Despite these studies, the positive charge localization mechanism that occurs in oxidized PPy has not been given a proper description at the quantum level.

The purpose of this study is to investigate the energetics of reduced and oxidized *n*-Py oligomers and the positive charge localization as a function of oligomer length (*n*). Results in these areas are pertinent for studies of polaron and bipolaron formation.<sup>17–19</sup> To that end, the geometrical structures of *n*-Py (n=1-9,12,15,18,20,24) and infinite PPy chains were studied in their reduced and oxidized phases within the hybrid DFT framework with large basis sets. This paper is organized as follows: Section II describes the methodology used as well as the results for the Py and bipyrrole molecules. Sec. III describes the geometrical configurations

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TABLE I. IR-active spectrum of anti-gauche and syn-gauche bipyrrole (str=stretch, i-r=inter-ring, rd=ring deform, ipb=in-plane bend, oopb=out-of-plane bend, oopr=out-of-plane rotation, and ripr=ring in-plane rotation).

Evet <sup>a</sup>	anti-ga	uuche	syn-gauche		
$(cm^{-1})$	(cm <sup>-1</sup> )	I <sub>IR</sub>	(cm <sup>-1</sup> )	$I_{\rm IR}$	Assignment
			a		
	3697	9.8	3692	57.4	N—H str
	3286	0.0	3285	0.0	C—H str
	3262	1.3	3268	9.1	C—H str
	3246	0.3	3252	0.25	C—H str
1618	1674	0.0	1671	0.4	C—C i-r str
1479	1523	1.2	1522	10.2	C—C, C—N str
1453	1477	1.6	1457	4.9	C—N, C—C str
1410	1450	0.3	1430	4.8	C—N, C—C str
1303	1345	1.8	1323	7.9	C-C str, N-H ipb
1263	1314	0.0	1287	0.8	CH ipb
1118	1162	1.5	1158	9.0	C—N—C—H ipb
1098	1132	1.8	1127	22.4	Н—С=С—Н
1029	1071	1.6	1065	29.0	H—C—C—H ipb
960	990	0.2	986	1.3	rd, C—H ipb
880	915	0.3	921	3.4	rd
	444	0.8	394	0.2	ripr
392	392	0.0	359	3.0	Ring ip transl
	902	0.18	910	0.1	C—H oopb
789	819	77.3	847	16.9	C—H oopb
727	736	170.3	738	22.3	C—H oopb
669	671	1.8	704	0.6	Ring def
584	642	49.6	654	30.5	Ring def
	623	107.2	624	31.4	N—H oopb
	121	0.6	122	0.2	Ring oopb
	63	3.6	b		Ring oopr
3365	3697	73.2	3691	19.5	N—H str
	3286	10.1	3284	10.7	C—H str
3120	3262	12.8	3268	2.4	C—H str
3100	3247	19.0	3251	15.7	C—H str
1527	1581	39.2	1589	30.4	C=C str
1425	1471	4.6	1485	7.4	N—C=C
1415	1443	13.0	1454	12.3	Н—С—С—Н
	1431	12.7	1439	1.7	C—C str
1252	1294	9.8	1313	4.9	C—H, N—H ipb
1147	1179	0.2	1173	0.2	Ring breath
1105	1138	55.7	1146	27.8	H—C—C—H, H—C—N—H
	1096	31.9	1091	13.8	C—H, N—H ipb
1034	1064	52.9	1061	36.1	C—H ipb
894	931	12.7	924	12.5	rd
	905	2.7	908	0.1	rd, C—H oopb
	130	2.5	117	1.2	Ring ipr
	902	0.2	903	1.0	C—H oopb
795	835	11.8	835	59.6	C—H oopb
692	736	13.4	736	155.2	C—H oopb
652	706	1.9	675	0.2	C—H, C—C i-r oopb
030	641	5.6	635	1.1	C—H, N—H oopb
448	623	22.7	597	135.6	C—H, N—H oopb
550	351	1.7	433	3.7	Ring oopb

<sup>a</sup>References 11 and 26.

and electronic properties of reduced n-Py. Sec. IV and V contain the study of charged n-Py without dopants and oxidized n-Py with dopants, respectively. Section VI contains the results of infinite PPy. Section VII presents the conclusions of this paper.

#### **II. PYRROLE AND BIPYRROLE**

DFT and the hybrid Becke–Perdew–Wang 1991 approach were used throughout this study, which includes local and nonlocal correlation functionals.<sup>20,21</sup> A triple valence ba-

![](_page_130_Figure_0.jpeg)

![](_page_130_Figure_1.jpeg)

FIG. 1. (Color) Stable bipyrrole isomers showing the torsion angles. [(a) and (b)] Neutral 2-Py; [(c) and (d)] oxidized 2-Py<sup>+</sup>.

sis set (6-311G) containing 8*s*, 7*p*, and 1*d* Gaussians contracted as (62111111, 3311111, and 3) was adopted in all calculations.<sup>22</sup> The GAUSSIAN 03 package<sup>23</sup> was used throughout. This level of theory reproduces very well the experimental geometry<sup>24</sup> of the neutral Py monomer with a maximum error in geometry variables of 0.8%. The Py molecule is a  $C_{2v}$  planar structure with a strong dipole moment of 1.98 D in the direction of the N—H bond and diagonal quadrupole matrix elements of -23.4, -26.5, and -34.1 D Å. The infrared active vibrational frequencies of the two bipyrrole isomers are given in Table I. The agreement of calculated frequencies with experiment<sup>25</sup> is excellent, as indicated by an average ratio of calculated to experimental results of 0.96.

The reduced phase of *n*-Py oligomers and PPy is insulating, charge neutral, and displays the benzenoid alternation of single-double C—C bonds. An alternative realization of the reduced phase is the benzenoid C—C bond alternation attained by electric neutralization of trapped anions  $(A^-)$  with solvent cations  $(C^+)$ . Anions or cations that remain in the polymer matrix during polymerization are called *dopants*. The oxidized phase of PPy (the polymer is positively

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charged) is the conducting phase displaying conjugated chains with quinoid single-double C—C bond alternation. The change from benzenoid to quinoid structures is promoted by the migration of electrons to the electronegative dopants ( $A^-$ ). In the oxidized state, *n*-Py and PPy chains are cations.

The geometrical structure of bipyrrole, as well as that of larger oligomers, is modulated the most by the rotational degree of freedom around the inter-ring C-C bond. In principle, reduced 2-Py may have four possible isomers: two puckered structures anti-gauche and syn-gauche and two planar structures anti and syn. The oxidized 2-Py may have only two planar isomers: anti and syn. Energetics along the rotational path yields the stability of rotational isomers as a function of the torsion angle. For neutral 2-Py, the global minimum corresponds to the anti-gauche C2 geometry (torsion angle= $153^{\circ}$ ), which is more stable by 0.033 eV than the planar anti form (180°), 0.122 eV more stable than the syngauche form  $(50^\circ)$  and 0.18 eV more stable than the syn form  $(0^\circ)$ . Additionally, a normal mode frequency analysis shows that only two neutral isomers are stable, e.g., the antigauche isomer ( $C_2$  with a torsion angle of 153°) and the syn-gauche isomer ( $C_2$  with a torsion angle of 50°) shown in Figs. 1(a) and 1(b). Once relaxed, the binding energy of the anti-gauche isomer becomes -119.32 eV, and the syngauche is 0.07 eV less stable. Therefore, these two neutral isomers can coexist in thermal equilibrium at temperatures of about 700 K. These results are in excellent agreement with MIDI-4 self-consistent field pioneer calculations.<sup>11</sup> For oxidized 2-Py with a +e charge, the two stable isomers are the anti  $(C_{2h})$  and the syn  $(C_{2v})$  planar forms shown in Figs. 1(c)

TABLE II. Vibrational spectrum of anti charged bipyrrole (str=stretch, i-r=inter-ring, rd=ring deform, ipb =in-plane bend, oopb=out-of-plane bend, oopr=out-of-plane rotation, and ripr=ring in-plane rotation).

				anti 2-Py <sup>+</sup> ( $C_{2h}$ )					
	h		a <sub>u</sub>			b <sub>u</sub>			
$(cm^{-1})$	$(cm^{-1})$	(cm <sup>-1</sup> )	$I_{\rm IR}$	Assignment	(cm <sup>-1</sup> )	$I_{\rm IR}$	Assignment		
3680	952	952	1.8	C—H oopb	3680	178.8	N—H str		
3300	880	884	15.6	C—H oopb	3300	8.3	C-H str		
3282	787	787	220.1	C—H oopb	3282	9.8	C-H str		
3269	687	675	210.4	N—H oopb	3268	0.0	C—H str		
1682	672	632	0.0	C—N oopb	1545	100.9	C—H, N—H ipb		
1521	577	587	10.7	C-C=C oopb	1502	56.8	C=C, C-N str		
1503	302	122	3.5	Ring oopb	1413	369.6	rd		
1417		68	4.3	Ring oopr	1400	1.4	C—H, N—H ipb		
1393					1224	4.8	rd		
1308					1181	6.5	Ring breath		
1184					1156	107.3	C—H, N—H ipb		
1123					1110	94.4	C—H ipb		
1113					1062	13.6	C—H. N—H ipb		
969					920	44.0	rd		
891					880	5.6	rd		
459					155	1.4	ripr		
406							Ľ		

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TABLE III. Vibrational spectrum of syn charged bipyrrole (str=stretch, i-r=inter-ring, rd=ring deform, ipb=in-plane bend, oopb=out-of-plane bend, oopr=out-of-plane rotation, ripr=ring in-plane rotation, and ript=ring in-plane translation).

				syn	2-Py <sup>+</sup> $(C_{2v})$				
<i>a</i> <sub>1</sub>		<i>a</i> -	$b_1$			<i>b</i> <sub>2</sub>			
(cm <sup>-1</sup> )	$I_{\rm IR}$	Assignment	$(cm^{-1})$	(cm <sup>-1</sup> )	$I_{\rm R}$	Assignment	(cm <sup>-1</sup> )	$I_{\rm IR}$	Assignment
3691	156.2	N—H str	954	956	1.5	C—H oopb	3682	0.1	N—H str
3302	1.8	C—H str	883	885	19.3	C—H oopb	3301	6.7	C—H str
3286	4.9	C—H str	785	790	178.7	C—H oopb	3283	5.4	C—H str
3277	0.9	C—H str	681	674	241.5	N—H oopb	3275	0.3	C—H str
1682	6.5	C=C i-r str	591	627	0.6	C-N-C oopb	1544	65.2	C—H, N—H ipb
1514	43.8	N—H ipb	583	577	26.2	C-C-C oopb	1510	31.8	C=C, C-N str
1498	1.6	rd	301	119	1.5	ring oopb	1421	317.3	C-C str
1416	23.9	C-C, N-H ipb	49				1386	8.7	C—H, N—H ipb
1389	13.4	C—H ipb					1296	3.9	C—H ipb
1239	6.2	C-N str					1173	1.0	Ring breath
1169	38.4	Н-С-М-Н					1156	24.0	Н-С-И-Н
1126	31.7	Н-С-С-Н					1104	69.0	Н-С-С-Н
1111	15.5	C-C str					1059	14.6	C—H ipb
966	1.6	rd					912	49.0	rd
902	1.1	rd					875	0.4	rd
407	0.0	ript					456	0.1	ripr
160	0.1	ripr							

and 1(d). The charged anti  $C_{2h}$  isomer (6.75 eV above the neutral  $C_2$  anti-*gauche*) is the global minimum, which is lower in energy by 0.144 eV than the charged syn  $C_{2v}$  isomer. A high torsional energy barrier of 1.146 eV makes the transition between the two charged isomers not thermally possible.

Table I lists the calculated normal mode IR-active frequencies for the two neutral bipyrrole isomers, and Tables II and III contain similar information for the positively charged 2-Py<sup>+</sup> isomers. The results for the neutral isomers are in very good agreement with experiment<sup>11,26</sup> (Table I, columns 1, 2, and 5). It is to be noted that at the time of the experiments, the symmetry assignment given to neutral bipyrrole was  $D_{2h}$ , only based on the frequency assignments of infinite chains. Our comparison shows that the agreement between experiment and calculation for anti-gauche or syn-gauche bipyrrole isomers is excellent. Therefore, the identification of the molecular symmetry through that IR experiment should be  $C_2$ . A frequency scaling factor can be defined as the ratio between the calculated and experimental frequencies, which, based on values in Table I, is on average 0.97. Additionally, Tables II and III contain the non-IR active frequencies of the  $a_g$  and  $b_g$  modes in the case of the anti  $C_{2h}$  charged isomer and of the  $a_2$  mode in the case of the syn  $C_{2v}$  charged isomer.

#### III. STRUCTURE AND ENERGETICS OF REDUCED *n*-Py OLIGOMERS

A geometry optimization of the larger reduced n-Py was performed for all sizes with n up to 24. The search for the structures of lowest energy was conducted for each oligomer size with the following strategy. A multitude of oligomer structures from molecular dynamics trajectories using an inhouse potential model<sup>27</sup> were used as initial geometries for the optimization to a minimum of the energy, which was performed with the Berny algorithm and redundant internal coordinates.<sup>28</sup> Because the most stable isomer of neutral bipyrrole is the anti-*gauche* form, only repetitions of this form were optimized for larger *n*-Py oligomers. Combinations of anti-*gauche* with syn-*gauche* forms were not attempted. All geometrical optimizations of the electronic states include the harmonic frequency calculations to ensure finding of minima. Multiple configurations were not minima but rather saddles of different orders, which are not reported in this paper. Some of these unstable geometries were chains with

![](_page_131_Figure_9.jpeg)

FIG. 2. (Color) Optimized structures for reduced n-Py (n=6, 9, 12, 15, 18, and 24).

#### 164903-5 *n*-pyrrole oligomers

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Reduced Oxidized q<sup>12+</sup>  $q^{2+}$  $q^{3+}$  $q^{4+}$  $q^{8+}$  $q^{10+}$  $q^{5+}$ Singlet Triplet  $q^{6+}$  $\Delta_{\rm HL}$  ${}^{3}E_{b}$  $\Delta_{\rm HI}$ n-Py  ${}^{1}E_{\mu}$  $E_{\mu}$ 1 -62.09 6.87 3.87 3.42 24.03 2 -119.32 5.21 2.84 3.24 18.72 3 -176.56 4.46 2.45 2.45 16.50 4 4.07 2.30 2.01 15.20 -233.80 5 -291.042.22 14.34 3.84 1.83 6 24.94 39.24 -348.283.69 2.19 1.64 13.73 9 -519.993.46 2.15 1.44 12.60 21.92 33.73 64.78 12 -691713 36 2.15 1 33 11 93 30.67 57.26 92.18 15 -863.43 3.31 1.29 11.48 19.08 28.71 52.41 120.95 2.14 39.62 -1035.14 18 3.29 2.14 1.28 11.16 49.02 76.71 150.82

TABLE IV. Binding energies and HOMO-LUMO energy gap for n-Py in the reduced phase and m+ oxidized phases (m=2-6, 8, 10, and 12). Energies are in eV; all energies are referred to the ground state of the neutral oligomer (second row).

wavy shapes almost degenerate in energy with the ground state. The ground states of the n-Py neutral oligomers are singlet electronic states.

The C—C single-double conjugation in *n*-Py is believed to result in a stiff backbone reluctant to bend and twist. Indeed, the picture that most experimentalists have of reduced *n*-Py is that of planar oligomers.<sup>26,29</sup> This belief is a result of semiempirical quantum mechanical approximations such as INDO that are not computer intensive and can be readily calculated in any type of computational platform. Our calculations are based on a better quantum approximation that predicts a different paradigm displayed in Fig. 2. This figure shows the optimized bent configurations of reduced 6-, 9-, 12-, 15-, 18-, and 24-Py. Notice that the torsion angle, as defined for 2-Py, continues to be approximately 153° between neighboring monomers. However, the end-to-end distance and the radius of gyration are substantially different from those in planar chains. This chain bending is one of the reasons why PPy, irrespective of the fabrication process,<sup>1,2,30</sup> tends to form amorphous rather than crystalline arrays of stacked chains.<sup>26</sup> This effect has also an important role in the volume contraction seen experimentally when an oxidized PPy sample is reduced. These bent conformations are in qualitative agreement with those reported recently within density functional calculations with smaller basis sets.

Although the point group of reduced Py is  $C_{2v}$ , larger chains present a loss of symmetry; the even-*n*-Py reduced oligomers are  $C_2$  (see Fig. 2) and odd-*n*-Py are  $C_s$ . Chains are less symmetric, reflecting the bending of the backbone away from a plane. Binding energies of the ground singlet state  ${}^{1}E_{b}$ , the first excited trimer state  ${}^{3}E_{b}$ , and the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) energy gap  $\Delta_{\rm HL}$  are reported in Table IV (columns 2–5). The binding energy of the triplet state is reported relative to that of the singlet state. The  $\Delta_{\rm HL}$  for the monomer and dimer are larger than the experimentally reported<sup>31</sup> values of 5.97 and 4.49 eV, respectively. This is to be expected for small molecules as one of the deficiencies of DFT. Figure 3(a) illustrates the binding energy per monomer of singlet states of *n*-Py showing a sharp increase for small chains and a slow asymptotic behavior for large chains toward the limiting energy of an infinite chain of -57.17 eV/monomer. Figure 3(b) is a plot of  $\Delta_{\rm HL}$  showing a sharp decrease as short oligomers increase the number of monomers. A slow asymptotic trend of  $\Delta_{\rm HL}$  toward the experimental energy gap of 3.2 eV (Ref. 32) is apparent as oligomers with 15 or more monomers increase in length.

The dependence on the oligomer chain length of both the radius of gyration  $R_g$  (average distance squared of monomers from the oligomer center of mass) and the end-to-end distance  $d_{\text{end-end}}$  are depicted in Figs. 3(c) and 3(d). As expected based on the bent conformations shown in Fig. 2, the radius of gyration as a function of chain length [solid line in Fig. 3(c)] increases less rapidly than  $R_g$  of planar chains [dashed line in Fig. 3(c)]. Accordingly, the end-to-end distance is dramatically shorter [solid line in Fig. 3(d)] than that in planar chains [dashed line in Fig. 3(c)]. In the triplet state [triangles in Figs. 3(c) and 3(d)], both  $R_g$  and  $d_{\text{end-end}}$  are closer to the planar chain values.

![](_page_132_Figure_9.jpeg)

FIG. 3. Properties of reduced *n*-Py oligomers as a function of the number of monomers. (a) Binding energy per monomer, (b) HOMO-LUMO energy gap, (c) radius of gyration, and (d) end-to-end distance.

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![](_page_133_Figure_1.jpeg)

FIG. 4. Distribution of bond lengths and bond orders along the backbone of reduced and oxidized 12-Py. Arrows mark the position of the C—C interring bonds.

The C—C bond length as a function of the C—C position in the 12-Py chain is depicted in the left top panel of Fig. 4 as an example of the oligomer benzenoid chains. The numbering of C—C bonds is sequential, starting with the double bond at one of the two chain ends. Arrows point to inter-ring C—C bonds. The Wiberg bond index<sup>33,34</sup> was calculated for the C—C bonds along the *n*-Py chain with results for 12-Py depicted in Fig. 4 (right top panel). There is a clear correlation between the bond length and bond order, reinforcing the expectation that intermonomer C—C single bonds are longer than the intramonomer C—C single bonds and have a substantially lower bond order. Additionally, the two end monomers in the oligomers display shorter C—C double bonds with higher bond orders.

The vibrational normal mode frequencies of the ground state and their IR-active intensities for *n*-Py (n=3-6, 9, and 12) are shown in the Appendix (Fig. 8). These spectra correspond to the equilibrium structures shown in Fig. 2. IR active frequencies of *n*-Py are predominantly distributed in two spectral regions: 700–1600 and 3000–4000 cm<sup>-1</sup>. The far IR region is associated with motions involving several atoms in each ring, whereas most C—H and N—H stretching modes are in the near IR region. These vibrational spectra indicate that the two IR spectral regions are not sensitive to the size of the oligomer. Hence, reduced *n*-Py with different *n* have very similar vibrational spectra. As expected, the intensity of modes in these two spectral regions increases as the oligomer size increases.

#### IV. STRUCTURE AND ENERGETICS OF OXIDIZED *n*-Py OLIGOMERS

A thorough conformational optimization was implemented for positively charged *n*-Py oligomers as a function J. Chem. Phys. 129, 164903 (2008)

of the sustained positive charge Q. For these charged oligomers, ground states are doublets or singlets depending on Q being odd or even. The positive charge distributions for different degrees of oxidation are based on the Mulliken analysis of the geometry-optimized ground state wave function of each oligomer. For oxidized *n*-Py, the torsion angle is gradually increased from 153° as more positive charge Q is added to the backbone until the angle reaches 180° (planar chain) when the ratio  $Q/n \ge 1/3$ . For Q/n below 1/3, the *n*-Py oligomers may have out-of-plane structures with torsion angles other than 180° between them. Although not systematic, a study was carried out for these twisted oxidized *n*-Py configurations. Results indicate that out-of-plane backbones lead to oxidized *n*-Py isomers with high binding energies, which in several cases are saddles of the energy landscape.

The findings in this work show that high level oxidized *n*-Py  $(Q/n \ge 1/3)$  even-membered oligomers display a  $C_{2h}$ symmetry and odd-membered oligomers display a  $C_{2v}$  symmetry. However, low level oxidized oligomers (Q/n < 1/3)are bent with a smaller curvature than in neutral oligomers. For example 12-Py<sup>6+</sup> and 12-Py<sup>4+</sup> are planar with no puckering between the nearest neighbor rings, whereas in 12-Py<sup>2+</sup> the torsion angle is increased from 153° (see Fig. 2) to 169°, as shown in Fig. 5. The effects of the increased oxidation level on the binding energy of oxidized oligomers (referred to the neutral) is summarized in Table IV (columns 6 and up). The effect of the increased oxidation level on the single/ double C-C bond lengths and bond order structures is illustrated in Fig. 4. When *n*-Py is incipiently oxidized (Q/n)< 1/3), the benzenoid conjugation of reduced *n*-Py is partly replaced with incipient trends of the quinoid structure. For example, in 12-Py<sup>2+</sup> the benzenoid conjugation is still predominant, with inter-ring C-C single bonds being shorter and with C-C double bonds being expanded. However, as the ratio Q/n becomes  $Q/n \ge 1/3$ , then regions of quinoid alternation become clear. These quinoid regions span three monomers, as shown in Fig. 4 for 12-Py4+ and 12-Py6+. Two of quinoid regions are visible in 12-Py4+, indicating that the positive charge localized on each of these regions is +2e. In the case of 12-Py6+, there are three quinoid regions, and again each region localizes a +2e charge. If the charge is

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FIG. 5. (Color) Optimized structures of oxidized 12-Py<sup>m+</sup> (m=2, 3, and 4) and 15-Py<sup>m+</sup> (m=3, 4, and 5).

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164903-7 *n*-pyrrole oligomers

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FIG. 6. Distribution of charge per monomer along the backbone of oxidized 12-Py. (a) Various oxidation levels and (b) charge localization due to dopants.

increased further as in 12-Py<sup>8+</sup>, then the extent of the +2*e* charge localization is shorter, barely covering two monomers. The energy of oxidized oligomers increases linearly by 0.92 eV/(+*e*). The vibrational spectra of oxidized *n*-Py are similar to the neutral spectra, with the exception that frequencies in the 700–1600 cm<sup>-1</sup> are two orders of magnitude more intense.

The conformational dependence on oxidation level findings is confirmed by analyzing the distribution of charge per monomer along the chain. Based on the Mulliken population analysis, the total charge on each monomer shows an increasing degree of localization in multiple regions of the chain as the oxidation level is increased. This effect is depicted in Fig. 6(a) showing two regions of localization in 12-Py<sup>4+</sup>, three regions in 12-Py<sup>6+</sup>, and four regions in 12-Py<sup>8+</sup>. The charge localization takes place in multiples of +2*e*, which could be identified with the bipolaron.<sup>17-19</sup> Electron conduction then would take place by charge hopping between these localized regions.

Oxidation is attained experimentally with dopants. Typical oxidizing dopants include iodine, arsenic pentachloride, iron (III) chloride, and NOPF<sub>6</sub>, which are electronegative compounds. A rough simulation of the effects of doping can be calculated within the hybrid DFT methodology used in this work by placing close to the chains high electron affinity atoms such as fluorine. The localization of positive charge will then take place around the positions where these electronegative atoms are located. In 12-Py, for example, if several F atoms are located symmetrically above and below the planar chain at three or four backbone positions where charge is peaked in Fig. 6(a), then oxidation takes place, yielding 12-Py<sup>+6</sup> or 12-Py<sup>+8</sup>. As shown in Fig. 6(b), negative charge is transferred from Py atoms at these backbone positions to the fluorine atoms.

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![](_page_134_Figure_7.jpeg)

FIG. 7. Electronic band structure of infinite chains of reduced and oxidized PPy.

The oxidation level influences the HOMO-LUMO energy gap in n-Py. The calculated energy gap for reduced 12-Py is 3.36 eV, in agreement with the experimental<sup>32</sup> value of 3.2 eV for bulk PPy. Additionally, for every +2e acquired by the oligomer upon oxidation, there is one localized state created in the gap. For 12-Py, upon oxidation the HOMO-LUMO gap decreases from 3.36 eV to 0.29, 0.73, 0.95, or 1.04 eV for every +2e increase in the oxidation level. For oxidation levels where Q/n < 1/3, the positive charge is delocalized along the backbone carbon atoms, and the new state created in the energy gap is close in energy to the HOMO. However, as oxidation reaches Q/n=1/3, charge localization occurs, and this effect results in level repulsion between the HOMO and the gap-localized states. For infinite PPy, these gap-localized states form a band, which may eventually overlap the valence band for the polymer to be conducting.

#### V. PPy INFINITE CHAIN

The electronic band structure of infinite chains was studied within the same hybrid DFT approach. For reduced PPy, a  $C_{2v}$  planar four-monomer chain was used in the unit cell of the periodic array. Figure 7 shows 16 bands around the Fermi energy, with all energies relative to the Fermi energy located at zero. Each band contains 80 k-points. The Fermi energy was determined as that energy for which the sum of the Fermi functions associated with each of the eigenvalues composing the bands was equal to the number of electrons. The energy band gap of the reduced PPy is 3.17 eV, which is in excellent agreement with the experimental value of 3.2 eV. Two oxidation levels of PPy were considered. For +1e oxidation, the PPy was obtained by placing two F atoms 2.2 Å away from the center of a monomer in the unit cell, one above and one below. For +2e oxidation, two  $F_2$  dimers were placed in similar locations. The localized new band due to the charge is mainly an extended *p*-band formed by the carbon p-orbitals perpendicular to the plane of the monomers. The energy band gap shows a marked dependence with the oxidation level, decreasing from 1.78 eV for +1e to 0.57 eV for +2e. Although fluorine is a strong electronegative element, because the dopants were placed far

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away from the monomers, we did not fully attain a  $\pm 1e$  or  $\pm 2e$  charge transfer with either two F or two F<sub>2</sub>, but rather  $\pm 1.08e$  and  $\pm 1.48e$  were obtained. For this reason, as seen in Fig. 7, the Fermi energy is still in the band gap and the valance band does not merge or cross the new localized band as expected in a conductor material. Increasing the basis set size to include diffuse *d*-functions does not change significantly the band structure shown in Fig. 7.

#### **VI. CONCLUSION**

In summary, this is an exhaustive set of structural and energetic results for *n*-Py oligomers (n=1-24) in both the reduced and oxidized phases. Outstanding features of the reduced oligomers are their notoriously bent spatial conformations, which result in strong reductions in their radius of gyration and end-to-end distance as compared to planar oligomers. As a result of oxidation (charge Q), these oligomers become increasingly planar until the critical value of Q/n=1/3 yields an oxidation level in which the oligomers are planar. This critical oxidation level is also accompanied by a spatial localization of positive charge, which is usually referred to as a polaron. Below the critical value, the oxidized oligomers present a delocalized positive charge distributed along the oligomer backbone C atoms. The vibrational spectra of n-Py oligomers display two fairly size-insensitive IR spectral regions at 700-1600 and 3000-4000 cm<sup>-1</sup>, which only change slightly with oxidation. As expected, if in the proximity of n-Py several electronegative dopants are included in the calculation, Q localizes in the neighborhood of the dopant and one localized state in the HOMO-LUMO gap appears for every +2e in the oxidation level. The energy band gap of infinite PPy is in excellent agreement with experiment. Additionally, the trend of a decreasing band gap with increasing oxidation level is clearly demonstrated.

Altogether, this study provides a comprehensive and complete compendium of the effects that reduction-oxidation changes produce in the electronic structure, conformation, energetics, and vibrational spectra on *n*-Py and infinite PPy chains.

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#### **APPENDIX: VIBRATIONAL ANALYSIS**

The vibrational normal mode frequencies of the ground state and their IR-active intensities for *n*-Py (n=3-6, 9, and 12) are shown in Fig. 8.

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![](_page_135_Figure_10.jpeg)

FIG. 8. IR-active vibrational spectra of reduced n-Py (n=3, 4, 5, 6, 9, and 12).

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# Curriculum Vitae

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Yafei Dai, Estela Blaisten-Barojas, "Density Functional Study of the Photodetachment Spectra of Zinc and Calcium Cluster Anions", American Physical Society March Meeting, New Orleans, LA, March 2008

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