COMPUTATIONAL STUDIES OF BONDING AND PHOSPHORESCENT PROPERTIES OF
GROUP 12 OLIGOMERS AND EXTENDED EXCIMERS

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Density functional (χα, BLYP, BPW91, B3LYP and B3PW91), MP2 and CCSD(T) methods in combination with LANL2DZ or cc-pVxZ-PP (where x=D(double), T(triple) Q(quadruple), and 5 quintuple) basis sets have been employed in computing electronic transition energies of zinc and cadmium monomers. CCSD(T)/aug-cc-pV5Z-PP combination finds values that are 150 cm⁻¹ from the experimental value for the zinc monomer and 240 cm⁻¹ remove from the cadmium monomer excitation experimental value. These method/basis set combinations are also used to find spectroscopic values (r_e, D_e, ω_e, ω_εx_e, B_e, and T_e) that rival experimental values for dimers and excimers. Examples of this can be seen with the CCSD(T)/aug-cc-pV5Z-PP combination phosphorescent emission results. The values found are within 120 cm⁻¹ of the zinc emission energy and 290 cm⁻¹ of the cadmium emission energy. While this combination rigorously models spectroscopic constants for monomers, dimers, and excimers, it does not efficiently model these constants for larger clusters with available modern computational resources. It is important to show spectroscopic trends (bonding, phosphorescent excitation and emissions) as clusters increase as the monomer and dimer emission energies do not model solid state metalophilic interactions and phosphorescence. The MP2/LANL2DZ combinations show qualitative cooperative bonding trends in group oligomers and extended excimers as size increases and shape
change. Changes in excitation and emission energies are also shown as a function of size and shape of the clusters.
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CHAPTER 1
MODELING BONDING AND PHOSPHORESCENT PROPERTIES IN GROUP 12 MONOMERS, DIMERS AND EXCIMERS

1.1 Introduction

According to molecular orbital (MO) theory, closed shell systems, such as the group 12 $d^{10}s^2$ dimers, should not have interactions other than van der Waals forces. However, many experimental and theoretical studies have found interaction which are stronger than van der Waals interactions (typical $D_e$ of less than $10^2$ cm$^{-1}$) can occur in the ground state of closed shell metal complexes.\textsuperscript{1} Closed-shell interactions which are stronger than van der Waals forces also have been shown to be important in recent studies of noble gas complexes.\textsuperscript{2} Several theories have been made as to why zinc and cadmium dimers should have stronger than expected bonding. Hoffmann has suggested hybridization of $s$, $p$, and $d$ orbitals may be the cause as to why these interactions may be stronger than expected.\textsuperscript{3} Another manner of looking at these interactions has been proposed by Pyykkö, who suggests that hybridization alone cannot be the ultimate reasoning behind the greater interaction strength. Relativistic effects cause the $s$ orbital to expand while the $p$ and $d$ orbitals contract causing greater correlation of the electrons and, thus, increases the interaction, commonly referred to as metallophic interactions, between these metals atoms. Pyykkö concludes that scalar relativistic effects cause these interactions to be stronger than what is to be expected by van der Waals interactions alone.\textsuperscript{4}
Two criteria which are important in defining metallophilic interactions are bond length and dissociation energy. These criteria must be modeled free of method error and remain systematic independent of system size to show strength is from metallophillic interactions. It is therefore important to utilize a computational approach that is able to describe these properties within chemical accuracy (defined as 0.01 Å for $r_{e}$, 350 cm$^{-1}$ for $D_e$ and 2000 cm$^{-1}$ for electronic transitions) while balancing memory and disk space requirements of modern computers, so as to make these computations feasible for larger systems. Rigorous characterization of spectroscopic constants of zinc and cadmium monomer and dimers will also allow for an improved knowledge of group 12 species. Establishing a systematic computational approach that can provide accurate spectra and better understanding of molecular interactions will enable improved design using similar group 12 complexes in several areas including photonics (LEDs and LASER materials), telecommunications, photocatalysts, environmental sensors, optical writing, photo magnetic switches, DNA photocleavage agents, probes in biological systems, and various conducting and semiconducting applications.$^5$

Many previous studies have found closed shell transition metal complexes to have interesting photophysical properties such as bright phosphorescence bands with rather large Stokes shifts assigned to metal-metal bonded excimers and exciplexes.$^6-^{16}$ These properties indicate a significant change in geometry from the ground electronic state to the low-lying phosphorescent excited state. As shown in Chart 1.1, an electron from the $\sigma^*$ antibonding orbital is excited either to a $\sigma$ bonding orbital giving rise to the $^{3}\Sigma^{+}_{u}$ state, according to the Russell-Saunders notation, or to a
π bonding orbital, resulting in the $^3 \Pi_g$ state. The transfer causes the bonding to change from a weak metallophilic interaction to a covalent bond. Going down group 12 from Zn to Hg, modeling bonding strengths and phosphorescent trends in both ground and low lying excited states assist in the understanding of elemental size trends and increased relativistic effects.\textsuperscript{17}

Chart 1.1. Qualitative MO diagram for zinc and cadmium dimer.
Many previous studies from the 1970s through the 1990s investigated the zinc and cadmium dimer bonding and spectroscopy in the ground state and the excited state with highest levels of methods feasible. The computing resources of the time, however, largely limited these calculations to that made greater approximations than is necessary in modern studies. In 2005, Gropen and coworkers performed an investigation of the ground and excited states of the zinc dimer. While this study has used high level methods such as (CISD) that included spin orbit coupling, small DZ level basis sets are employed to compute the spectroscopic values. Recent improvements in computing power and the development of the correlation consistent basis sets for group 12 metals has allowed for computations of spectroscopic constants such as $r_e$, $D_e$, $\omega_e$, $\omega_e\chi_e$, and $B_e$ that closely resemble experimental values. The investigations of both Peterson and Puzzarini and Yu and Dolg provided accurate ground state bonding constants for the zinc and cadmium dimers using CCSD(T). These studies were, however, limited to the ground state.

Recently, a study by Omary et al., reported a study that accessed various computational treatments in predicting photophysical and molecular spectroscopic parameters. Another Omary group study also reported an experimental/computational study in which computations a priori have predicted tuning of ligand-containing gold-phosphine complexes to achieve blue phosphorescence (which was verified experimentally in the same study). Encouraged by the results obtained by Omary et al., this study seeks to provide spectroscopic constants that rival experiment results for electronic, vibrational, and rotational transitions for zinc and cadmium
monomers and dimers as well as $r_e$ for dimers for both the ground state and low-lying excited states. Results for the zinc and cadmium elements should have greater agreement with experimental values than previous studies of mercury elements when using computations that do not include spin-orbit coupling.\textsuperscript{34,36} The j-j coupling scheme in the $^3P$ states of the monomers is shown in Chart 1.2, showing states in the presence and absence of spin-orbit coupling.

Chart 1.2. Atomic state splitting with (left side) and without (right side) LS coupling.

Spin-orbit coupling increases down the group and thus, individual sub-states have a larger SO-splitting energy. As a result of this weak but important coupling in the monomers, the forbidden transition of $^1S \rightarrow ^3P$ becomes more allowed through the mixing of $^1P$ and $^3P$ states.\textsuperscript{30} It can also be seen that the greater amount of mixing of the $^1P$ and $^3P$ Cd and Hg monomers causes a greater lowering of the $^3P_1$ sub-state than is seen in the Zn monomer. An error arises in results from using computations that do not model the spin-orbit coupling. Spin-orbit coupling effects become greater down a
group and thus this should affect cadmium results more so than the zinc results. As a result zinc results should more closely resemble the experimental results, even in the absence of spin-orbit coupling effects modeled in previous studies.\textsuperscript{25,31}

1.2 Computational Methods

Closed shell ground states were treated by using coupled cluster with single, double and perturbative triple excitations (CCSD(T))\textsuperscript{32} and second order Møller-Plesset perturbation theory (MP2).\textsuperscript{33} Closed shell interactions such as van der Waals or metallophilic interactions are not well-described by conventional density functional theory (DFT) due to the inability of these methods to properly treat long range electron correlation effects. DFT methods were only employed for excited state computations.\textsuperscript{34} The relevant low-lying paramagnetic excited state dimers and monomers were described with CCSD(T) and MP2, as well as density functional theory, using two GGA methods (BLYP, BPW91), two hybrid methods (B3LYP and B3PW91) and an exchange only method ($\chi\alpha$, (0.7$S$)).\textsuperscript{35-39}

Scalar relativistic effects were included through the use of relativistic electron core potentials (RECP) to represent core electrons and were not treated explicitly. The ECP replaces chemically inactive core electrons with a pseudopotential, allowing the basis sets for the transition metals to only explicitly treat the outermost electrons and enabling a more computationally cost effective computation. The closed shell computations were treated with spin-restricted and pure singlet wave functions. Triplet excited states were treated with a restricted-open shell Hartree-Fock (ROHF) wave function within RMP2 and RCCSD(T) methods. In DFT methods, the unrestricted Kohn-
Sham (UKS) functional was implemented. All calculations were performed using the MOLPRO quantum chemistry package.\textsuperscript{40}

Three types of effective core potential (ECP) and basis set combinations were used in this work. The first combination, commonly referred to as LANL2DZ, employs a double-$\zeta$ (DZ) contracted Gaussian-type orbital (CGTO) basis set that treats only $3d$ and $4s$ electrons explicitly for the zinc atom or $4d$ and $5s$ electrons in the case of the cadmium atom. The core electrons are modeled by the use of an ECP. These basis sets were developed by Hay and Wadt.\textsuperscript{41} The second set of basis set/ECP combinations are the correlation consistent (cc) series of CTGO basis sets. These basis sets abbreviated, as cc-pVxZ-PP or aug-cc-pVxZ-PP (where $x=$D (2), T (3), Q (4) and 5), were developed by Peterson and Puzzarini.\textsuperscript{26} The aug-cc-pVxZ-PP basis sets treats $3s$, $3p$, $4s$ and $3d$ electrons explicitly for zinc or $4s$, $4p$, $5s$ and $4d$ electrons for cadmium. The core is treated with the ECP developed by the Stuttgart group.\textsuperscript{42} The complete basis set (CBS) limit is approximated by use of the Feller extrapolation\textsuperscript{43} given by:

\begin{equation}
E(n) = E(\infty) + Ae^{-Bn}, \quad (1)
\end{equation}

where $n$ is zeta level and $A$ and $B$ are fitting parameters. At the CBS limit, the remaining error is from the choice of the computational method and allows for a direct comparison of methods to be made. This extrapolation will allow for an improved insight into how the approximations made in these methods affect the prediction of spectral data for these closed shell systems.\textsuperscript{44} The third basis set/ECP combination also uses the same Stuttgart ECP as the correlation consistent basis sets mentioned above. This set, referred to as the Stuttgart basis set in this investigation, however, uses a
basis set that has also been developed by the Stuttgart group. This basis set is approximately equivalent to an augmented valence triple-ζ quality CGTO basis set. This basis set has been included in this work for the sake of comparison of the correlation consistent basis set to a non-correlation consistent basis set with a comparative ECP.

The absorptions and emissions were computed using the Franck-Condon transition, a vertical transition between the singlet gerade \( (1\Sigma^+_g) \) ground state and the two lowest lying triplet excited (the forbidden \( 3\Pi_g \) and the allowed \( 3\Sigma^+_u \)) states. The absorptions were found using the vertical transition at the optimized singlet \( r_e \), while the emissions were calculated using the vertical transition at the optimized triplet \( r_e \). Vibrational and rotational spectral constants were taken from the Dunham analysis, taking 7-9 single point calculations around the \( r_e \).\(^45\) The Dunham analysis was also performed with counterpoise corrected points to eliminate any artifacts of basis set superposition error (BSSE).\(^46\) The BSSE arises from over-description of the molecule relative to the molecular fragments. To correct for this effect the BSSE energy is subtracted from the molecular energy. The BSSE energy is given by:

\[
\Delta E_{CP}(R) = E_{AB} - E_{A}^{\{AB\}} - E_{B}^{\{AB\}}, \quad (2)
\]

where \( R \) represents distance between A and B, \( E_{AB} \) represents the energy of the complex and \( E_{A}^{\{AB\}} \) represents the energy of fragment A in the presence of the basis sets for both the A and B fragments.
1.3 Results and Discussion

1.3.1 Monomers

The study of zinc and cadmium monomers will be used to gauge the accuracy of methods and ECP/basis set combination in the prediction of ground and excited state energies as well as show periodic trends before moving onto bonding and spectroscopic trends of group 12 dimers. The monomer transitions have been computed with \textit{ab initio} and DFT methods paired with the three ECP/basis combinations mentioned in the methods section.

From Figures 1.1-1.3, as well as excitation energies obtained for Hg by Omary \textit{et. al.}, the importance of the basis set and ECP used to obtain results can be observed.\textsuperscript{25} As Figure 1.1 suggests, zinc and cadmium monomer excitation energies ($T_e$) computed with the LANL2DZ basis set are not within chemical accuracy with the exception of B3LYP. The B3LYP/LANL2DZ combination results in an excitation that is only 80 cm\textsuperscript{-1} away from the experimental excitation value. It can also be noted the combination of CCSD(T)/LANL2DZ does not provide results within chemical accuracy. While CCSD(T) tends to find excitation energies that are more accurate than B3LYP for transition metals, the underestimation of the excitation energy due to the use of the LANL2DZ basis set along with the overestimation of B3LYP for the excitation energy results in an energy that is very close to the experiment due to cancellation of errors. The larger ECP of LANL2DZ, with all of the method except B3LYP is seen to have energies that are farther from experiment than is the case of the smaller Stuttgart ECP. The use of the smaller ECP of the Stuttgart predicts excitation energies ($T_e$) that are
within chemical accuracy with the use of MP2 (1240 cm\(^{-1}\) from experimental zinc excitation) and CCSD(T) (220 cm\(^{-1}\) from experimental zinc excitation) methods with little extra computational cost.

Figure 1.1. Zinc atomic excitation energies computed with LANL2DZ and Stuttgart type basis sets.
Figure 1.2. Zinc atomic excitation energies with selected basis sets.
Comparing the $T_e$ computed with the Stuttgart basis set to $T_e$ computed the correlation consistent basis sets shows the importance of extrapolating energies to the complete basis set (CBS) limit. While the Stuttgart basis set gives ($T_e$) that are within chemical accuracy, energies obtained using aug-cc-pVxZ-PP basis sets are closer to experimental values at the CBS limit. At the CBS limits, the $T_e$ are 840 cm$^{-1}$ of the experimental value at the MP2 level of theory and are within 150 cm$^{-1}$ of the experimental value for CCSD(T). Note that while using a basis set of at least triple-$\zeta$ level in combination with DFT methods, $T_e$ that are within chemical accuracy are
obtained. For example, the $\chi\alpha$/aug-cc-pvTz-PP $T_e$ of the zinc monomer is 1790 cm$^{-1}$ from experiment, the BPW91/aug-cc-pvTz-PP excitation for zinc monomer is 1020 cm$^{-1}$ from experiment, and B3PW91/aug-cc-pvTz-PP excitation for zinc monomer is 390 cm$^{-1}$ from experiment. Excitation energies computed with DFT methods do not necessarily show convergence towards a limit as it generally known that DFT does not systematically improve with increasing basis set size.$^{47}$

The importance of extrapolation to the CBS limit is also illustrated in Figures 1.2 and 1.3. The $T_e$ for the cadmium monomer using the MP2 method along with the aug-cc-pVDZ-PP basis set results in a transition energy that is only 150 cm$^{-1}$ from the experimental value. While MP2 overestimates the transition energy at the CBS limit, the aug-cc-pVDZ-PP underestimates the transition energy and the estimation errors are canceled to create a result that appears close to the experimental value for the wrong reasons, a result commonly referred to as a Pauling point. Upon extrapolation to the CBS limit the results of MP2 are actually 1100 cm$^{-1}$ away from the experimental value, a result that is still within chemical accuracy but farther from the experimental value then the smaller aug-cc-pVDZ-PP basis set.

$T_e$ obtained with the smaller Stuttgart ECP with at least a triple-$\zeta$ level basis set in combination with CCSD(T) are within several hundred cm$^{-1}$ for all group 12 monomers. These results establish the importance of a reasonably-sized ECP, such as the Stuttgart ECP, in evaluating the transition energies of these monomers. $T_e$ computed with larger sized ECP, such as that in the case of the LANL2DZ basis set,
both in this study and in previous work fail to produce excitation energies within chemical accuracy.

Extrapolated CBS limit values using either MP2 or CCSD(T) methods and both augmented and nonaugmented series of correlation consistent basis sets are well within the limit of chemical accuracy for transitions. At the CBS limit, excitations computed with the CCSD(T) method are closer to experiment, only 240 cm\(^{-1}\) for the cadmium dimer, versus 1100 cm\(^{-1}\) from the experimental value computed with the MP2 method. Excitations computed with the CCSD(T) method are within \(~200\) cm\(^{-1}\) of experimental values for both zinc and cadmium systems.

DFT methods finds values for the monomer transition energies that are also within chemical accuracy but at a fraction of the computational cost compared to MP2 and CCSD(T). The choice of functional proves to be fairly influential on the excitation energy. Results with the \(\chi_{\alpha}\) functional show chemically accurate \(T_e\) for only a few selective basis sets, for example the cadmium monomer is 1030 cm\(^{-1}\) away from the experimental value while the zinc monomer excitation is 2250 cm\(^{-1}\) away from experimental value. \(T_e\) for zinc and cadmium are not close to experimental when using the LYP functional. For example use of BLYP/aug-cc-pV5z-pp results in a \(T_e\) which 3650 cm\(^{-1}\) away from the zinc experimental value and 3590 cm\(^{-1}\) away from the value for the cadmium experimental value. \(T_e\) computed with either DFT methods using PW91 correlation methods results that compare well with experimental energies when used in combination with correlation basis sets of at least triple-\(\zeta\) level quality. Inclusion of exact exchange as in the case of the hybrid methods can be seen to have an important
effect in achieving excitation energies comparable to experiment. The B3PW91 method is found to be the most accurate DFT method for both zinc and cadmium monomer Te, being within ~600 cm\(^{-1}\) of experimental values.

1.3.2 Equilibrium Geometries of Dimers

Bonding in group 12 ground state dimers is seen to be caused by weak metallophilic interactions. Potential energy curves for the ground states of these molecules show very shallow minima due to electron correlation enhanced by relativistic effects. It is therefore extremely important to use methods capable of showing long range correlation effects as well as using basis sets that properly treat relativistic effects. While post Hartree-Fock \textit{ab initio} methods, such as MP2 and CCSD(T) are capable of properly describing long range electron correlation, previous papers have failed to show evidence that commonly used DFT methods can accurately account for electron correlations influence in weak dispersion type interactions such as metallophic bonding. These previous studies have observed DFT to find repulsive curves for molecules with dispersion force interaction.\(^{48}\)

Several recent investigations, however, have indicated that certain DFT methods, such as \(\chi\alpha\) may be able to account for the interactions.\(^{49,50}\) This current study has thus evaluated both \textit{ab initio} methods and DFT methods for ground state interactions using the ECP/basis set combinations mentioned in the methods section to evaluate these methods at a variety of levels. In the tables, methods showing repulsive curves for these ground state interactions are represented by dashes indicating the inability of a
method to show bonding interactions. χα has indeed shown an ability to model weak metallophilic interactions, as shown for the zinc and cadmium dimer \( r_e \) 3.719 Å and 3.956 with aug-cc-pV5Z-PP, respectively.

### Table 1.1. Zinc dimer counterpoise corrected bond distance \( (r_e) \) and dissociation energy \( (D_e) \) values.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis Set</th>
<th>( 1\Sigma_g^+ ) ( r_e (\text{Å}) )</th>
<th>( 2\Sigma_u^+ ) ( D_e (\text{cm}^{-1}) )</th>
<th>( 3\Sigma_u^+ ) ( r_e (\text{Å}) )</th>
<th>( 3\Pi_u ) ( D_e (\text{cm}^{-1}) )</th>
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<td>LANL2DZ</td>
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<td>2.7154</td>
<td>4553.3</td>
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<td>205.3</td>
<td>2.4730</td>
<td>9046.3</td>
</tr>
<tr>
<td></td>
<td>aug-cc-pVDZ-PP</td>
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Table 1.2. Cadmium dimer counterpoise corrected bond distance ($r_e$) and dissociation energy ($D_e$) values.

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The level of basis set used for these interactions, along with the amount of BSSE inherent to these basis sets can be very influential on bond length and dissociation energy. For example, before accounting for BSSE, CCSD(T)/LANL2DZ in bond lengths of 4.673 Å and 4.121 Å, respectively for the zinc and cadmium dimers. Having corrected for the BSSE effect, the CCSD(T)/LANL2DZ combination is shown to have a very limited ability to describe metallophilic interactions in the ground state zinc and cadmium dimers, resulting in bond lengths of 5.201 Å for the zinc dimer and 5.321 Å for the cadmium dimer, results that are over an angstrom longer than the experimental results.
The importance of BSSE correction can also be noted in the convergence of bond lengths and other spectral properties with respect to increasing basis set size. When these properties are uncorrected smooth convergence to the CBS limit does not occur. However, upon BSSE correction, convergence to the limit does occur. The reason for this comes from smaller, more incomplete basis sets appearing to show greater effects from BSSE. This will cause smaller basis sets to appear closer to the CBS limit when uncorrected.\(^{52}\)

Upon correction for BSSE effects, extrapolation to the CBS limit can be used to determine an appropriate method for modeling the ground state dimer. It is shown that dimers computed with the MP2 method estimate bond lengths that are too short. For example, using the aug-cc-pV5Z-PP basis set the computed \(r_e\) value for \(\text{Zn}_2\) is 3.539 Å versus the experimental value of 4.19 Å, and dissociation energy is higher than expected, computing a value of 413 cm\(^{-1}\) compared to the experimental value of 279 cm\(^{-1}\). The underestimation of bond lengths and overestimation of dissociation energies when using MP2 has been previously shown in other studies of dispersion type interactions.\(^{52}\)

Results by Peterson and Puzzarini using the CCSD(T) method and cc-pVxZ-PP basis sets for the ground state zinc and cadmium dimers also show bond lengths that are noticeably shorter than those from experiment, finding a value of 3.913 Å for the \(\text{Zn}_2\) \(r_e\) in comparison to the longer experimental value 4.19 Å. The BSSE corrected CCSD(T)/aug-cc-pV5Z-PP combination also computes a lower dissociation energy (193 cm\(^{-1}\)) than the experimental values (279 cm\(^{-1}\)). It is noted by Peterson and Puzzarini
that the bond lengths between their study and the experiment may differ due to the experiment’s treatment of the spectral data as pure van der Waals interactions instead of as stronger metallophilic interactions. This treatment will lead to bond lengths that are longer than should be expected for true metallophilic bonding. The error in dissociation energy is unable to be determined at this time but is in line with other references. 26,52

Relativistic effects trends in bonding strength of the ground state dimers can be observed for these species. Calculations using any of the methods point to a stronger bond in the case of the cadmium dimer as compared to the zinc dimer. An example of this trend may be seen in the CCSD(T)/aug-cc-pV5Z-PP combination for the zinc dimer $D_e$ value of 193 cm$^{-1}$ compared to the cadmium dimer $D_e$ value of 297 cm$^{-1}$.

Upon photoexcitation of the dimer to low lying excited states the bonding is observed to significantly change from these weak metallophilic interactions to covalent type bonding. Examples of this can be seen in the zinc dimer bond lengths at the CCSD(T)/aug-cc-pV5Z-PP level; the ground state bond is 3.913 Å, while the excited states are covalently bonding, as seen by the shorter bond lengths of 2.508 Å for the $^3\Sigma_u$ excited state and 2.344 Å for the $^3\Pi_g$ excited state. For both zinc and cadmium dimers, low lying non-emissive $^3\Pi_g$ state has a larger increase in bonding than the low lying emissive $^3\Sigma_u^+$ states. The excitation will also lead to a substantial change in the dissociation energy as can be seen in the zinc dimer dissociation energies computed at the CCSD(T)/aug-cc-pV5Z-PP level. While the ground state is shows dissociation energies on the order of metallophilic bonding (193 cm$^{-1}$ and 297 cm$^{-1}$ for zinc and
cadmium dimers, respectively), the excited state dissociation energies are increase
covalent strength dissociation energies in both the \( ^3\Sigma_u^- \), (9475 cm\(^{-1}\) and 8436 cm\(^{-1}\) respectively) and the \( ^3\Pi_g \) (11371 cm\(^{-1}\) and 9777 cm\(^{-1}\), respectively).

While the bond length and dissociation energy for these low lying states of
mercury have been well classified by experiment, fewer accurate references for zinc and
cadmium bond lengths and dissociations exist.\(^{53-55}\) Those lengths that are found are
often given as bond lengths relative to the ground state or other excited states.
Experimental bond lengths, having been determined by fitting of vibrational frequencies
and are given as difference in length between \( ^3\Sigma_u^+ \) and \( ^3\Pi_g \) states. Comparing the
relative bond lengths of our calculated dimers show a good comparison to these
experimental numbers in the CCSD(T) and B3PW91 methods as long as basis sets of at
least triple-\( \zeta \) level are employed. The relative comparison for the zinc dimer
(\( \Delta r_e( ^3\Pi_g \rightarrow ^3\Sigma_u^+) \)) show good agreement with the experimental \( r_e \) value of 0.18 Å. The
CCSD(T)/aug-cc-pVTZ-PP combination results in a \( \Delta r_e \) 0.16 Å, while the B3PW91/aug-
cc-pVTZ-PP combination results in a value of 0.18 Å. The cadmium dimer \( \Delta r_e( ^3\Pi_g \rightarrow ^3\Sigma_u^+) \) also agrees well with the experimental \( \Delta r_e( ^3\Pi_g \rightarrow ^3\Sigma_u^+) \) value of 0.16 Å.
CCSD(T)/aug-cc-pVTZ-PP computes a \( \Delta r_e \) of 0.16 Å, and the B3PW91/aug-cc-pVTZ-PP
computes a \( \Delta r_e \) of 0.19 Å.

1.3.3 Excimer Phosphorescence

The methods that provide the best agreement between experiment and theory
for the zinc and cadmium monomer energies and for the dimer bond lengths and
dissociation energies also are useful in the description of absorptions and phosphorescent emissions for dimers. Though MP2 does provide absorptions and phosphorescent emission energies that are within what has often been consider to be within chemical accuracy (.25eV or 2000 cm\(^{-1}\)) the method does not perform as well as CCSD(T). For example, the zinc dimer emission computed with MP2/aug-cc-pV5Z-PP is 1070 cm\(^{-1}\) from experiment while CCSD(T)/aug-cc-pV5Z-PP is only 120 cm\(^{-1}\) from experimental.

Figure 1.4. Zinc dimer absorption and emission energies with selected basis sets.
Figure 1.5. Cadmium dimer absorption and emission energies with selected basis sets.
For absorption energies, both in this study and in previous studies, the conventional DFT methods show an inability to find accurate values for dispersion type interactions. DFT methods’ inability to optimize ground state geometries causes a need to use a value found in another manner. The MP2 and CCSD(T) methods may also have problems finding accurate absorption energies if computed ground state values are used to compute the transition. While these methods are capable of finding a minimum bond length for ground state dimers, the shallow potential found for the ground state causes there to be uncertainty in the ground state minimum bond lengths that will be used to compute the absorption energies. In the previous Omary et al. study of mercury clusters, these limitations led to the computations of absorptions at the experimental bond lengths. Encouraged by the achievement of chemically accurate absorptions in the previous Omary study, this study has utilized the same approach to finding the absorption energies.

Table 1.3. BSSE corrected spectra for emitting state for zinc dimers.

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| Literature Ref(51) | 30.66 | 21.10 | 9.56 |

† SS-Stokes Shift
BPW91 and B3PW91 show absorptions and emissions within chemical accuracy for both zinc and cadmium dimers. The other DFT methods using the LYP exchange or the S exchange ($\chi_\alpha$) compute absorption energies that do not agree with the experiment. B3PW91 demonstrates ability to find accurate absorption and emission energies for zinc dimers, being 1740 cm$^{-1}$ from the experimental absorption and 620 cm$^{-1}$ from the experimental emission.

Regardless of method choice, the LANL2DZ basis set does not find absorption or emission energies that agree with experiment stemming from an exorbitant ECP size. Improvement in all cases is seen upon implementation of basis sets employing the smaller Stuttgart ECP. Another point to note is that absorptions and emissions do not necessarily converge to a limit with respect to increases in the size of the correlation consistent basis set. While both the ground state and excited state energies can be seen to converge to a limit, the difference in energies between them may not converge due to the rate of which these states converge. If at least a triple-zeta level basis set is used in conjunction with CCSD(T), BPW91, or B3PW91 electronic transition energies that are within chemical accuracies also result. When comparing to the experimental data, the absorption and emission deviate further from experimental results as one goes down the group from Zn to Hg. An example of this can be seen in emission energies of zinc and cadmium computed at the aug-cc-pV5Z-PP level. While both within chemical accuracy, zinc is only 120 cm$^{-1}$ from the experimental value while cadmium is 290 cm$^{-1}$ from the experimental value. This should not be overly surprising
as the computational methods used do not include spin-orbit coupling. Zn, which is
affected the least by spin-orbital coupling, shows absorptions and emission agreeing
closest to experiment, while Hg, which is affected the most by spin-orbital coupling will
show the greatest amount of deviation from experiment. It is also important in the
case of all three dimers of the group to note the spin-orbit coupling in the electronic
transitions studied. While it is true that only \( \Delta S=0 \) spin state transitions are allowed,
these spin-orbital coupling effects cause mixing of states in the transition, allowing the
phosphorescence transition to become more allowed.\(^{57}\)

Large changes in geometry upon photoexcitation, such as those discussed
earlier, can also be quantified by changes in spectral properties such as the magnitude
of the Stokes shifts, and changes in the vibrational energies. It is important to be able
to accurately model these effects in the calculations. Stokes shifts are based upon a
difference between the excited state and the ground state, therefore the methods that
are able to describe both the excited state and ground state well are methods that are
most likely to provide Stokes shifts for both elements that are comparable to
experiment when using the CCSD(T)/aug-cc-pV5Z-PP combination, resulting in a
difference between computed and experiment of 480 cm\(^{-1}\) for zinc and 1370 cm\(^{-1}\) for
cadmium. The Stokes shift for the zinc dimer computed with MP2 and B3PW91 are
1564 cm\(^{-1}\) and 1062 cm\(^{-1}\), while the experiment is 1174 cm\(^{-1}\). The vibrational constants
are also well described by CCSD(T) and B3PW91 methods at the aug-cc-pV5Z-PP level.
The CCSD(T) result by Peterson to be 2 cm\(^{-1}\) from the experimental ground state
vibrational constant of 25.9 cm\(^{-1}\). As the \( ^3\Sigma_u^+ \) excited state bonding becomes covalently
bound, the experimental $\omega_e$ is seen to increase to 174±5 cm$^{-1}$. The computed values of $\omega_e$ are 191 cm$^{-1}$ with CCSD(T)/aug-cc-pV5Z-PP and 177 cm$^{-1}$ utilizing B3PW91/aug-cc-pV5Z-PP. Taking into account all spectroscopic constants, it is seen that CCSD(T) and B3PW91 methods result in closest agreement to the experimental values.

1.4 Conclusions

This study uses CCSD(T) levels of theory combined with CBS extrapolations in order to obtained more reliable theoretical bond lengths and spectral properties than have been previously calculated. Both the theoretical ground state and excited state values for bond lengths and spectra accurately reproduce experimental values. The results are seen to less be less accurate as spin orbit coupling increase. This effect is due to the neglect of spin orbit coupling. This increase however, is not so extreme as to warrant the dismissal of the theoretical spectral data, which is still close to experiment with respect to previous studies.
1.5 References


31 (a) Moore, C. E. *Atomic Energy Levels*; United States Dept of Commerce, National


CHAPTER 2

BONDING AND PHOSPHORESCENCE IN LINEAR, 2-DIMENSIONAL, AND 3-DIMENSIONAL OLIGOMERS AND EXCIMERS: COOPERATIVITY WITH METALLOPHILIC AND EXCIMERIC BONDING

2.1 Introduction

Chapter 1 studies show the ability to accurately model monomer and dimers. Studies on group 12 homonuclear monomers dimers provide excitations and emissions that are within 1000 cm\(^{-1}\) of experimental results when using coupled cluster singles, doubles and pertabative triples, (CCSD(T)), method in combination with the cc-pv5z-pp basis set.\(^1\),\(^2\) However, obtaining similar results for larger clusters becomes computationally challenging in both time and processor power.

Chapter 2 seeks to extend these results to larger clusters. Computational studies of bond distances\((r_e)\), bond dissociation energies\((D_e)\), excitation energy and phosphorescent emission energies of group 12 systems as a function of cluster size have been examined. These spectroscopic properties can vary greatly with metallophilicity as cluster size is increased. It is therefore important to model various cluster size as spectroscopic properties can vary with the aggregation of the atoms.\(^3\)\(^-\)\(^5\)

It has been shown that dimer computations can be used as a model for dilute solutions, but at increased concentrations and in solid state complexes that absorb and emit light at various wavelengths that are not well described by the dimer models.\(^3\)

In order to understand the photophysics of varying cluster sizes, it is first important to be able to model the progression in bond strength and geometry as the
number in the atoms are increased. There have previously been many studies have
modeled the electronic structures of the ground state of group 12 clusters as a function
of cluster size. 6-10 In small clusters, interactions are van der Waals type resulting in
an insulator type material. 11 As the number of atoms in the cluster increase, bond
strength changes from van der Waals type interactions to covalent type bonds and
eventually metal-metal interactions that are seen in bulk-systems of group 12 metals. 12
An estimation of whether bonding is van der Waals or covalent has been for clusters
ranging from 4-50 atoms. Many sources believe this transformation of bond strength
occurs due to a broadening of the atomic bandwidths allowing for an overlap of the s
and p orbitals, which allows for the covalent bonding to happen with an open orbital
space. As the overlap increases, the bond strength will increase and spectroscopic
properties will thus change as a result of this increased interactions. 13-15

The inability to agree on the exact cluster size where the bonding change occurs
may stem from attempts to find an absolute definition for bond strengths. Bonds are
often found to be a mix of several different bond types. Bond strengths in metal-metal
clusters have been observed to be cooperative in nature, thus the actual bond strength
does not change at just one point but occurs gradually as more atoms are added to the
clusters. 16

Interaction of the atom in the group 12 metal clusters may explain properties
such as magnetism, luminescence, atomic and electronic structures, and stability of the
electronically charged clusters. To better understand these properties, one must first
be able to accurately model the interactions of the atoms in the metal clusters. Previous
investigations have used high level quantum mechanic methods, such as CCSD(T) to for small molecules. The larger clusters are than modeled with semi-empirical methods that compare well with CCSD(T) results for small clusters. The accuracy of the larger clusters is therefore dependent on the ability of these approximations to estimate the rate of change in bonding as the cluster size increase. Another study performed by Kitamura used density functional theory (DFT) to model the cluster growth trends. While DFT can properly model the covalent and metallic bonding of the medium to large size metal clusters, studies have shown the difficulty overall that prior DFT methods can hance in describing long-range dispersion forces. A systematic approach to modeling the changes in the group 12 clusters structure and spectroscopy may be difficult with either of these approaches. This study will examine the use of MP2, which will allow both small and large clusters to be systematically compared.

To date, excited state complexes have not been studied to the same extent as the ground state structures. Triplet state structures may be more difficult to interpret based on the amount of cooperativity in the bond length alone. While the bond order of the ground state is equal to zero regardless of the number of atoms in the cluster, bond order in the triplet excited states varies with cluster size. For example the order is 1/2 for the dimer, 1/3 for the trimer, 1/4 for the tetramer, and so forth. Previous studies have shown cooperativity in the excited states of smaller mercury cluster by evaluating energies per individual bonds of excited states.

Excited states with higher than triplet spin (quintet) have also been studied previously by Wilson and coworkers. The cooperativity, absorptions and emission were
shown to be well modeled with the chosen treatment of MP2/LANL2DZ. This paper focuses on an accurate method for modeling the interactions of the ground and lowest-lying triplet excited states of $d^{10}s^2$ clusters. An ideal method should also be able accurately model clusters of different sizes and bond types in order to appropriately characterize the changes in bonding. While CCSD(T) can accurately model both dispersion and covalent bonding, the size of clusters modeled in this study makes CCSD(T) impractical. As stated above, DFT and semi-empirical methods may be accurate for larger clusters but may not systematically treat clusters of various size. Our previous studies have found MP2/LANL2DZ to be an appropriate model for smaller mercury clusters (up to 4 atoms). Encouraged by these results, this study has expanded the focus on larger clusters (up to 10 atoms) and also includes zinc and cadmium multinuclear systems.

A systematic approach will allow an evaluation of relativistic effects on structural development. In small clusters, mercury bonds have been shown to be the strongest, which is seen in both experimental and computational studies. The opposite trend, however, is seen in large sized clusters. This build up can be shown to be directly related to the s-p orbital interactions of the group 12 clusters. The p orbital contracts the most in the mercury when compared to other group 12 atoms, while the s expands the most. This causes there to be the most interaction in the s-p orbitals of the mercury. The mercury dimer therefore show the most amount of p orbital bonding. While this causes strength in the dimer bond, it hinders the bond strength for the 3-dimensional mercury structures. In contrast, the zinc clusters, which have bonding
mostly comprised of s orbitals interacting, have a large amount delocalization of
electronic density in 3-dimensional structures and bond strength increases readily.

This paper systematically addresses the structural and spectral differences of
M$_{2-10}$, where M=Zn, Cd, or Hg. Linear and 3-dimensional structures are examined, both
as a model of cooperativity and spectral constants as a result of linear aggregation of
closed-shell complexes, such as (RNC)AuCl, and as a model for both bond strengths
and electronics transition as the cluster changes from a linear to 3-dimensional
structure. Results show an ability to model the structural impact in these clusters, for
both the ground state and low-lying excited states and the limits of the aggregation of
the atoms of the clusters

2.2 Computational Methods

All computations in this study were carried out using the Gaussian program
suite. Computations were performed for Zn$_n$, Cd$_n$, and Hg$_n$ (where n=2-8 atoms)
species with linear, or D$_{∞h}$ symmetry. Several representative systems have also been
computed in linear and 3-dimensional structures to gain insight into structural effect of
bonding and spectroscopy. It is necessary to choose a method that models electron
correlation interactions in order to accurately describe the dispersion forces seen in the
ground state of these systems. The Møller-Plesset second order, MP2$^{23-25}$, method has
been found to be a qualitatively accurate method for these closed-shell systems by
Burda et. al.$^{26}$ and Wilson and coworkers.$^2$ This method has also been employed in this
study. Exciplexes have been model with restricted-open Møller-Plesset second order
(ROMP2) method. Importance of using ROMP2 instead of unrestricted Møller-Plesset second order.\textsuperscript{27}

A 12-electron ECP with double-\(\zeta\) (DZ) quality contracted Gaussian-type contracted orbital (CGTO) basis set, commonly referred to as LANL2DZ, was used in this work. The ECP and CTGO parameters have been developed by Hay and Wadt. In the case of each atom only the outside \(d^{10}s^2\) electrons are treated explicitly while the remaining electrons are represented by a pseudo-potential.\textsuperscript{28}

To ensure the cooperativity trends are not due to basis set superposition error (BSSE) several test calculations have been ran using counterpoise corrections. These calculations have been done for Zn\(_n\), Cd\(_n\) and Hg\(_n\) clusters with \(n=2, 4,\) and 7 atoms.

Frequency computations were also run to ensure the clusters were minima. While the linear structures are not necessarily global minima, the linear models may well represent the aggregation of closed-shell atoms in polymers and complexes. Only structures that were found to be global minima have been included in the results section unless denoted otherwise.

2.3 Results and Discussion

2.3.1 Bond Length

2.3.1.1 Ground State Bonding

As stated above in the methods section, the MP2 method has been chosen because this method accounts for electron correlation effects responsible for van der Waals type interactions seen in closed-shell ground states. When choosing this
method, it is essential to realize that MP2 is known to underestimate bond lengths while overestimate the stability of bonds. The LANL2DZ basis set is a small basis set and has also been shown to incorrectly approximate bond lengths and dissociation energies. These errors are due to basis set superposition error and can be corrected for by using the counterpoise correction method, as follows:

\[ \Delta E_{CP}(R) = E_{AB} - \left( E^{A}_{A} + E^{B}_{B} \right), \]  

(1)

where \( R \) represents distance between A and B, \( E_{AB} \) represents the energy of the complex and \( E^{A}_{A} \) represents the energy of fragment A in the presence of the basis sets for both the A and B fragments. To verify that metalophilic trends remain significant in the absence of BSSE, several sample clusters were counterpoise corrected. Upon counterpoise correction, the bond strengthening with cluster size remained significant. While this method/basis set combination makes it impossible to use these values as absolute answers the trends should remain valid as these errors will carry throughout the systems. The results give qualitative evidence for metallophilicity in small cluster of Zn\(_n\), Cd\(_n\), and Hg\(_n\) (where \( n = 2-8 \) atom clusters).

The cooperativity of the ground state clusters can be shown in Tables 2.1a-2.3a as demonstrated by shortening of bonds in all three group 12 systems. The group 12 dimers have bond lengths that would suggest weak dispersion force. As the cluster size increases, the bond lengths shorten from approximately 0.3 Å in zinc clusters to over 0.80 Å in center bond of the cadmium cluster.

The shortening of the bonds can be seen to level out as the size of the cluster increases. An example of this effect in the zinc clusters is shown in Table 1a. As the
zinc cluster increases in size from the dimer to the trimer the bond length decreases by approximately 0.1 Å. The exterior bonds of the tetramer through octamer, however, are shown to remain fairly close in length.

Table 2.1: Bonding and spectroscopic constants of zinc clusters (a) \(^1\Sigma\) (b) \(^3\Sigma\) (c) \(^3\Pi\) (d) high spin states.

**(a)**

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**(b)**

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<th>(E/\text{Bond}) (cm(^{-1}))</th>
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Table 2.2: Bonding and spectroscopic constants of cadmium clusters (a) $^1\Sigma$ (b) $^3\Sigma$ (c) $^3\Pi$ (d) high spin states.

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Table 2.3: Bonding and spectroscopic constants of mercury clusters (a) $^1\Sigma$ (b) $^3\Sigma$ (c) $^3\Pi$ (d) high spin states.

(a)

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2.3.1.2 $^3\Sigma$ Excited State Bonding

As noted in the introduction section, the bond order of the excited states will decrease as the number of bonds in the excited state increase. This makes accessing cooperativity of excited states based solely on the length of bonds more difficult. As shown in tables 2.1b-2.3b, the bonds of the sigma state are dependent on the size of the cluster. As the clusters increase in size the bond lengths become longer instead of shorter, as is the case in the ground state. Delocalization of the triplet electron can be seen in figures 2.1-2.3 as the cluster increases. The covalent bonding can be seen to be more localized in the central atoms of the zinc, cadmium and mercury clusters as the clusters increase in size. Tables 2.1-2.3 show exterior bonds approaching longer bond lengths similar to those seen in metallophilic bonding of the ground state.

2.3.1.3 $^3\Pi$ Excited State Bonding

The $^3\Pi$ excited state is also seen to have an increase in the bond length as the cluster size increase. The delocalization in the $^3\Pi$ excited state is shown to be less extensive than in the case of the $^3\Sigma$ excited state. While the excited state bonding is delocalized, it is only delocalized over a maximum of 4 central atoms of the group 12 clusters. Exterior bond of the pi excited states also approach metallophilic bonding as the covalent bonding is not delocalized over all bonds. The approach to longer bond lengths of the exterior bonds is more rapid than the sigma state as is shown in tables 2.1-2.3.
Figure 2.1. Zinc cluster $^3\Sigma$, $^3\Pi$ and high spin SOMO diagrams.
Figure 2.2. Cadmium cluster $^3\Sigma$, $^3\Pi$ and high spin SOMO diagrams.
Figure 2.3. Mercury cluster $^3\Sigma$, $^3\Pi$ and high spin SOMO diagrams.

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2.3.1.4 High Spin Excited State Bonding

In the high spin excited clusters, all atoms have an excited electron. The interactions are covalent in nature as all atoms have an unpaired of electrons on the s and p orbital causing there to be one bond between all atoms. The bonds lengths in the high spin excited state clusters are similar in length to that of the excited dimer. The bond lengths remain fairly constant with the growth of the clusters. This may not be surprising as the bonds are all covalent in nature and the overall bond order per atom is constant. Cooperativity does not seem to have a large effect on the length of the bonds, as they do not decrease substantially with the increasing of cluster size. This may be due to cooperativity stemming from the delocalization of electrons from the s to the p orbitals. In the case of the high spin clusters, the atoms comprising the clusters should exhibit a splitting of the two highest energy electrons between the s and p orbital. Therefore, while adding more atoms may decrease the s-p gap, it does not strength the interaction that are already a combination of s and p orbital interactions.

2.3.2 Bond Energy

2.3.2.1 Ground State Dissociation Energy

Dissociation per bond can be used to qualify the change in bonding strength from dispersion forces for the smaller cluster to more covalent bonding as the cluster size increases. The extent of this change can be observed in tables 2.1-2.3. Zinc clusters are shown to be the least affected by the increasing size of the cluster. The dimer is shown to have relatively weak dissociation energy of only 234 cm$^{-1}$. With the
addition of an atom in the trimer, the dissociation energy is seen to increase by approximately 50 cm\(^{-1}\)/bond. As the cluster is increased by another atom to the tetramer, the dissociation energy per bond is only increased another 15 cm\(^{-1}\)/bond. The next addition to a pentamer increases the dissociation energy per bond by another 10 cm\(^{-1}\)/bond. As the cluster size is increased the change in dissociation per bond is seen to level off to only a difference of 5 cm\(^{-1}\)/bond between the heptamer and octamer.

Figure 2.4. \(D_e/\text{bond}\) in \(^1\Sigma\) state as a function of cluster size.

The dissociation per bond in the mercury clusters is seen to have a greater change from the dimer to the trimer, changing from 768 cm\(^{-1}\)/bond to 919 cm\(^{-1}\)/bond. The change from the trimer to tetramer is shown approximately 90 cm\(^{-1}\)/bond. The
overall change from the dimer to decamer is seen to be greater than in the case of zinc and does not level out as greatly.

The relative change in dissociation per bond can be seen to have the greatest magnitude in the cadmium clusters. The change from dissociation per bond in the dimer, $374 \text{ cm}^{-1}/\text{bond}$ increases to dissociation per bond of $469 \text{ cm}^{-1}$ in the trimer. The change in the dissociation per bond as the cluster size increases is observed to have the least amount of leveling of with the increased stability in bonding. This may be due to cadmium clusters’ ability to greater delocalize the electrons. As clusters increase past the octamer, the dissociation per bond may eventually level off as covalent bonding becomes a stabilizing factor.

2.3.2.2 $^3\Sigma$ Excited State Bond Energy

The bonding energy of the excited state can be seen to mirror the amount of delocalization of covalent bonding. The covalent bonding is seen to be delocalized over all atoms in zinc clusters smaller than the hexamer. The bond energy is seen to steadily increase with the delocalization. The covalent bonding is delocalized over both bonds in the trimer, thus the bonding energy per bond is seen to increase substantially from the bonding energy of the dimer, $-21.6 \times 10^3 \text{ cm}^{-1}/\text{bond}$ verses $-17.0 \times 10^3 \text{ cm}^{-1}/\text{bond}$, respectively. The increase is also substantial from the trimer to the tetramer, a difference of $1.7 \times 10^3 \text{ cm}^{-1}/\text{bond}$. The trend can be seen to follow the same pattern as the delocalization of bonding does. The amount of delocalization as well as the energy per bond changes less with the addition of each atom to the cluster.
size. When the delocalization of the covalent bonding ceases to increase after the zinc hexamer, the change in energy per bond is seen to level off. The mercury clusters can also be observed to have a decrease in delocalization as the cluster size is increased. The decrease in delocalization is not as significant as in the case of zinc but is shown to start diminishing after the pentamer cluster. Figure 2.3 shows the highest sigma SOMO of the mercury octamer contains the majority of the electron density localized on the interior clusters with only a small amount of electron density on the outermost to atoms. The change in energy per bond is seen to decrease as the clusters are increased past the tetramer.

Figure 2.5. Energy per bond in $^3\Sigma$ as a function of cluster size.
2.3.2.3 $^3\Sigma$ Excited State Bond Energy

The bonding energy of the pi state for all group 12 elements is shown to mirror the delocalization of the bonding. The bond energies in the pi state increases drastically from the dimer to the tetramer as covalent bonding is fully delocalized. Examples of this are shown in all the clusters. For example, the energy per bond for the dimer, trimer, and tetramer zinc clusters are $-17.9 \times 10^3$ cm$^{-1}$, $-22.0 \times 10^3$ cm$^{-1}$ and $-23.7 \times 10^3$ cm$^{-1}$, respectively. The pentamer and larger sized clusters shows increasing in bond energy, however, the change in energy as the cluster size increases is diminished, as the bonding is not fully delocalized over the outermost atoms of the clusters. Examples of this are shown in the energy per bond changes in the zinc pentamer, hexamer and heptamer. Energy per bond in the pentamer, hexamer and heptamer are $-24.5 \times 10^3$ cm$^{-1}$, $-25.2 \times 10^3$ cm$^{-1}$, and $-25.6 \times 10^3$ cm$^{-1}$, respectively.
2.3.2.4 High Spin Excited State Bond Energy

The energy per bond of the high spin excited states in the zinc, cadmium and mercury clusters is higher than the energy of an excited state dimer. This may indicate the ferromagnetism of these clusters provides a stabilizing factor. As the cluster grows the energy per bond remains somewhat constant. This may indicate a lack of cooperative effects in the covalently bonding high spin clusters. The lack of cooperativity may be due to the s and p orbitals being already occupied and thus there is no delocalization of the s orbital electronic density into the p orbitals. Without the cooperative effects, the bonds are not strengthened and thus the energy remains somewhat constant as a covalent interaction.
2.3.3 Phosphorescent Absorption and Emissions

2.3.3.1 Absorption Energies

Absorption energies in all elements are shown to mirror the bonding in the ground state clusters. As the progression of bonding delocalization is shown to decline as the cluster grows larger in size, the change in absorption energy is also shown to diminish. An exception to this can be observed in the ground state of the zinc dimer. The zinc cluster absorption energies are shown to oscillate in energy as the cluster size is increased. Examples of this can be seen in the dimer, trimer and tetramer absorption energies of $32.2 \times 10^3$ cm$^{-1}$, $28.1 \times 10^3$ cm$^{-1}$ and $31.1 \times 10^3$ cm$^{-1}$.

Figure 2.7. Absorption energy as a function of cluster size.

This oscillation of absorption energies is a result of the stability differences in even numbered clusters verses an odd numbered of clusters, due to varying levels of
electron delocalization. Looking only at the even-numbered clusters, it can be shown the energy progressively decreases as the size increases. An example of this is shown in the zinc dimer, tetramer and hexamer clusters. The absorption energies are $32.2 \times 10^3$ cm$^{-1}$, $31.1 \times 10^3$ cm$^{-1}$, and $30.7 \times 10^3$ cm$^{-1}$, respectively. Looking only at the odd clusters, a decreasing progression in the absorption energies is also shown. Examples of this can be seen in the zinc trimer, pentamer and heptamer clusters. These even/odd stability effects have little consequence on the cadmium clusters’ absorption energies. The absorption can be seen to decrease as the cluster size increases in the cadmium. Examples of this are shown in the dimer, timer and tetramer clusters. The respective absorption energies are $27.6 \times 10^3$ cm$^{-1}$, $25.0 \times 10^3$ cm$^{-1}$ and $20.1 \times 10^3$ cm$^{-1}$. In the mercury clusters, even/odd effects are not seen in the smaller clusters as the change in energy is greater than the oscillation energy. For example the absorption energies in the dimer, trimer and tetramer clusters are $31.7 \times 10^3$ cm$^{-1}$, $29.8 \times 10^3$ cm$^{-1}$ and $28.3 \times 10^3$ cm$^{-1}$. Another important result can be shown by comparing the dimer and octamer clusters. A several thousand inverse centimeter difference in absorption energy between the dimer and octamer clusters is shown in all three cluster types. The zinc dimer absorbs at $32.2 \times 10^3$ cm$^{-1}$, whereas the octamer has an absorption energy of $30.4 \times 10^3$ cm$^{-1}$. A greater difference is seen in the mercury cluster. The dimer absorption energy is $31.7 \times 10^3$ cm$^{-1}$ while the octamer absorption energy is $26.6 \times 10^3$ cm$^{-1}$. The largest difference is seen in the cadmium, as clusters show full delocalization up to the decamer cluster. As is the case in bond energy, the absorption is also seen to change throughout the cluster series that have been studied. Decreasing magnitude of
absorption energies of the cadmium clusters is much more subtle than the zinc or mercury clusters. The dimer absorbs at $27.6 \times 10^3 \text{ cm}^{-1}$ while the octamer absorption energy is over $10 \times 10^3 \text{ cm}^{-1}$ lower at $17.4 \times 10^3 \text{ cm}^{-1}$. It is shown that cooperativity effect has a significant impact on the absorption energies of the metal clusters.

2.3.3.2 Sigma ($^3\Sigma^-\Sigma$) Emission Energies

The sigma emission is shown to be a dependant of electron delocalization. Examples of this are shown in the zinc clusters. In figures 2.1-2.3 and 2.8 the delocalization and emission energies are shown to be a function of cluster size. The changes in emission energies is shown to change most dramatically in the dimer though tetramer clusters. The respective emission energies are $17.8 \times 10^3 \text{ cm}^{-1}$, $13.0 \times 10^3 \text{ cm}^{-1}$ and $10.6 \times 10^3 \text{ cm}^{-1}$.
As is the case of the electron density, as shown in figure 2.1, the emission energy is found to oscillate in clusters larger than the pentamer. The electron density of odd clusters that are larger than a pentamer is predominately delocalized over the five central atoms. The even numbered clusters larger in size than the hexamer show delocalization primarily over the central six atoms. The emission energies are shown to mirror this even-odd delocalization pattern. The pentamer has an emission energy of $9.2 \times 10^3$ cm$^{-1}$, the hexamer has an emission energy of $8.8 \times 10^3$ cm$^{-1}$, the heptamer has a greater difference with an emission of $7.9 \times 10^3$ cm$^{-1}$. The cadmium shows no sign of oscillation in the even and odd clusters in the dimer through the octamer computations, as the delocalization of electron density are continuous throughout the series. The emission energy shows signs of diminishing as the cadmium clusters get larger, at a similar rate as the cessation of the electron delocalization.
It is evident when comparing electron delocalization of the mercury sigma SOMO shown in figure 2.3 with the mercury emission energy plot of figure 2.8 the effect the electron delocalization has on the sigma emission energy. As the delocalization decrease in the larger clusters, the change emission energy is seen to diminish.

2.3.3.3 Pi (\(^{3\Pi-\Sigma}\)) Emission Energies

As was discussed in the bond energy section, the bonding of the pi excited state is localized on only the inner most atoms of the zinc, cadmium and mercury clusters. The odd numbered clusters larger than the pentamer show electron density on only the three central atoms of the cluster. In the even numbered clusters larger than the hexamer, electron density is primarily on the four inner most atoms. The density is seen to oscillate between three and four central atoms with even and odd number of atoms. The emission energies are also seen to have this similar pattern as the clusters are increased in number of atoms.
While there is a substantial change in emission energy from the dimer to the tetramer, the change in emission energy ceases with the cessation of electron delocalization. An example of this can be seen in the zinc clusters. The dimer, trimer and tetramer pi emission energies are $14.8 \times 10^3$ cm$^{-1}$, $9.6 \times 10^3$ cm$^{-1}$ and $8.7 \times 10^3$ cm$^{-1}$. There is a change of over $6.0 \times 10^3$ cm$^{-1}$ in the emission energies in emission energy from the dimer to the tetramer. The change from the pentamer to octamer, however, is very minimal. The emissions energies are $6.2 \times 10^3$ cm$^{-1}$, $6.1 \times 10^3$ cm$^{-1}$, $5.6 \times 10^3$ cm$^{-1}$ and $5.6 \times 10^3$ cm$^{-1}$ for the pentamer, hexamer, heptamer, and octamer zinc clusters.
2.3.3.4 High Spin Emission Energies

Emission energies of the high spin excited state clusters are shown to continuously rise with cluster size. The change bonding and energy are not shown to diminish in the high spin states. The energies per bond are shown to be continuous in magnitude. The emission energies per bond are seen to grow with the increased number of bonds in the cluster, mirroring the full delocalization of the electron delocalization. In all cases it is very important to model the emission energies for the clusters instead of simply modeling the solid state as a dimer emission. Zinc decamers, for example, have an emission energy of $70.0 \times 10^3 \text{ cm}^{-1}$, while the dimer only has an emission energy of $32.2 \times 10^3 \text{ cm}^{-1}$. Clearly, the importance of cluster size and electron density is demonstrated.

2.3.4 Change from Linear to 3-dimensional Structures

2.3.4.1 Ground State Bonding in 3-dimensional Structures

The linear clusters are not always the lowest energy geometry. This does not mean the computations using linear geometries are useless. Many luminescent compounds show linear aggregation as metal-metal interactions grow. It is, however, also important to model the ground and excited state structures as multi-dimensional structures to fully understand the interaction of metal clusters and how these interactions are built upon as the cluster size grows.

The bonding strength and structure of closed shell clusters will be affected by two competing factors. If a bond is made of $p$ type atomic orbitals, the bond will be
more stabilized in a linear environment and 3-dimensional build up of the structure is hindered. While the mercury atoms have more $p$ orbital characteristic in the valence bond than the zinc or cadmium atoms, the electron density of the mercury clusters is still primarily in the $s$ orbitals. Therefore, stabilization from $p$-orbitals overlapping in a linear fashion will not be a major contributor to the ground state structure in any of the group 12 clusters.

A second factor, increased electron delocalization through increased bonds per atoms, is much more influential in the group 12 and other closed shell clusters. If the electronic density is primarily in the $s$ orbital, bonding will be most stabilized by delocalization of electrons. 3-dimensional structures will allow for the most bonds per atom in the cluster and thus the most delocalization of electron density will be attained by forming 3-dimensional structures. Delocalization of electron density is obtained by the overlap of the orbitals in the clusters. The bond lengths of the dimer and trimer are seen to be the bond length typical of a dispersion interaction. The HOMO diagrams shown in table show the bent trimer to have an increased amount of bonding due to delocalization of the electron density. Comparison of this structure to the linear trimer clearly shows the importance of bond number per atom in delocalization of density. Comparing of the orbital population shows the bent trimer to have more electron delocalization from the $s$ to $p$ orbitals.
Figure 2.10 3-dimensional structures of (a) zinc (b) cadmium and (c) mercury ground state.

‡ Transition State, used for comparison to 3-D structure
Table 2.4: (a) 3-dimensional structures of (a) zinc (b) cadmium and (c) mercury ground state.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>MP2 Energy (Hartee)</th>
<th>Absorption Energy $(10^3 \text{ cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
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<td>IIa</td>
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<td>IIIa</td>
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<tr>
<td>IVa</td>
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<td>Va</td>
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<tr>
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<tr>
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<td>IVc</td>
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</tr>
<tr>
<td>Vc</td>
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<td>27.3</td>
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</tbody>
</table>

As the cluster size is increased to the tetramer, the possible configurations will be either the rhombus or 3-dimensional figures. While the rhombus is a transition state and thus not a minima, it has been left in table 4 for comparison sake. If the bonds were comprised of p orbitals overlapping, the rhombus would be favored. As previously stated, however, all of the ground structure atoms have a majority of electron density in the s orbital with only a slight amount of p orbital delocalization. The 3-dimensional
structure is therefore favored], as it encompasses 3 bonds per atom instead of only 2 bonds per atom, as is the case of the rhombus. The greater electron delocalization allows for an increase in the bonding in all of the group 12 clusters. Zinc clusters increase the greatest extent from the trimer to the tetramer. The bonding in the C2v trimer is seen to be 4.287 Å, while the 3-dimensional tetramer is shown to have bond lengths of 2.819 Å. This result compares well with ground state computations of previous studies.13 The amount of change seen suggests a change from van der Waals to covalent strength bonding. While the bond lengths in cadmium and mercury tetramers also contract, the magnitude is not as great. As was the case in the linear clusters, cooperativity effects are noted in the 3-dimensional states. In these three cluster types, bond lengths averages can be seen to decrease in length, as the bonding is strengthened by delocalization of electronic density. Bond lengths of the zinc pentamer are shown to be greater than an angstrom shorter than the dimer’s bond length. The cadmium also see significant change from the dimer to the pentamer bond lengths. While the change in length is not as drastic in mercury clusters, the bond lengths are still shorten by 0.4 angstrom in the mercury.

2.3.4.2 Absorption Energies

As was the case of the linear state clusters, it can be noted that absorption follows the trend of electronic delocalization of the clusters. Unlike the linear clusters however, there is no leveling off or oscillation of the absorptions in the 3-dimensional zinc clusters. This may be attributed to the ability of the 3-dimensional structures to
fully delocalize the electronic density, through the increased number of bonding interaction of the 3-dimensional structures. 3-dimensional structures of all three cluster types are shown to have a large diminish in magnitude of the absorption energy as the cluster size grows. An example of this can be seen in the zinc clusters. In the linear clusters, the absorption energy is seen to only decrease by $4.3 \times 10^3 \text{ cm}^{-1}$, from the dimer to the pentamer clusters. In the 3-dimensional clusters, this decrease in absorption energy is $11.1 \times 10^3 \text{ cm}^{-1}$. It is clearly shown that both cluster size and structure have a significant impact on the electronic delocalization and thus, the absorption energies of the clusters.

2.3.4.3 Excited State Distortions of 3-Dimensional Clusters

Upon photoexcitation of an electron into the lowest orbital, the bond order is changed from a formally closed-shell cluster to a partially covalent bonded system. Several structural consequences result from this change in electronic bonding structure. The first consequence is similar to the linear arrangement and the bond lengths of the excited state are seen to contract, indicating the bonding is more covalent in nature. A second consequence of this is the excited state bonding has an increased amount of interaction arising from the overlap of the atomic p orbitals. In the 3-dimensional ground state, the bonding was made of primarily s orbital interactions and thus the stabilization of these orbitals was primarily from an increased number of interactions, causing the structures to shift to 3-dimensional structures as soon as possible. In the case of the excited state, the bonding interaction contains more p orbital characteristics.
and thus bonding is not only stabilized by number of bonds but also by structural arrangements that favor p orbital overlap.

Figure 2.11 3-dimensional structures of (a) zinc (b) cadmium and (c) mercury triplet (T₁) excited state.
Table 2.5: (a) 3-dimensional structures of (a) zinc (b) cadmium and (c) mercury excited ($T_1$) state.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>MP2 Energy (Hartee)</th>
<th>Absorption Energy ($10^3$ cm$^{-1}$)</th>
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<td>IVc</td>
<td>-207.3980940</td>
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</tr>
</tbody>
</table>

This change in bonding interactions can be noted in the teteramer cluster of all three cluster types. In the ground state of all of the clusters, the 3-dimensional tetramer was the most stable structure. In the excited state however, the tetramer structures become planar as to increase the amount of p orbital overlap, allowing for delocalization through the p as well as s orbitals. Larger excited state clusters also show a preference for point groups that favor p orbital overlap over number of bonds per atom.

This preference may be best noted in the excited state ($T_1$) cadmium hexamer distortion to a D$_{4h}$ symmetry. The D$_{4h}$ distortion is favored by both the C$_{2v}$ and O$_h$ ground states of the cadmium hexamer. While the C$_{2v}$ provides the most number of bonds per atom, the D$_{4h}$ arrangement allows more overlap of the p orbitals of the excited state and thus is more preferred.
2.3.4.4 Emission Energies of 3-Dimensional Clusters

Emission energies of the 3-dimensional clusters show a similar trend to the linear cluster. As the electron density is delocalized over the cluster, the emission energies are shown to decrease in magnitude. As the 3-dimensional clusters are shown to have an increased amount of electronic delocalization with cluster when compared with the ground state, the emission energy is also shown to decrease at a substantial faster rate than is the case of the linear clusters. The effect structural change in clusters is shown to have a huge impact on emission energies. Zinc clusters, which show the greatest change in bonding strengths also show the greatest change in emission energies. An example of this is shown in the pentamer cluster. The linear structure has an emission energy of $9.2 \times 10^3 \text{ cm}^{-1}$ while the 3-dimensional structure has an emission of $4.7 \times 10^3 \text{ cm}^{-1}$, a difference of $4.5 \times 10^3 \text{ cm}^{-1}$. This effect is not as dramatic in the cadmium, which only shows a difference of $1.7 \times 10^3 \text{ cm}^{-1}$ between the linear and 3-dimensional structures. The difference in the magnitude of these changes stems from the amount of change in electronic density of the clusters.

2.4 Conclusion

The MP2 method has been shown to attain systematic results for all element type and cluster size studied. The effect of size and structure of clusters has been demonstrated to have important impact on bond strengths and spectral data. Structures have been shown to be most stabilized by increased number of bonds
causing increased s orbital overlap in the ground state, while excited states may be more stabilized by increased p orbital overlap. These trends have also been shown to be systematic due to the amount of delocalization shown in the group 12 elements. Cooperative effects have been demonstrated in ground and triplet excited states but not in the high spin excited states. This effect has been shown to be due to electron delocalization of s electronic density into the p orbitals.
2.5 References


2 Determan, J. J.; Omary, M. A.; Wilson, A. K. manuscript in progress.


27 DeYonker, N. J.; Williams, T. G.; Wilson, A. K.; results to be presented in future ccCA paper.
