Stability, Electronic Structure, and Nonlinear Optical Properties in Clusters and Materials: A Synergistic Experimental-Computational Analysis

Maksim Kulichenko

Utah State University

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STABILITY, ELECTRONIC STRUCTURE, AND NONLINEAR OPTICAL PROPERTIES IN CLUSTERS AND MATERIALS: A SYNERGISTIC EXPERIMENTAL-COMPUTATIONAL ANALYSIS

by

Maksim Kulichenko

A dissertation submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemistry

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2022
ABSTRACT

Stability, Chemical Bonding, and Nonlinear Optical Properties
in Atomic Clusters and Materials

by

Maksim Kulichenko, Doctor of Philosophy

Utah State University, 2022

Major Professor: Dr. Alexander I. Boldyrev
Department: Chemistry and Biochemistry

The main objective of Chemistry as a science is an understanding of the behavior of matter which, in turn, is essential for the creation of new chemical species with desired properties. Recent advances in synthetic equipment offer a wide range of opportunities for the discovery of useful compounds. However, experimental material discovery mostly relies on a trial-and-error approach which slows the process down. At the same time, various, if not most, properties of molecules and materials are dictated by their electronic structure. The explosive development in computational resources makes it possible to efficiently analyze electronic wavefunctions and systematically characterize chemical structures. Thus, this dissertation presents a series of projects – both joint studies with experimentalists and purely theoretical ones – devoted to the rationalization of electronic structure properties in atomic clusters and materials. Chemical bonding analysis is an essential part of each presented project and is used for the interpretation of stability and electronic properties in a chemically intuitive manner via the concept of multicenter bonds.
In particular, the presented work can be considered the steps towards further generalization of the unified chemical bonding theory.

We analyzed geometry, stability, and electronic structure of the following systems: \( \text{IrB}_3^- \), \( \text{BiB}_n^- \) \((n=6-8)\), \( \text{Au}_9\text{Zn}^- \) doped clusters; \( \text{SO}_4^{2-}(\text{H}_2\text{O})_n \) \((n=1-40)\) solvated dianion; \( \text{X}_4\text{O}_3 \) electrides \((\text{X}=\text{Alkaline earth metals})\); \( \text{MgO} \) and \( \text{MoS}_2 \) crystals. Multicenter bonding approach accompanied by other electronic structure analysis techniques has proven its predictive, explanatory, and illustrative power in characterization of structural stability, charge distribution, and photoelectron spectra in these systems. Our findings led to the discovery of non-trivial bonding patterns and charge transfer mechanisms in the abovementioned chemical species. Along with characterization of newly synthesized charged clusters, we identified new aspects of electronic structure in widely known and used chemical systems. In particular, we showed that 2D \( \text{MoS}_2 \) is \( \sigma \)-aromatic (which has been experimentally proven shortly thereafter) and made theoretical clarifications regarding charge transfer and stabilization mechanisms of hydrated \( \text{SO}_4^{2-} \) dianion. A part of this research deals with highly polarizable electride-like systems that possess nonlinear optical properties and, thus, have plenty of potential applications in electron-emitting devices, hydrogen storage, ammonia synthesis, etc.

(251 pages)
The main objective of Chemistry as a science is an understanding of how and why certain atoms are bonded together and what effects these bonds cause. Modern computational chemistry offers a wide range of tools that greatly assist the exploration of vast chemical space replacing expensive trial-and-error experimental approaches. Computational chemistry may serve to characterize newly synthesized compounds and provide atomic scale insights inaccessible to experimentalists’ vision. Moreover, predictive power of computational chemistry may be used as a guidance for future experiments and for the rational design of new compounds with desired properties.

This dissertation demonstrates the capabilities of joint experimental and theoretical approaches in the characterization of atomic clusters. Bonding and stability analysis in such systems is crucial for understanding the relations between various atomic-scale changes and resulting alterations in chemical properties. This work also makes use of predictive power of modern theoretical methods to probe new chemical species with peculiar electronic properties. A common thread through the projects presented here has been a rationalization of size- and composition-dependent properties of chemical systems based on the analysis of their electronic structure. An essential part of this dissertation is the
deciphering of electronic structure via chemical bonding analysis which helps explain various properties in a chemically intuitive manner.
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# CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT ........................................................................................................ iii</td>
</tr>
<tr>
<td>PUBLIC ABSTRACT .......................................................................................... v</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS ....................................................................................... vii</td>
</tr>
<tr>
<td>LIST OF TABLES ............................................................................................ xiii</td>
</tr>
<tr>
<td>LIST OF FIGURES .......................................................................................... xiv</td>
</tr>
<tr>
<td>CHAPTER 1 INTRODUCTION ............................................................................ 1</td>
</tr>
<tr>
<td>1-1. Theoretical tools for chemical bonding deciphering ......................... 1</td>
</tr>
<tr>
<td>1-2. Aromaticity ............................................................................................ 3</td>
</tr>
<tr>
<td>1-3. Stability and Chemical Bonding in Clusters ....................................... 4</td>
</tr>
<tr>
<td>1-3.1. Atomic clusters .................................................................................. 4</td>
</tr>
<tr>
<td>1-3.2. Hydrated sulfate clusters $\text{SO}_4^2- (\text{H}_2\text{O})_n (n = 1\text{--}40)$ .... 7</td>
</tr>
<tr>
<td>1-4. Nonlinear Optical Properties ............................................................... 8</td>
</tr>
<tr>
<td>1-4.1. MgO surface with periodic defects ................................................... 8</td>
</tr>
<tr>
<td>1-4.2. Molecular electrides .......................................................................... 9</td>
</tr>
<tr>
<td>References .................................................................................................... 9</td>
</tr>
<tr>
<td>CHAPTER 2 $\sigma$-AROMATICITY IN THE MoS$_2$ MONOLAYER ................... 21</td>
</tr>
<tr>
<td>Abstract ........................................................................................................ 21</td>
</tr>
<tr>
<td>2-1. Introduction ........................................................................................... 21</td>
</tr>
<tr>
<td>2-2. Computational Methods ....................................................................... 23</td>
</tr>
<tr>
<td>2-3. Results and Discussion ......................................................................... 24</td>
</tr>
<tr>
<td>2-4. Conclusions ........................................................................................... 29</td>
</tr>
<tr>
<td>References .................................................................................................... 29</td>
</tr>
<tr>
<td>Tables and Figures ....................................................................................... 40</td>
</tr>
</tbody>
</table>
Abstract ........................................................................................................................................... 97
5-1. Introduction .................................................................................................................................. 98
5-2. Methods ...................................................................................................................................... 100
  5-2.1. Photoelectron Spectroscopy ................................................................................................. 100
  5-2.2. Computational Details ........................................................................................................... 101
5-3. Results ....................................................................................................................................... 103
  5-3.1. Experimental Results ............................................................................................................ 103
  5-3.2. Theoretical Results ............................................................................................................... 103
5-4. Discussion .................................................................................................................................. 104
  5-4.1. Confirmation of the Global Minimum of Au9Zn− ................................................................. 104
  5-4.2. Chemical Bonding in the D3h Au9Zn− ................................................................................... 106
5-5. Conclusions ............................................................................................................................... 108
References ......................................................................................................................................... 108
Tables and Figures ............................................................................................................................. 120

CHAPTER 6 HYDRATED SULFATE CLUSTERS SO42−(H2O)n (n = 1–40): CHARGE DISTRIBUTION THROUGH SOLVATION SHELLS AND STABILIZATION .......................................................................................................................... 124

Abstract ........................................................................................................................................... 124
6-1. Introduction .................................................................................................................................. 125
6-2. Computational Methods ............................................................................................................. 126
6-3. Results and Discussion .............................................................................................................. 127
6-4. Conclusions ............................................................................................................................... 131
References ......................................................................................................................................... 132
Tables and Figures ............................................................................................................................. 136

CHAPTER 7 PERIODIC F-DEFECTS ON THE MgO SURFACE AS POTENTIAL SINGLE-DEFECT CATALYSTS WITH NON-LINEAR OPTICAL PROPERTIES ......................................................................................................................... 139

Abstract ........................................................................................................................................... 139
7-1. Introduction .................................................................................................................................. 140
7-2. Computational methods ............................................................................................................. 142
7-3. Results and discussion ............................................................................................................... 145
  7-3.1. Electronic properties ............................................................................................................ 145
  7-3.2. Optical properties ................................................................................................................. 147
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-4.</td>
<td>Conclusions</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>Tables and Figures</td>
<td>164</td>
</tr>
<tr>
<td><strong>8</strong></td>
<td><strong>CHAPTER 8 DESIGNING MOLECULAR ELECTRIDES FROM DEFECTIVE UNIT CELLS OF CUBIC ALKALINE EARTH OXIDES</strong></td>
<td>169</td>
</tr>
<tr>
<td>8-1.</td>
<td>Introduction</td>
<td>170</td>
</tr>
<tr>
<td>8-2.</td>
<td>Computational Methods</td>
<td>172</td>
</tr>
<tr>
<td>8-3.</td>
<td>Results and Discussion</td>
<td>173</td>
</tr>
<tr>
<td>8-3.1.</td>
<td>$X_3O_3$ Isomers</td>
<td>173</td>
</tr>
<tr>
<td>8-3.2.</td>
<td>Bonding Analysis</td>
<td>174</td>
</tr>
<tr>
<td>8-3.3.</td>
<td>Electronic Properties</td>
<td>176</td>
</tr>
<tr>
<td>8-4.</td>
<td>Conclusion</td>
<td>177</td>
</tr>
<tr>
<td>8-5.</td>
<td>References</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>Tables and Figures</td>
<td>190</td>
</tr>
<tr>
<td><strong>9</strong></td>
<td><strong>CHAPTER 9 SUMMARY</strong></td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>197</td>
</tr>
<tr>
<td><strong>APPENDICES</strong></td>
<td>200</td>
<td></td>
</tr>
<tr>
<td><strong>CURRICULUM VITAE</strong></td>
<td>229</td>
<td></td>
</tr>
</tbody>
</table>
# LIST OF TABLES

Table 3-1. Experimental ADEs and VDEs and the calculated values along with the final neutral states and valence-electron configurations for the two IrB$_3^-$ low-lying isomers. ................................................................. 56

Table 4-1. Experimental VDEs and Comparison with the Calculated Values for the Global Minimum of BiB$_6^-$ ................................................................. 89

Table 4-2. The experimental VDEs and comparison with the calculated values for the global minimum of BiB$_7^-$. ............................................................................. 90

Table 4-3. The experimental VDEs and comparison with the calculated values for the global minimum of BiB$_8^-$. ............................................................................. 90

Table 4-4. Comparison of the experimental ADE and VDE$_1$ with calculated values at the PBE0/aug-cc-pVTZ and CCSD(T)/def2-TZVP levels of theory for the global minima (GM) of BiB$_n^-$ ($n = 6$–$8$) and the VDE$_1$ for low-lying isomers. ................. 91

Table 5-1. Comparison of the experimental and calculated VDE$_1$ for the global minimum $D_{3h}$ structure, and the two low-lying isomers, Iso1 and Iso2, of Au$_9$Zn$^-$. ...... 120

Table 6-1. ONs of multi-centered bonds .................................................................................. 136
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>(A) 1c–2e s-lone pairs of S atoms, ONs = 1.9</td>
</tr>
<tr>
<td>2-2</td>
<td>Sigma-aromatic orbital inside of the hexagonal MoS$_2$ ring.</td>
</tr>
<tr>
<td>2-3</td>
<td>ELF of MoS$_2$. The isosurface value is 0.4.</td>
</tr>
<tr>
<td>2-4</td>
<td>Left: ELF slice with 001 Miller indices; the sliced plane contains Mo atoms; three Mo and three S atoms are placed for convenience purposes. Right: ELF slice with 100 Miller indices. Purple triangles indicate the same point sliced in different directions.</td>
</tr>
<tr>
<td>2-5</td>
<td>Isolated MoS$_2$ cluster model.</td>
</tr>
<tr>
<td>2-6</td>
<td>Left: three 1c–2e lone pairs on Mo atoms, ONs = 1.6. Right: 2c–2e Mo–Mo bonds; only 3 out of 6 are depicted for convenience purposes.</td>
</tr>
<tr>
<td>2-7</td>
<td>Left: Triangle-like structure of the MoS$_2$ isolated cluster. Right: schematic representation of σ-aromaticity electron distribution. Dotted lines indicate missing rings in the cluster model.</td>
</tr>
<tr>
<td>2-8</td>
<td>3c–2e σ-aromatic bond inside the hexagonal ring. ON = 1.8</td>
</tr>
<tr>
<td>2-9</td>
<td>Extended isolated MoS$_2$ cluster model.</td>
</tr>
<tr>
<td>3-1</td>
<td>Photoelectron images and spectra at a) 2.3305 eV (532.00 nm) and b) 3.4958 eV (354.67 nm). The vertical lines denote vibrational progressions. The insert in (a) shows the vibrational assignments for band X. The double arrow below the images shows the laser polarization.</td>
</tr>
<tr>
<td>3-2</td>
<td>High-resolution photoelectron images and spectra at a) 1.3471 eV (920.38 nm), b) 1.3722 eV (903.54 nm), c) 1.3910 eV (891.33 nm), and d) 1.4399 eV (861.06 nm). The vertical lines denote fundamental vibrations; hot band transitions are labeled. The double arrow below the images shows the laser polarization.</td>
</tr>
<tr>
<td>3-3</td>
<td>Optimized structures for the ground states and low-lying isomers for IrB$_3$ and IrB$_3$. Bond lengths are given in Å. Relative energies are given in eV at the TPSS level followed by the ROCSD(T) values in brackets.</td>
</tr>
</tbody>
</table>
Figure 3-4. Displacement vectors and computed vibrational frequencies of the observed vibrational modes of isomers A.2, N.1, and N.2 (see Figure 2-3). The values in brackets are the measured frequencies. ................................................................. 60

Figure 3-5. Adaptive natural density partitioning (AdNDP) analysis for isomers N.1 (b) and N.2 (c). The AdNDP result of B₃⁺ (a) is given for comparison. The solid and dashed boxes emphasize the σ and π bonds, respectively, in the two isomers of IrB₃ that are similar to those in B₃⁺ (a). ................................................................. 61

Figure 4-1. Photoelectron spectrum of BiB₆⁻ at 266 nm (4.661 eV). The vertical bars correspond to computed VDEs at the PBE0/aug-cc-pVTZ level of theory. .......... 92

Figure 4-2. Photoelectron spectrum of BiB₇⁻ at 266 nm (4.661 eV). The vertical bars correspond to computed VDEs at the PBE0/aug-cc-pVTZ level of theory. The longer bars correspond to transitions to triplet final states; the shorter bars correspond to transitions to singlet final states. ................................................................. 92

Figure 4-3. Photoelectron spectrum of BiB₈⁻ at 266 nm (4.661 eV). The vertical bars correspond to computed VDEs at the PBE0/aug-cc-pVTZ level of theory. .......... 93

Figure 4-4. Global minima and low-lying isomers of (A) BiB₆⁻, (B) BiB₇⁻, and (C) BiB₈⁻. Relative energies are given in kcal/mol at the PBE0/aug-cc-pVTZ + ZPE level and the CCSD(T)/def2-TZVP level [in brackets]. ................................................................. 93

Figure 4-5. Low-lying isomers of (A) BiB₆⁻, (B) BiB₇⁻, and (C) BiB₈⁻. Relative energies are given in kcal/mol at the PBE0/aug-cc-pVTZ + ZPE level of theory. .......... 94

Figure 4-6. AdNDP bonding analysis for BiB₆⁻. ON stands for occupation number. .............................................................................................................. 94

Figure 4-7. AdNDP bonding analysis of BiB₇⁻. ON stands for occupation number. ...... 95

Figure 4-8. AdNDP bonding analysis of BiB₈⁻. ON stands for occupation number. ...... 95

Figure 4-9. AdNDP bonding analysis for the half-sandwich global minimum of neutral BiB₇⁻. ON stands for the occupation number................................. 96

Figure 4-10. AdNDP bonding analysis for the half-sandwich global minimum of neutral BiB₈⁻. ON stands for the occupation number................................. 96

Figure 5-1. Photoelectron spectroscopy of Au₆Zn⁻ at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV). ........................................................................................................ 121

Figure 5-2. Global minimum (GM) and low-lying isomers of Au₆Zn⁻ and their relative energies. All energies are in kcal/mol at the CCSD(T)/def2-
TZVP//PBE0/def2-TZVP, PBE0/def2-TZVP (in parentheses), and PBE0/TZ2P (in brackets) levels

Figure 5-3. Comparison of the simulated spectrum for the global minimum of $D_{3h}$ Au$_9$Zn$^-$ with the experimental spectrum at 193 nm. The simulated spectrum is obtained via the GKT approach at the PBE0/TZ2P SO-ZORA level.

Figure 5-4. Kohn–Sham MO correlation diagram between Zn$^{2+}$ and Au$_9^{3+}$ for $D_{3h}$ Au$_9$Zn$^-$ at the PBE0/TZ2P SR-ZORA level via the ADF program. The energy levels in magenta, blue, red, and green denotes to the MOs derived from 4s(Zn), 3d(Zn), 6s(Au), and 5d(Au) AOs, respectively. Electrons on the occupied MOs are represented by dots.

Figure 5-5. Contour plots of the 6s-based HOMO (34e') and HOMO–1 (20a1') of the $D_{3h}$ Au$_9$Zn$^-$ at the PBE0/TZ2P SR-ZORA level via the ADF program.

Figure 5-6. AdNDP bonding patterns of $D_{3h}$ Au$_9$Zn$^-$. ON is the occupation number.

Figure 6-1. SO$_4^{2-}$(H$_2$O), SO$_4^{2-}$(H$_2$O)$_2$, and SO$_4^{2-}$(H$_2$O)$_3$ structures. Hereinafter, S atoms are green, O atoms are red, and H atoms are blue. Dotted lines indicate H bonds.

Figure 6-2. Dependence of the sulfate charge on the water molecule number.

Figure 6-3. Mean hydrogen bond length between water molecules and the sulfate ion, $r_{OH}^{ws}$, for the putative global minimum structures of SO$_4^{2-}$(H$_2$O)$_n$ clusters as a function of the number of water molecules, $n$.

Figure 6-4. VDE of system SO$_4^{2-}$ with point charges in respect to the number of modeled water molecules. Red line: linear fitting of $n = 0$–12 region. Blue line: linear fitting of $n = 13$–40 region.

Figure 6-5. (a) SO$_4^{2-}$(H$_2$O)$_{18}$ cluster; (b) first solvation shell attributed to one oxygen atom; (c) first and the second solvation shell attributed to one oxygen atom.

Figure. 7-1. a: pristine MgO unit cell. b: unit cell of MgO slab with every second surface oxygen atom removed. c: 2x2x1 supercell of slab with the same defect superstructure. d: 1x1x1 supercell slab with every eight surface O removed.

Figure. 7-2. Phonon spectrum of MgO slab with multiple defects.

Figure. 7-3. Left: bonding analysis of MgO slab with multiple defects. Right: bonding analysis of MgO slab with rare defects.
Figure 7-4. Left: band structure of MgO slab without defects. Right: band structure of MgO with multiple F-defect. Fermi-levels are set as zeroes. In both cases vacuum gap is added in z-direction. ................................................................. 165

Figure 7-5. Pair correlation function of MgO slab with multiple defects.................. 166

Figure 7-6. Imaginary and real parts of optical dielectric function $\varepsilon_{\|}$ of MgO slab with every second oxygen removed from the surface. .................................................. 166

Figure 7-7. Imaginary and real parts of optical dielectric function $\varepsilon_{\perp}$ of MgO slab with every second oxygen removed from the surface. .................................................. 166

Figure 7-8. Calculated $\text{Im}X^{(2)}_{333}$ ($2\omega, \omega, \omega$) spectra with the intra-($2\omega)/(1\omega)$ and inter-($2\omega)/(1\omega)$ band contributions of MgO slab with every second oxygen removed from the surface. ........................................... 166

Figure 7-9. Absolute value of the second-order nonlinear susceptibility $X^{(2)}_{333}$ ($2\omega, \omega, \omega$) of MgO with multiple defects. .............................................................. 166

Figure 7-10. Calculated $\text{Im}X^{(2)}_{311}$ ($2\omega, \omega, \omega$) spectra with the intra-($2\omega)/(1\omega)$ and inter-($2\omega)/(1\omega)$ band contributions of MgO slab with every second oxygen removed from the surface. ........................................... 166

Figure 7-11. Absolute value of the second-order nonlinear susceptibility $X^{(2)}_{311}$ ($2\omega, \omega, \omega$) of MgO with multiple defects. .............................................................. 166

Figure 8-1. Geometry representation for a potential electride structure derived from a defective unit cell of a cubic ionic crystal. The transparent vertex corresponds to a missing anion. Electrons are expected to be localized in this vacancy. ................. 190

Figure 8-2. GM of Be$_4$O$_3$. Left: AdNDP 2c-2e Be–Be bond, ON = 1.95 |e|. Right: ELF thermal slice in a molecule plane. O atoms are red, Be atoms are white. ................. 190

Figure 8-3. GM structures and electride-like 3c-2e bonds of X$_2$O$_3$ global minima (X = Mg, Ca, Sr, Ba). Side and top orientations. All systems are of $C_{3v}$ symmetry. ONs of 3c-2e bonds are $\sim 1.90$ |e|. Contour value is 0.041. Color legend: O is red, Mg is green, Ca is yellow, Sr is orange, Ba is blue. .................................................. 190

Figure 8-4. Electron localization function slice in M-M-O plane. .......................... 191

Figure 8-5. Total first hyperpolarizability, $\beta_{\text{tot}}$, (blue) and excitation energy (red) graphs................................................................. 191
CHAPTER 1
INTRODUCTION

1-1. Theoretical tools for chemical bonding deciphering

Modern computational resources and theoretical methods enable efficient and systematic exploration of vast chemical space. Quantum chemistry offers a wide range of high accuracy tools that operate within the concept of molecular orbitals (MO). Although MOs proved themselves as a useful tool for calculating various properties of chemical compounds, they are delocalized over entire molecule and do not provide descriptive chemical bonding patterns. Thus, the rigorous language of the delocalized MOs is often assisted by various localization schemes.

As proposed by Foster and Boys,1 Edmiston and Ruedenberg,2 Pipek and Mezey,3 the possibility of such localization procedures is based on the fact that the wave function is invariant under unitary transformations. Valence bond (VB) theory proposed by Heitler, London, Slater, and Pauling,4,5 – an alternative to the MO theory – incorporates bonding concepts such as hybridization and resonance structures. At the same time, some chemical bonding techniques avoid references to the “chemical bonds” as objects that do not have physical definition. They include but not limited to quantum theory of atoms in molecules (QTAIM)6 and local quantum-mechanical functions such as Fermi Hole (FH), electron localization function (ELF) and their variations.7-15 Moreover, chemical bonding analysis can be performed using various flavors of bond orders and indices proposed by Coulson,16 Wiberg,17 Mayer,18,19 Giambiagi20 and Sannigrahi.21 Multiple electron-sharing indices such as Fulton’s index (ESI),22,23 Mayer’s bond-orders,18,19,24-26 and delocalization indexes (DI)27-29 reflect the degree of electron delocalization in atomistic systems.
One of the most popular chemical bonding and charge assignment techniques is natural bonding orbital (NBO) analysis proposed by Weinhold.\textsuperscript{30} The method is based on the diagonalization of the blocks of the first-order density matrix in the basis of natural atomic orbitals. It aims to construct the Lewis structure of a given system in an \textit{a priori} manner.\textsuperscript{31}

Developed by Zubarev and Boldyrev, Adaptive Natural Density Partitioning (AdNDP)\textsuperscript{32} algorithm is one of the recent tools capable of deciphering bonding in molecules, clusters, and solids. The method is a generalization of the NBO analysis. AdNDP helps to express chemical bonding in terms of both classical Lewis-like bonds (lone pairs and two-center (2c-2e) bonds) and delocalized bonding elements (nc-2e). When it is impossible to completely explain a bonding pattern in terms of a single Lewis structure, AdNDP avoids resonance descriptions and provides multicenter bonds in addition to the Lewis-like elements. The bond delocalization option gives a chemical bonding pattern consistent with the electron counting and the symmetry of a system. Thus, AdNDP is the primary tool for bonding deciphering throughout this dissertation.

The focus of this work is the study of atomistic systems and their electronic structure. Chemical bonding analysis is an essential part of each presented project as the interpretation of various structural and electronic properties is assisted by the concept of multicenter bonds providing chemically intuitive pictures. From the fundamental point of view, this thesis is a contribution to the understanding of how and why certain elements are bonded together and what effects these bonds cause.
1-2. Aromaticity

In organic chemistry, aromaticity is a property of planar conjugated cycloalkenes that are stabilized due to the delocalization of $\pi$-electrons. To date, aromaticity has proved itself as a reliable indicator of electronic and structural stability in various chemical systems.\textsuperscript{33-38} Since 1931, when Hückel introduced the $4N+2$ electron counting rule, this concept has been extended to various compounds beyond conjugated organic molecules.\textsuperscript{39,40} Aromaticity in inorganic compounds is a fairly new field of research. For a long time, these nontrivial species existed as metastable and short-lifetime systems in laser beams or just remained as theoretical predictions. An important contribution to the concept of aromaticity was made in 2018, when Saito and coworkers synthesized a bottleable doubly aromatic benzene derivative $[\text{C}_6(\text{SePh})_6]^{2+}$.\textsuperscript{41} Its unconventional aromatic behavior was supported not only by theoretical chemistry but also by electron paramagnetic resonance and X-ray analysis. These results further proved that aromaticity is applicable to various inorganic compounds. In the late 20\textsuperscript{th} century, Fowler and Ugalde used the $\pi$-aromaticity concept to describe unusual stability in boron clusters.\textsuperscript{42} Later on Robinson and coworkers used this concept for stability analysis in gallium complexes.\textsuperscript{43,44} Subsequently, Boldyrev, Wang and coworkers discovered aromatic behavior in a series of all-metal clusters.\textsuperscript{45,46} Thereafter, aromaticity was observed in various transition metal compounds with diverse stoichiometries and compositions.\textsuperscript{43,44,47–57}

Nowadays, aromaticity is used as a versatile tool for stability and bonding analyses in atomic clusters,\textsuperscript{58–73} all-metal systems,\textsuperscript{45,74–77} Zintl phases,\textsuperscript{78–81} and solid state compounds.\textsuperscript{82–85} Chapters 2-5 of this dissertation also deal with aromaticity in inorganic compounds.
Thus, the first project described in this dissertation is devoted to transition metal dichalcogenide (TMD) material MoS$_2$ and chemical bonding pattern in it (Chapter 2). TMD materials have been extensively studied during recent decades and, among them, MoS$_2$ has received the most attention due to its unique mechanical$^{86,87}$ and electronic$^{88-92}$ properties. MoS$_2$ is one of the most studied materials in the world and has found applications as a catalyst$^{91}$ and a lubricant.$^{86,87}$ And yet, some of its electronic structure aspects still remain unclear. Chapter 2 reports the complete bonding picture in a MoS$_2$ monolayer via aromaticity concept.

1-3. Stability and Chemical Bonding in Clusters

1-3.1. Atomic clusters

The search for new nanostructures is one of the defining aspects of modern nanoscience and technology. Atomic clusters represent a special class of nano-objects, an intermediate form of matter between molecules and materials with unique size- and composition-dependent properties. Understanding chemistry of these exotic species is of great importance for nanotechnology where atomic-scale manipulations are used to tune specific properties. In a broad sense, bonding and stability analysis in such systems is crucial for understanding the relations between various atomic-scale changes and resulting alterations in stability, reactivity, and other essential properties.

At the same time, bare atomic clusters are hard to synthesize in a “bottleable” form because they are thermodynamically metastable. This often hinders their in situ characterization. Experimental observation of clusters requires special techniques like matrix isolation or anion photoelectron spectroscopy. Bare atomic clusters can also be
liganded and stabilized in solids. Therefore, joint experimental and theoretical efforts are needed for their accurate characterization.

Chapters 3-5 are devoted to the structural and electronic analysis of negatively charged IrB₃, BiBₙ (n=6-8), and Au₉Zn clusters in collaboration with Prof. Lai-Sheng Wang (Brown University) whose group did the experimental part of the research. The gas-phase clusters are produced using anion photoelectron spectroscopy (PES) experiments. Clusters are generated using laser vaporization technique and then analyzed via a mass spectrometer. The desired cluster stoichiometry is mass-selected and photodetached by a laser. The photoelectrons are analyzed in a magnetic-bottle photoelectron apparatus. Such experiments allow detecting global minima and, in some cases, coexisting low lying isomers. Their photoelectron spectrum serves as an “electronic fingerprint” which can be compared with the calculated electron detachment energies of theoretically predicted low lying isomers.

Various algorithms for structural global minimum search (GM) exist. In this dissertation, Coalescence Kick (CK) and Adaptive Force-Field-Assisted Coalescence Kick (AFFCK) are used as the most suitable methods for GM searches of small to medium size clusters. CK and AFFCK are based on generating large enough number of starting geometries (with some physical and symmetry constraints) of a certain stoichiometry and subsequent ab initio optimization. Additionally, AFFCK method employs preliminary force field pre-optimization in order to accelerate further ab initio calculations.

Once theoretical results agree with experimental ones, GM’s structure, stability, and electronic properties can be explained via ab initio methods. Subsequently, structural and
compositional trends developed on the basis of such findings can be used for building chemical models.

1.3.1.1 IrB$_3^-$

Transition metals (TM) tend to form strong covalent bonds with boron. That is why transition metal borides have become an active field of search for ultrahard materials. However, their rational design needs deep understanding of atomic-scale bonding and stability trends in TM-B compounds. Small TM-B clusters are ideal systems for probing and testing these trends. Thus, Chapter 3 aims to elucidate the nature of B-Ir interactions. There have been limited previous studies on Ir-B interactions, and the nature of the stability and chemical bonding has not been completely understood even for the simplest iridium borides. Following experimental and theoretical procedures described above, we explored the potential energy surface of IrB$_3^-$, theoretically explained the PES spectrum, and analyzed the electronic structure of the observed low lying isomers.

1.3.1.2 BiB$_n^-$ ($n = 6$–$8$)

Bismuth is the heaviest stable metal in the periodic table. Due to its low toxicity relative to its neighbors, bismuth is considered a “green metal” and has received considerable attention in materials science and medicinal chemistry. As a heavy member of important III–V semiconductors, bismuth boride has unique electronic and optical properties with a wide potential for industrial applications. However, bulk bismuth borides have not been synthesized and there have been few experimental studies on bismuth–boron species.
Bismuth–boron clusters are ideal systems to probe the chemical bonding between Bi and B. They will lay the foundation to synthesize bulk bismuth borides or new bismuth–boron nanostructures. Thus, Chapter 4 is devoted to the joint experimental and theoretical study of BiB$_n^-$ ($n = 6$–8) clusters, their stability, and boron-bismuth chemical bonding.

1.3.1.3 \textit{Au}_9\textit{Zn}^-

Gold clusters have received significant attention over the past 2 decades\textsuperscript{120-124} because of the discovery of catalytic effects by gold nanoparticles.\textsuperscript{125,126} Among structural and electronic features, Au clusters are interesting by remarkable occurrence of planar σ-aromatic structures in pure and doped stoichiometries.\textsuperscript{127-132} The project reported in Chapter 5 is complementary in many ways to the studies on planar pure and doped golden clusters reported previously.\textsuperscript{127-132} Chapter 5 describes a collaborative study on the experimentally observed isomers of Au$_9$Zn$^-$. Using theoretical methods, we interpreted photoelectron spectra, performed the analysis structural and electronic stability, and examined aromatic patterns in the bonding picture.

1-3.2. \textit{Hydrated sulfate clusters SO}_4^{2-}\textit{(H}_2\textit{O})_n (n = 1–40)

Solvated species can be seen as a different form of clusters. These systems consist of individual molecules or ions with a central molecule (or an ion) surrounded by, e.g., water or ammonia molecules. The fragments are usually bonded by noncovalent interactions rather than strong covalent bonds. These clusters are ubiquitous in soils and atmospheric aerosols on Earth and across the Solar System.\textsuperscript{134-139} Therefore, atomic-scale study of these systems is crucial for environmental chemistry and for reliable modeling of atmospheric processes.
A prominent example of such systems is hydrated $\text{SO}_4^{2-}$ dianion. Interestingly, an isolated sulfate dianion is unstable due to a strong Coulomb repulsion between the two excess electrons.\textsuperscript{140-142} Lai-Sheng Wang and coworkers discovered that three water molecules are needed to stabilize this doubly charged system.\textsuperscript{142}

Chapter 6 of this dissertation reports a systematic study of $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ ($n = 0-40$) hydrated clusters to understand the nature of $\text{SO}_4^{2-}$ stabilization upon its hydration. We analyzed a dianion-water charge transfer and the role of a cage effect induced by surrounding water molecules.

1-4. Nonlinear Optical Properties

Nonlinear optics (NLO) is a sub-discipline of modern optics which describes various nonlinear effects that arise from the interaction of a laser with matter. In nonlinear media, the applied electric field $E$ causes nonlinear polarization response $P$. For example, this effect is used for second-harmonic generation – a process in which two photons interact with a nonlinear material and form a new photon with twice the energy of initial photons. NLO is extensively used in many fields such as optical computing, laser devices, optical communication, and image processing.\textsuperscript{143-151} Over the past 50 years, the search for new NLO materials has never stopped in an effort to develop new laser technologies and extend NLO applications. Chapters 7 and 8 show that defective cubic phases of alkaline earth oxides are good candidates for new types of nonlinear media.

1-4.1. MgO surface with periodic defects

Oxygen vacancies in MgO crystal (and other ionic compounds) contain a diffuse electron pair which is responsible for various electronic and catalytic properties.\textsuperscript{152-154}
Moreover, a diffuse electron density is a favorable condition for the emergence of nonlinear optical properties because such density is very responsive to the applied electric field. Chapter 7 describes stability and electronic properties of a defective MgO (001) surface. We proposed a strategy to extensively increase the efficiency of these defective sites by making them periodic on the MgO crystalline surface.

1.4.2. **Molecular electrides**

Electrides represent an unusual class of compounds where electrons are localized in space distinct from atomic positions and behave like diffuse anions. This type of localization makes electron density very flexible. Therefore, even a weak electric field causes significant nonlinear optical response. Since the first room-temperature stable electride was synthesized by Hosono in 2003, electrides have found plenty of applications in chemical reductants, electron emitting devices, electron-injection layers in organic LEDs, and boosting nitrogen dissociation for ammonia synthesis. To date, all synthesized electrides are bulk compounds. However, molecular size electrides have a potential to enhance the efficiency and extend their applications at nano scale. Chapter 8 describes a proposed strategy for designing molecular electrides as defective unit cells of cubic alkaline-earth oxides with a missing anion.

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CHAPTER 2

σ-AROMATICITY IN THE MoS$_2$ MONOLAYER$^1$

Abstract

Molybdenum disulfide is a prominent semiconductor that received a lot of attention due to its unique properties. Possessing a layered crystal structure, one can tune the band gap from indirect to direct while transforming the material from the bulk to monolayer structure. MoS$_2$ is a highly researched material. However, not all of the nature of this intriguing material is revealed yet. The aim of this work is to deepen the knowledge of the scientific community about MoS$_2$ by deciphering its bonding picture. In addition to 2-center bonds between neighboring Mo and S atoms, we showed that the remaining electrons are distributed over Mo atoms and form conjugated aromatic σ-bonds inside every hexagonal ring, which makes molybdenum the main carrier of σ-aromaticity in MoS$_2$ layer.

2-1. Introduction

Nowadays, the development of materials with tunable electronic and mechanical properties is a topical task in the field of nanoscience. The recent progress of experimental and theoretical techniques allows the fabrication and characterization of monolayer- and few-layer-scale structures that obtain different and unique properties as they transform from bulk to nanostructures. The need of the nanotechnology industry for materials with

desired properties is partially covered by transition metal dichalcogenides. Transition metal dichalcogenides (TMDs) form a big class of layered compounds with the general formula MX$_2$, where M stands for a transition metal, and X is a chalcogen. The neighboring layers interact via weak van der Waals forces,\(^1\) while M and X atoms within one layer have strong covalent bonding.\(^2,3\) TMD materials have been widely explored recently,\(^4\)–\(^12\) and amongst them, molybdenum disulfide (MoS$_2$)\(^13\)–\(^18\) received the most attention of researchers from different chemical and physical disciplines. The configuration of stacked layers exhibits properties of a dry lubricant, which found an application in aerospace technologies.\(^19,20\) Besides its outstanding mechanical characteristics, this layered material has the ability to transform from an indirect band gap of 1.2 eV in bulk to a direct band gap of 1.9 eV in the monolayer.\(^21,22\) Due to its unique electronic\(^23\)–\(^31\) and optical\(^18,32\) properties including tunable band gap,\(^16,33,34\) MoS$_2$ is one of the most intensively studied materials in the world. Different crystal phases\(^6,35\) of this TMD compound have a great variety of potential applications in solar batteries,\(^36\)–\(^41\) sensors, and detectors\(^42\)–\(^52\) due to the high band-edge excitation of d–d transitions. Despite the continuously growing number of publications dedicated to MoS$_2$, some of its fundamental aspects still remain unclear. The aim of this work is to provide a convincing bonding picture for the MoS$_2$ monolayer.\(^53,54\) In this paper, we perform the bonding analysis of this material and show that there are aromatic σ-bonds inside hexagonal rings. Mo atoms are the main carriers of this aromaticity.
2-2. Computational Methods

Solid-state calculations of the MoS$_2$ monolayer were performed within the density functional theory (DFT) formalism using the generalized gradient approximation with the Perdew–Burke–Ernzerhof exchange-correlation functional revised for solids (PBEsol) and the projected augmented wave approach, as implemented in the Vienna Ab-initio Simulation Package (VASP). The following lattice constants were used for the pristine MoS$_2$ unit cell (Figure 2-1): $a = b = 3.192$ Å, $c = 20.0$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 60^\circ$.

The first step is preparatory calculations for bonding analysis performed using a $3 \times 3 \times 1$ supercell with a 350 eV kinetic energy cutoff and $11 \times 11 \times 1$ $\Gamma$-centered Monkhorst–Pack $k$-point sampling. The vacuum gap is added only in the $z$-direction, and the monolayer remains continuous. The unit cell of $3 \times 3 \times 1$ size is chosen for computational convenience. Then, periodic natural bond orbital (NBO) and SSAdNDP calculations were performed for the bonding analysis. Periodic NBO, like the standard NBO code, enables the assignment of $1c$–$2e$ bonds (lone pairs) and $2c$–$2e$ bonds (2-centered 2-electron bonds). The SSAdNDP code, which is an extension of AdNDP for solid-state calculations, allows the recognition of multicenter delocalized bonds ($nc$–$2e$, $n > 2$). AdNDP works within the concept of electron density overlapping. AdNDP, particularly SSAdNDP, was successfully applied as a bonding decoder to many one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) systems including those with aromatic properties. Both NBO and AdNDP use the concept of occupation numbers (ONs), which represent the amount of electron density localized on a multicenter bond. The closer these values to 2.0, the more reliable a bonding picture is. A User-Directed Search procedure implemented in SSAdNDP (UD-SSAdNDP) allows solving nontrivial bonding cases. Comprehensive guidelines and
examples to UD search can be found in the Supporting Information of the following literature. ⁷⁴,⁷⁵

We chose the def2-TZVP ⁷⁶ basis set for the projection of PW for the electron density matrix used in SSAdNDP calculations to be in precise agreement with the initial PW results. The MN15L ⁷⁷/def2-TZVP level of theory was used for isolated cluster calculations via Gaussian16 ⁷⁸ software.

2-3. Results and Discussion

Periodic NBO and SSAdNDP showed that as was expected, every Mo atom is bonded to six neighboring S atoms by 2-center–2-electron (2c–2e) bonds (Figure 2-1B) with ONs = 1.8 |e|. This implies that every S is bonded to three Mo atoms by 2c–2e bonds. Additionally, every sulfur has a lone pair (1c–2e) on it (Figure 2-1A) with ONs = 1.9 |e|. For the purpose of this work, we simplified the description of 2c–2e Mo–S bonds to the Lewis-like level. It does not affect in any way the main idea of the current paper – the presence of σ-aromaticity inside hexagonal rings. What matters is that every such 2c–2e bond requires 2 electrons as well as every lone pair. Therefore, after localization of all lone pairs and 2c–2e bonds 18 out of 162 valence electrons remain unlocalized in our unit cell. We tested 1c–1e bonds on S and 1c–2e bonds on Mo atoms in both spin-polarized and closed-shell configurations but occupation numbers (ONs) of such bonds are about 0.4–0.5 |e|, which does not look very convincing. This indicates the presence of conjugated multicenter bonds.

After testing several bonding combinations, we say without any doubt that the MoS₂ monolayer possesses sigma aromaticity inside every hexagonal ring, that is, 3c–2e
multicenter bonds over 3 Mo atoms with ONs being $\sim 1.5 \, |e|$ (Figure 2-2). As we can see in Figure 2-2, these sigma bonds in some way consist of $3d_{x^2}$ molybdenum orbitals connected in the center of the ring. The $\sigma$-bonding is quite nontrivial since we observed that the major contribution to these $\sigma$-bonds comes from Mo atoms, i.e., when localizing conjugated orbitals like 9c–2e bonds over 3 molybdenum and 6 sulfur atoms, the ONs are just slightly higher being $\sim 1.6 \, |e|$. Therefore, we refer these conjugated sigma systems as 3c–2e sigma bonds localized over Mo atoms. Alvarez et. al. 79 showed that Mo covalent radius is $1.54 \, \text{Å}$, which, definitely, enables the overlapping of Mo electron density within the MoS$_2$ system.

It is worth mentioning that the energy difference between the closed- and open-shell configurations is just $5 \times 10^{-8} \, \text{eV}$ according to our level of theory. Both configurations give absolutely the same bonding pattern.

The reader may set a fair point that the picture of the 3c–2e orbital is not smooth. The problem likely lies in the periodic NBO projection code since d-metals like molybdenum are always tricky subjects in the field of quantum chemistry calculations. Indeed, the average value of the “spillover” output parameter of the projection code is 0.82, while its highest allowed value is 1.01. Once at least one of the spillover values exceeds this threshold, the results are not reliable anymore. Our value of 0.82 is below 1.01, so the results are trustworthy. However, based on our experience, when the system does not contain any d- or f- elements, the spillover values are of the order of $<10^{-3}$. That is why we assign the problem of the picture distortion to the interaction of d-electron density and projection code. Anyway, the code, definitely, works good enough for this system and qualitatively proves the presence of $\sigma$-aromaticity.
To further verify the presence of electron density inside the hexagonal ring, we performed Electron Localization Function (ELF) analysis. As can be seen in Figure 2-3, there is a triangle-like area of electron localization probability inside rings, which we interpret as the analog of the proposed delocalized σ-bond.

Thermal 2D-slices of ELF are presented in Figure 2-4. Noticeably, according to the thermal map, the highest ELF value inside the triangle area corresponds to the highest observable value around Mo atoms in all directions. This fact indicates that the remaining 18 electrons of the system indeed show delocalized behavior rather than lone pair character. The above-mentioned triangle-like area is marked with purple triangles in Figure 2-4. For the reader’s convenience, we indicated locations of Mo and S atoms in 2D-slices.

The analysis of the isolated cluster model is complicated by nontrivial periodic conditions; however, such complexity even supports our idea to some degree. Let us consider one solitary neutral ring with S atoms being bonded by Mo from all three directions (Figure 2-5). The system contains 72 valence electrons. 48 of them are localized in a trivial way as six 1c–2e lone pairs on S and 18 2c–2e bonds between every S and Mo. Then, AdNDP reveals one lone pair on each Mo located on “triangle” vertices (Figure 2-6, left). No other lone pairs were found either on S or Mo as well as in solid-state calculations. Interestingly, we have found six 2c–2e bonds between Mo atoms with ONs = 1.8 |e| that form an outer frame (Figure 2-6, right). These six Mo–Mo bonds are likely to be formed by the electrons that molybdenum shares with sulfur in the periodic system. This fact once more indicates the strong electron density overlapping of Mo atoms.

66 electrons are localized to this point meaning that 6 electrons, or 3 bonds, remain unlocalized yet. For symmetry reasons, we initially tried to localize the remaining bonds
over three triangles as shown in Figure 2-7 (left). 3c–2e localization over 3 Mo atoms is not very convincing with an ON of just 1.3 |e|. When the S atoms are treated alongside with Mo, that is, when the complete 5c–2e triangle is considered, the ON is increased to 1.6 |e|. However, the bond shape (see Supporting Information (SI) of the original paper, Figure S1) makes no sense in terms of potential periodic extension (Figure 2-9). Indeed, the 5c–2e bond expectedly disappears when a bigger cluster with more rings is considered (see SI of the original paper, Figure S2) with the ON being reduced to 1.4 |e|.

The ON of the 3c–2e σ-bond inside the ring (Figure 2-8) is 1.8 |e|, and this bond does not break any symmetry and periodicity rules.

In addition, 4 electrons remain unlocalized yet. We believe that there is no way to localize them symmetrically because of the extremely complicated periodic conditions in the solid state, which are impossible to model within the isolated neutral cluster model. In qualitative approximation, every above-mentioned triangle (Figure 2-7) is a part of three neighboring hexagonal rings. Considering the presence of a 3c–2e σ-bond inside every ring, the triangle formally possesses 1/3 electron density of every σ-bond, i.e., 2/3 |e|. A schematic representation is given in Figure 2-7(right). In sum, there are 2/3 × 3 = 2 |e| on each triangle that came from three neighboring rings. In this cluster model, there are three triangles and only one ring. Roughly speaking, 2/3 |e| are withdrawn from each triangle to form one 3c–2e σ-bond inside a ring, while the remaining 4/3 |e| have nowhere to go due to the lack of periodicity. In total, 4/3 × 3 = 4 electrons remain unlocalizable since there are not enough rings in the isolated cluster model. The same bonding pattern is observed when a bigger cluster model is considered (Figure 2-9) with more unlocalizable bonds.
Obviously, such an explanation aims at giving an understanding of why 4 electrons remain unlocalized rather than provide the physical insight into electron distribution.

The extended isolated cluster model (Figure 2-9) allows shedding some light on the 2c–2e bonding nature between Mo and S atoms. For example, let us consider the Mo atom, marked by a red circle in Figure 2-9, which experiences an approximated solid-state surrounding. According to the NBO analysis, it forms the following 2c–2e bonding combination with each S atom: 46% of electron density are attributed to Mo and 54% to S. 20% of molybdenum density are formed by p-electrons and 77% of d-electrons, while 18% of sulfur density comes from s-electrons and 81% from p-electrons. These numbers indicate that two-center bonding shows mostly covalent behavior between the d-electrons of molybdenum and the p-electrons of sulfur. However, sulfur forms 3 covalent bonds with neighboring molybdenum atoms but possesses 4 p-electrons. Interestingly, the NBO analyses in the cluster model show that the s-lone pair on sulfur is approximately 50% s-density and 50% p-density. These facts alongside with solid-state NBO charges, $\text{Mo}^{0.96+}\text{S}_2^{0.48-}$, and ELF analysis make reasonable the idea of covalent bonding between Mo and S, leaving the resonance interpretation possible, i.e., two single sulfur 3p-electrons interact with two Mo atoms through covalent bonds, and the paired 3p-electrons coordinate with one Mo atom that provides an empty orbital. Additionally, sulfur s-density is involved to a certain degree. As we can see, the 2c–2e bonding picture is complex in its electron involvement but can be simplified to the Lewis-like level.

The further discussion of the 2c–2e bonding nature is beyond the scope of the current research. As we mentioned above, what matters is electron counting. Indeed, the simplified
Lewis-like bonding model via AdNDP is independent of the presence of any resonances and takes into account only electron counting.

2-4. Conclusions

As we found using the SSAdNDP approach, there are 2c–2e bonds between Mo and S as well as one lone pair on each S in the MoS$_2$ monolayer. Next, we found that the only way to localize the remaining electrons is to conjugate the 3c–2e σ-bonds inside every hexagonal ring. That is, three molybdenum atoms of every ring are the main carriers of the proposed σ-aromaticity. The Mo covalent radius of 1.54 Å enables electron density overlapping. ELF analysis and the isolated cluster model support the idea of σ-aromaticity inside hexagonal rings as well as Mo–Mo electron density overlapping.

We believe that the deciphering of the MoS$_2$ monolayer bonding picture is an essential step toward understanding the nature of this unique and multifunctional material. We hope that our observation may shed light on some important aspects of molybdenum disulfide in the future.

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Tables and Figures

Figure 2-1. (A) 1c–2e s-lone pairs of S atoms, ONs = 1.9 $|e|$. (B) 2c–2e Mo–S bond, ONs = 1.8 $|e|$. Hereinafter, Mo atoms are purple, and S atoms are yellow.

Figure 2-2. Sigma-aromatic orbital inside of the hexagonal MoS$_2$ ring.

Figure 2-3. ELF of MoS$_2$. The isosurface value is 0.4.
Figure 2-4. Left: ELF slice with 001 Miller indices; the sliced plane contains Mo atoms; three Mo and three S atoms are placed for convenience purposes. Right: ELF slice with 100 Miller indices. Purple triangles indicate the same point sliced in different directions.

Figure 2-5. Isolated MoS$_2$ cluster model.

Figure 2-6. Left: three 1c–2e lone pairs on Mo atoms, ONs = 1.6. Right: 2c–2e Mo–Mo bonds; only 3 out of 6 are depicted for convenience purposes.
Figure 2-7. Left: Triangle-like structure of the MoS$_2$ isolated cluster. Right: schematic representation of $\sigma$-aromaticity electron distribution. Dotted lines indicate missing rings in the cluster model.

Figure 2-8. 3c–2e $\sigma$-aromatic bond inside the hexagonal ring. ON = 1.8 $|e|$.

Figure 2-9. Extended isolated MoS$_2$ cluster model.
CHAPTER 3

HIGH-RESOLUTION PHOTOELECTRON IMAGING OF IrB$_3^-$: OBSERVATION OF A π-AROMATIC B$_3^+$ RING COORDINATED TO A TRANSITION METAL$^1$

Abstract

In a high-resolution photoelectron imaging and theoretical study of the IrB$_3^-$ cluster, two isomers were observed experimentally with electron affinities (EAs) of 1.3147(8) and 1.937(4) eV. Quantum calculations revealed two nearly degenerate isomers competing for the global minimum, both with a B$_3$ ring coordinated with the Ir atom. The isomer with the higher EA consists of a B$_3$ ring with a bridge-bonded Ir atom ($C_s$, $^2A'$), and the second isomer features a tetrahedral structure ($C_{3v}$, $^2A_1$). The neutral tetrahedral structure was predicted to be considerably more stable than all other isomers. Chemical bonding analysis showed that the neutral $C_{3v}$ isomer involves significant covalent Ir–B bonding and weak ionic bonding with charge transfer from B$_3$ to Ir and can be viewed as an Ir–($\eta^3$-B$_3^+$) complex. This study provides the first example of a boron-to-metal charge-transfer complex and evidence of a π-aromatic B$_3^+$ ring coordinated to a transition metal.

The electron deficiency of boron leads to unique delocalized bonds in boron compounds and clusters, which can exhibit π and σ double aromaticity. A review specifically focused on the double aromaticity of three-centered boron rings appeared in 2006.$^{[1]}$ The B$_3^-$ anionic cluster is the smallest possible doubly (π and σ) aromatic

The B$_3^+$ cation is only $\pi$-aromatic and has recently been observed in complexes with CO and N$_2$. A previous computational study suggested that B$_3^-$ might be stabilized by Na$^+$ to form an Na$^+$B$_3^-$ salt. Two alkali-stabilized boron clusters were observed previously, LiB$_6^-$ and LiB$_8^-$.

Both species had similar structures to their analogous pure boron cluster dianions, suggesting that it is possible to stabilize aromatic boron clusters with alkali metals. A theoretical study has examined the stability of the B$_3^-$ ring in sandwich complexes with alkali and alkali earth elements. It was found that only heterodecked sandwiches were stable when capped with cyclopentadienyl (Cp$^-$). Recently, a $\pi$-aromatic B$_3$ ring was synthesized as B$_3$R$_3^2-$ stabilized by Na$^+$ and sterically protected by bulky ligands. The bonding in B$_3$R$_3^2-$ was found to be identical to that in B$_3$H$_3^2-$, which is analogous to C$_3$H$_3^+$. Doubly aromatic three-membered-ring bishomotriborirane and triboracyclopropanate were also synthesized as lithium salts. Boranes with as few as three or four boron atoms are known, including several metalloboranes with iridium, although their bonding is quite different from the bare boron clusters.

Anion photoelectron spectroscopy (PES) has been shown to be a powerful technique to probe the electronic structure and chemical bonding of size-selected boron clusters. Combined with theoretical calculations, PES has also been used to elucidate numerous transition-metal-doped boron clusters. In particular, the PE spectrum of TaB$_3^-$ revealed that the Ta–B interactions are stronger than B–B interactions because its lowest-energy structure features a Ta atom inserted into a B–B bond of the B$_3$ ring. On the other hand, the lowest-energy structure of AuB$_3^-$ contained a B$_3$ ring with the Au atom bonded to an apex B atom, revealing a very different Au–B bonding mode that is
analogous to the H–B bond. Joint PES and theoretical studies of lanthanide-doped boron clusters have been reported recently, revealing both half-sandwich and inverse-sandwich complexes, as well as several transition-metal diboride clusters. Most recently, a small lanthanide-doped boron cluster, PrB3−, was found to be planar with Pr II[η2-B33−] coordination. The question we were trying to address in this study is whether three-membered aromatic boron rings can coordinate with a transition metal in η3-B3 coordination while retaining σ or π aromaticity.

Herein we report a high-resolution PE imaging (PEI) and theoretical study of the IrB3− cluster. Two isomers were observed in the PEI experiment. Theoretical calculations found two nearly degenerate low-lying isomers: a quasiplanar isomer with an η2-B3 moiety coordinated to Ir, and a tetrahedral structure with an η3-B3 moiety coordinated to Ir. In the neutral potential-energy surface, the tetrahedral structure was found to be much more stable than all other isomers owing to favorable Ir–B covalent bonding and weak electron donation from the B3 ring to Ir to form a (B3)+Ir− cluster with a π-aromatic B3+ moiety. This compound is the first example of a transition-metal-doped boron cluster in which the negative charge is donated from the boron ring to a metal center.

The PEI experiment was performed on a high-resolution photoelectron imaging apparatus. Figure 3-1 shows the reconstructed PE images and spectra measured at photon energies of 2.3305 and 3.4958 eV. The PE spectrum taken at 2.3305 eV (Figure 3-1 a) reveals two bands (X′ and X), each with well-resolved vibrational progressions around 1.3 and 2.0 eV. By varying the cluster temperature, we found that these two bands corresponded to two isomers, with band X′ coming from a slightly higher energy isomer because its relative intensity increased under hotter source conditions (see Figure S1 in the
Supporting Information of the original paper.\cite{19} Band $X'$ displays a single vibrational progression with the 0–0 transition centered around 1.32 eV. A second band with its 0–0 peak at 1.937(4) eV exhibits rich vibrational structures. More PES bands were observed in the 3.4958 eV spectrum ($A$–$E$, $A'$, and $B'$). The relative intensities of bands $A'$ and $B'$ were found to correlate with that of band $X'$ (see Figure S1 in the original paper), and they must come from the same isomer. All the observed bands and their binding energies are summarized in Table 3-1, where they are compared with the theoretical results.

Higher-resolution PE spectra for band $X'$ at lower photon energies are presented in Figure 3-2. The 1.3471 eV spectrum (Figure 3-2 a) shows several well-resolved vibrational features near the 0–0 peak, all coming from hot band transitions. A new intense vibrational peak was observed in the 1.3722 eV spectrum along with two weak hot band transitions (Figure 3-2 b). One more intense peak in Figure 3-2 c seems to come from a hot band transition. This peak was identified as a hot band because there are no symmetry-allowed modes close to this frequency (see below). Another intense peak was observed in the 1.4399 eV spectrum (Figure 3-2 d). This peak corresponds to a new vibrational mode (see below). The binding energies and angular distributions of all the observed vibrational transitions are provided in the Supporting Information (see Table S1 and Figures S2–S4 in the original paper).\cite{19}

Theoretical calculations were performed for $\text{IrB}_3^-$.\cite{19} The global minima of $\text{IrB}_3^-$ were searched using the coalescence kick method,\cite{20} the TPSS functional,\cite{21} and the lanl2dz basis set.\cite{22} The lowest-energy isomers were reoptimized at the TPSS/aug-cc-pVTZ-PP\cite{23} level of theory. Previous studies on $\text{TaB}_3^-$ and $\text{B}_3\text{Au}^-$ yielded satisfactory results using similar methods.\cite{12m,12n} All calculations were performed with the Gaussian 09
program. The three isomers within 0.2 eV of the global minimum are shown in Figure 3-3 (see Figure S5 in the original paper for all low-lying isomers within 2 eV of the global minimum). The lowest-energy anion at the DFT level (isomer A.1) consists of a B₃ ring with a bridge-bonded Ir atom. The second isomer (A.2) has a tetrahedral structure with a B₃ ring capped by the Ir atom. The third isomer (A.3) has a fan structure, which can be viewed as the Ir atom inserted into a B–B bond of a B₃ ring. Using the ROCCSD(T) method, we found that isomers A.1 and A.2 become nearly degenerate with A.2 being 0.01 eV more stable, while isomer A.3 is only slightly higher in energy. The ROCCSD(T) calculations were single-point calculations using the TPSS-optimized geometries, which are not necessarily the minimum on the ROCCSD(T) potential-energy surface. The most stable neutral structures are also shown in Figure 3-3. The tetrahedral structure with a singlet spin state (N.2) is significantly more stable than the two planar isomers (N.1 and N.3).

The adiabatic (ADE) and vertical detachment energies (VDE) were calculated for each isomer. The ADE for isomers A.2 and A.1 was calculated to be 1.20 and 1.86 eV, respectively, using the ROCCSD(T) method (Table 3-1). Isomer A.3 was found to have an ADE of 1.90 eV by the same method. Several calculated vibrational frequencies for isomers A.2, N.1, and N.2 are presented in Figure 3-4 (see Table S2 for the full list of vibrational frequencies).

The calculated ADE for the planar isomer A.1 agrees well with the 00 transition of band X (Table 3-1). The vibrational peaks in the X band are almost evenly spaced, but the alternating intensities of the peaks suggest that two modes are involved, with the frequency of one of the modes almost twice that of the other mode. The geometry changes from A.1
to N.1 (Figure 3-3) suggest that the two Franck–Condon active modes should be the Ir–B₃ stretching mode \( (\nu_3=529 \text{ cm}^{-1}) \) and the bending mode \( (\nu_4=292 \text{ cm}^{-1}) \), as shown in Figure 3-4. There should be a long bending progression off each stretching level. However, the \( 4^2 \) transitions overlap with the stretching transitions, thus resulting in the uneven vibrational profile. The \( \beta \) values for all of the vibrational peaks are around 0.5 (see Figure S4 in the original paper), thus indicating that the outgoing wave has some \( p \) character, which is consistent with the predicted detachment from the HOMO orbital that involves the 5d orbital of Ir (see Figure S6 in the original paper). The higher-binding-energy features in Figure 3-1 b can all be assigned using the TDDFT results (Table 3-1). We can rule out isomer A.3 because none of its calculated vibrational frequencies (see Table S2, Supporting Information in the original paper) match the experimental values.

The \( ^0_0 \) transition of band \( X' \) agrees well with the calculated ADE for the tetrahedral isomer A.2 (Table 3-1). The high-resolution spectra in Figure 3-2 yield accurate vibrational frequencies. Two fundamental progressions for neutral isomer N.2 can be assigned as the Ir–B₃ stretching mode \( ((370\pm10) \text{ cm}^{-1}) \) and B₃ breathing mode \( ((900\pm10) \text{ cm}^{-1}) \), in agreement with the structural changes from A.2 to N.2 (Figure 3-3). The measured frequencies agree well with the calculated values (Figure 3-4). Furthermore, we were able to estimate the corresponding vibrational frequencies for the A.2 anion isomer, as compared with the computed values in Figure 3-4. We can also assign several combination modes (see Table S1, Supporting Information in the original paper) using the calculated frequencies (see Table S2, Supporting Information in the original paper).\(^{[19]}\) The \( ^0_0 \) peak of band \( X' \) has a \( \beta \) value approaching 2 at high kinetic energies
owing to the contribution of the $5d_{x^2}$ orbital (see Figure S6 in the original paper), whereas nearly all peaks in Figure 3-2 have negative $\beta$ values owing to the interference of the outgoing $p+f$ wave (see Figure S4 in the original paper). The vibrational peaks involving the $10'$ transitions are significantly enhanced, probably as a result of vibronic coupling.

We performed adaptive natural density partitioning (AdNDP) analysis on the neutral species to elucidate the chemical bonding in each isomer (Figure 3-5). The planar N.1 isomer consists of two 5d lone pairs and four two-center–two-electron (2c-2e) bonds around the periphery from the B 2s and Ir 5d$_{yz}$ orbitals (Figure 3-5 b). There are also two 3c-2e bonds involving the B 2p and Ir 5d orbitals, as well as two 3c-1e bonds delocalized over the B$_3$ ring. The 3c-1e $\pi$ bond is reminiscent of the 3c-2e bonds in B$_3^+$ shown in Figure 3-5a for comparison. The two 3c-1e single-electron bonds are similar to the doubly aromatic $\sigma$ and $\pi$ bond in B$_3^-$; the single-electron bonds are consistent with lower stability of the planar open-shell IrB$_3$ neutral cluster. It is expected that this isomer would be more competitive in the closed-shell [IrB$_3$]$^{2-}$ system.

Our AdNDP analysis for the N.2 tetrahedral global minimum (Figure 3-5 c) reveals two 5d lone pairs and three 2c-2e Ir–B bonds. The three 3c-2e bonds mainly describe B–B bonding (see Figure 3-5a for B$_3^+$) with contributions also from the 5d$_{xy}$ or $5d_{x^2-y^2}$ orbitals, as emphasized in Figure 3-5 c. The 4c-2e bond involves bonding between the Ir 6s orbital and the $\pi$ bond in B$_3^+$, thus preserving the $\pi$ aromaticity in the tetrahedral N.2 isomer. This optimal bonding between Ir and the B$_3$ ring in the tetrahedral isomer underlies its considerable stability on the neutral potential energy surface. Natural bond orbital (NBO) charge analysis on N.2 gave $Q$(Ir)=$-0.394$ e, which indicates, surprisingly, that charge
is transferred from the B$_3$ unit to the metal. Therefore, isomer N.2 can be viewed approximately as (B$_3$)$_{\text{3+}}$Ir$^{-}$, which is the first example of the coordination of a B$_3^{\text{3+}}$ cation to a negatively charged transition metal. The surprising direction of charge transfer can be understood by the high electronegativity of iridium (2.20) as compared to boron (2.04). The ionic interaction provides further stabilization of the tetrahedral isomer. Interestingly, the structures of the MB$_3$$^{-}$ clusters depend on the nature of the interactions between M and B. The strong Ta−B bonding results in a fanlike global minimum for TaB$_3$$^{-}$, whereas the relatively weak Au−B bonding leads to a terminal Au−B bond in AuB$_3$$^{-}$. The Ir−B bonding is between the Ta−B and Au−B bonding, thus resulting in two nearly degenerate global minima with a side-on Ir−(η$_2^-$-B$_3$) structure and a tetrahedral Ir−(η$_3^3$-B$_3$) structure.

In conclusion, we have reported a high-resolution photoelectron imaging and computational study on the IrB$_3$− cluster. Photoelectron spectroscopy revealed the presence of two isomers in the cluster beam of IrB$_3$−. Two nearly degenerate low-lying isomers, with a quasiplanar η$_2^-$-B$_3$ moiety coordinated to Ir and an η$_3^3$-B$_3$ tetrahedral structure, were found computationally to compete for the global minimum in the anion. The computed electron binding energies and vibrational frequencies of these two isomers are in good agreement with the experimental results. In the neutral species, tetrahedral IrB$_3$ was found to be significantly more stable than any other isomers. Chemical bonding analysis revealed strong covalent bonding between Ir and B$_3$ in the tetrahedral isomer, in which the aromaticity of the B$_3$ unit is maintained. Surprisingly, it was further found that there is a small amount of charge transfer from the B$_3$ unit to Ir in the tetrahedral isomer. The current
study discloses the smallest π-aromatic system, B$_3$$^+$, stabilized by a negatively charged transition metal, which may be viable for bulk synthesis with suitable ligands.

References


[19] See supporting information of the original paper for experimental details, computational methods, temperature dependent spectra, detailed peak positions and angular distributions, all low-lying isomers, and calculated vibrational frequencies.


**Tables and Figures**

Table 3-1. Experimental ADEs and VDEs and the calculated values along with the final neutral states and valence-electron configurations for the two IrB$_3^-$ low-lying isomers.

<table>
<thead>
<tr>
<th>Isomer A.2/N.2</th>
<th>Experimental</th>
<th>Final State and Electronic Configuration</th>
<th>Theoretical ADE/VDE</th>
<th>Peak ADE/VDE$^a$</th>
<th>Final State and Electronic Configuration</th>
<th>TPSS</th>
<th>ROCCSD(T)</th>
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<tr>
<td>X'</td>
<td>1.3147(8)</td>
<td>$^1$A$_1$...4a$_1^2$3e$_1^2$45a$_1^2$4e$_1^2$6a$_1^2$5e$_1^4$7a$_1^0$</td>
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<td>ROCCSD(T)</td>
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<td>A'</td>
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<td>B'</td>
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<th>Isomer A.1/N.1</th>
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<th>Theoretical ADE/VDE$^a$</th>
<th>Peak ADE/VDE$^a$</th>
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<th>ROCCSD(T)</th>
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<td>X</td>
<td>1.937(4)/2.026(4)</td>
<td>$^3$B$_1$...4b$_2^2$1a$_2^2$8a$_1^2$9a$_1^2$3b$_1^1$</td>
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Figure 3-1. Photoelectron images and spectra at a) 2.3305 eV (532.00 nm) and b) 3.4958 eV (354.67 nm). The vertical lines denote vibrational progressions. The insert in (a) shows the vibrational assignments for band X. The double arrow below the images shows the laser polarization.
Figure 3-2. High-resolution photoelectron images and spectra at a) 1.3471 eV (920.38 nm), b) 1.3722 eV (903.54 nm), c) 1.3910 eV (891.33 nm), and d) 1.4399 eV (861.06 nm). The vertical lines denote fundamental vibrations; hot band transitions are labeled. The double arrow below the images shows the laser polarization.
Figure 3-3. Optimized structures for the ground states and low-lying isomers for IrB$_3^-$ and IrB$_3$. Bond lengths are given in Å. Relative energies are given in eV at the TPSS level followed by the ROCCSD(T) values in brackets.
Figure 3-4. Displacement vectors and computed vibrational frequencies of the observed vibrational modes of isomers A.2, N.1, and N.2 (see Figure 2-3). The values in brackets are the measured frequencies.
Figure 3-5. Adaptive natural density partitioning (AdNDP) analysis for isomers N.1 (b) and N.2 (c). The AdNDP result of B$_3^+$ (a) is given for comparison. The solid and dashed boxes emphasize the $\sigma$ and $\pi$ bonds, respectively, in the two isomers of IrB$_3$ that are similar to those in B$_3^+$ (a).
CHAPTER 4
PHOTOELECTRON SPECTROSCOPY OF SIZE-SELECTED
BISMUTH–BORON CLUSTERS: BiB\textsubscript{n}– (n = 6–8)\textsuperscript{1}

Abstract

Because of its low toxicity, bismuth is considered to be a “green metal” and has received increasing attention in chemistry and materials science. To understand the chemical bonding of bismuth, here we report a joint experimental and theoretical study on a series of bismuth-doped boron clusters, BiB\textsubscript{n}– (n = 6–8). Well-resolved photoelectron spectra are obtained and are used to understand the structures and bonding of BiB\textsubscript{n}– in conjunction with theoretical calculations. Global minimum searches find that all three BiB\textsubscript{n}– clusters have planar structures with the Bi atom bonded to the edge of the planar B\textsubscript{n} moiety via two Bi–B σ bonds as well as π bonding by the 6p\textsubscript{z} orbital. BiB\textsubscript{6}– is found to consist of a double-chain B\textsubscript{6} with a terminal Bi atom. Both BiB\textsubscript{7}– and BiB\textsubscript{8}– are composed of a Bi atom bonded to the planar global minima of the B\textsubscript{7}– and B\textsubscript{8}– clusters. Chemical bonding analyses reveal that BiB\textsubscript{6}– is doubly antiaromatic, whereas BiB\textsubscript{7}– and BiB\textsubscript{8}– are doubly aromatic. In the neutral BiB\textsubscript{n} (n = 6–8) clusters, except BiB\textsubscript{6} which has a planar structure similar to the anion, the global minima of both BiB\textsubscript{7} and BiB\textsubscript{8} are found to be half-sandwich-type structures due to the high stability of the doubly aromatic B\textsubscript{7}\textsuperscript{3–} and B\textsubscript{8}\textsuperscript{2–} molecular wheel ligands.

4-1. Introduction

The electron deficiency of boron results in a variety of bulk allotropes and compounds consisting of different three-dimensional (3D) cages. Over the past two decades, extensive research has been conducted on size-selected boron clusters using joint experimental and first-principle theoretical studies. Different from the bulk, small boron clusters have been found to process predominantly two-dimensional (2D) structures consisting of B₃ triangles decorated with tetragonal, pentagonal, or hexagonal holes. One of the most interesting 2D boron clusters is the C₆₀ B₃₆ cluster with a central hexagonal hole, providing the first experimental evidence of the viability of atom-thin 2D boron (borophene). Borophenes have been realized on metal substrates, becoming a new class of synthetic 2D materials. The B₄₀ cluster was found to have a cage structure marking the discovery of the first all-boron fullerene (borospherene), while the B₄₈⁻ cluster with a bilayer structure was the largest bare boron cluster interrogated experimentally up to date. Numerous metal-doped boron clusters have also been produced and studied, significantly expanding the structural diversity of nanoborons. The study on transition-metal-doped boron clusters revealed the existence of various structures including metal-centered borometallic molecular wheels, metallo-boronanotubes, and metallo-borophenes. The PrB₇⁻ cluster contains a half-sandwich structure featuring a B₇³⁻ moiety, which was also found recently in B₉O⁻. Dilanthanide boron clusters were found to form inverse sandwiches, while La₃B₁₈⁻ features the first spherical trihedral metallo-borospherene.

Bismuth is the heaviest stable metal element in the periodic table, but it has low toxicity relative to its neighbors. In fact, bismuth is considered a “green metal”, and it
has received increasing attention in chemistry, materials science, and medicinal chemistry. \textsuperscript{28−30} Being a heavy member of the important III–V semiconductor family, bismuth boride has unique electronic and optical properties with significant potentials for industrial applications. \textsuperscript{31−33} However, bulk bismuth borides have not been synthesized. Because of their large size discrepancy, the bismuth–boron bond is expected to be weak, although little is known. Only recently have a series of studies focusing on the bismuth–boron bonding been reported in BiBO\textsuperscript{−}, Bi\textsubscript{2}B\textsuperscript{−}, and BiB\textsubscript{2}O\textsuperscript{−}, which are found to contain a single Bi–B, double Bi≡B, and triple Bi≡B bond, respectively. \textsuperscript{34,35} Other than that, there have been few experimental studies on bismuth–boron species except a recent investigation on the dibismuth boride clusters of Bi\textsubscript{2}B\textsubscript{n−} (n = 2–4). \textsuperscript{36}

Bismuth–boron clusters are not only ideal systems to probe the chemical bonding between Bi and B, but they will also lay the foundation to synthesize bulk bismuth borides or new bismuth–boron nanostructures. In the current work, we report a joint photoelectron spectroscopy (PES) and theoretical study on a series of bismuth-doped boron clusters, BiB\textsubscript{n−} (n = 6–8). Well-resolved photoelectron spectra are obtained for all three clusters and are combined with theoretical calculations to elucidate their structures and bonding. The global minima of the BiB\textsubscript{n−} (n = 6–8) clusters are all found to have 2D structures featuring a Bi atom bonded to the edge of a planar B\textsubscript{n} motif. Chemical bonding analyses show that the elongated BiB\textsubscript{6−} cluster is doubly antiaromatic, while both BiB\textsubscript{7−} and BiB\textsubscript{8−} are doubly aromatic. Interestingly, the global minima of neutral Bi\textsubscript{7} and Bi\textsubscript{8} are three-dimensional (3D) half-sandwich-type structures as a result of the high stability and aromaticity of the B\textsubscript{7}\textsuperscript{3−} and B\textsubscript{8}\textsuperscript{2−} molecular wheel motifs.
4-2. Experimental and Theoretical Methods

4-2.1. Photoelectron Spectroscopy

The experiment was conducted by using a magnetic-bottle PES apparatus equipped with a laser-vaporization supersonic cluster source, the details of which have been published elsewhere.\textsuperscript{8,37} The BiB\textsubscript{n}\textsuperscript{−} (n = 6–8) clusters were produced by laser vaporization of a disk target prepared by mixing powders of bismuth and \textsuperscript{11}B-enriched boron (1/1 Bi/B molar ratio). The laser-induced plasma was cooled by a high-pressure He carrier gas seeded with 5\% Ar, initiating nucleation and cluster formation. The nascent clusters were entrained by the carrier gas and underwent a supersonic expansion to produce a cold cluster beam. The cluster temperature was expected to be below room temperature\textsuperscript{38} and could be varied slightly by controlling the resident time of the cluster in the nozzle.\textsuperscript{8} The Ar-seeded helium carrier was found to be better for cooling heavier clusters, as demonstrated previously by the observation of Ar-tagged Au\textsubscript{x}\textsuperscript{−} clusters.\textsuperscript{39} After passing a skimmer, anionic clusters were extracted from the collimated cluster beam and analyzed by time-of-flight mass spectrometry. The clusters of interest were mass-selected and decelerated before photodetachment by a laser beam from the fourth harmonic of a Nd:YAG laser at 266 nm (4.661 eV). Photoelectrons were collected at nearly 100\% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The photoelectron kinetic energy (E\textsubscript{k}) was calibrated by using the known spectrum of Bi\textsuperscript{−}. The resolution of the magnetic-bottle photoelectron analyzer was $\Delta E\textsubscript{k}/E\textsubscript{k} \approx 2.5\%$, that is, \textasciitilde 25 meV for 1 eV electrons.
4.2.2. **Theoretical Methods**

Global minimum searches were performed by using the AFFCK code, which was an efficient global optimization method through the introduction of an intermediate step where structures were optimized by using a classical force field generated on the fly within the algorithm. About 1300 starting geometries were generated for BiB$^{6-}$ and $\sim$2000 for BiB$^{7-}$ and BiB$^{8-}$. After the initial optimization at the PBE0/LANL2DZ level, the low-lying isomers were reoptimized at the PBE0/aug-cc-pVTZ level of theory (with the effective core potential for Bi) as implemented in Gaussian-16. Both singlet and triplet states for BiB$^{6-}$ and BiB$^{8-}$, and doublet and quartet states for BiB$^{7-}$, were tested for each generated structure. The one-determinant character of the global minimum wave functions was examined by the wave function stability test (stable = opt).

Vertical detachment energies (VDEs) and adiabatic detachment energies (ADEs) were calculated by using two approaches: (1) time-dependent DFT (TD-DFT) at the PBE0/aug-cc-pVTZ level of theory and (2) CCSD(T)/def2-TZVP. The first vertical detachment energy (VDE$_1$) was calculated as the energy difference between the neutral and anion at the optimized anion geometry. The ADE was computed by using the optimized anion and the optimized neutral for the corresponding anion structure. Spin–orbit effects were not treated explicitly in the current work, which might affect the accuracy of the computed detachment energies. However, the overall agreement between the theoretical VDEs and the experimental spectral patterns is quite good, as shown below.

The adaptive natural density partitioning (AdNDP) method was used for the chemical bonding analyses as a time-proven probe for deciphering delocalized bonding in various chemical systems. The algorithm works within a concept of occupation
numbers (ONs), such that the closer an ON of a certain bond is to 2.0 (1.0 for single-electron bonds), the more reliable the bonding picture is.

4-3. **Photoelectron Spectra of BiB\(_n^-\) (n = 6–8)**

The photoelectron spectra of BiB\(_n^-\) at 266 nm are shown in Figures 4-1, 4-2, 4-3 for \(n = 6–8\), respectively. The observed PES bands are labeled with letters (X, A, B, ...), and the detailed VDEs are shown in Tables 4-1, 4-2, 4-3, along with their theoretical VDEs and electron configurations. In each spectrum, band X represents the transition from the anionic ground state to the electronic ground state of the corresponding neutral, while bands A, B, ... indicate transitions from the anionic ground state to excited states of the corresponding neutral species.

4-3.1. **BiB\(_6^-\)**

The photoelectron spectrum of BiB\(_6^-\) displays three well-resolved bands, as shown in Figure 4-1. Band X gives rise to the first VDE at 2.62 eV. The ADE is estimated to be 2.46 ± 0.04 eV from its onset, which also represents the electron affinity (EA) of the corresponding neutral BiB\(_6\). Following a large energy gap, band A at 3.65 eV is intense and sharp with a short vibrational progression and a vibrational spacing of \(\sim 1120\) cm\(^{-1}\). A broad band B is observed at 4.26 eV.

4-3.2. **BiB\(_7^-\)**

The photoelectron spectrum of BiB\(_7^-\) (Figure 4-2) is congested with more complicated features because it is open-shell. The strong band X is broad, yielding a VDE of 3.21 eV and an estimated ADE of 3.03 ± 0.06 eV. A broad band A with an unresolved
shoulder closely follows band X at a VDE of 3.42 eV. Band B at 3.81 eV is sharp, and it contains a short vibrational progression with a spacing of \( \sim 490 \) cm\(^{-1}\). A weaker and broad band C is observed with a VDE of 4.04 eV. At the high binding energy side, two closely spaced bands, D and E, are observed at 4.39 and 4.47 eV, respectively. The weak band \( X' \) on the low binding energy side at 2.84 eV is likely from a low-lying isomer.

4-3.3. \( BiB_8^- \)

The photoelectron spectrum of \( BiB_8^- \) displays a relatively simple spectral pattern with three well-resolved bands, as shown in Figure 4-3. The sharp band X yields a VDE of 3.13 eV and an ADE of 3.07 \( \pm \) 0.03 eV. The shoulder on the high binding energy side of band X is likely an unresolved vibrational peak. A relatively broad band A is observed at 3.64 eV. The intense and sharp band B gives a VDE of 4.18 eV and a vibrational progression with a frequency of 570 cm\(^{-1}\). There were very weak signals at the low binding energy side around \( \sim 2.7 \) eV (not labeled), which could be due to a low-lying isomer.

4-4. Theoretical Results

The global minima of \( BiB_n^- (n = 6–8) \) along with several low-lying isomers are displayed in Figure 4-4. More low-lying structures are given in Figure S1 of the original paper.

4-4.1. \( BiB_6^- \)

The global minimum of \( BiB_6^- \) was found to be a closed-shell 2D structure with \( C_1 \) symmetry (\(^1\)A, Figure 4-4A) at the PBE0 level. The \( B_6 \) motif is similar to the global minimum of the bare \( B_6 \) cluster with some in-plane distortions.\(^{56}\) The valence MOs for
the $C_1$ BiB$_6^-$ are displayed in Figure S2 (Supporting Information in the original paper). The HOMO–LUMO gap is computed to be 2 eV at the PBE0/aug-cc-pVTZ level, indicating the global minimum of BiB$_6^-$ is a stable electronic system. The first low-lying isomer (Iso1) can be considered as the triplet excited state of the global minimum. It is almost degenerate with the global minimum at the PBE0 level but is much higher in energy at the CCSD(T) level. The second low-lying isomer (Iso2) is a 3D half-sandwich type structure, which is 5.0 kcal/mol higher in energy at the PBE0 level but becomes even lower in energy than the $C_1$ 2D global minimum. The true global minimum can only be determined by comparison with the experimental data. The ADE and VDE$_1$ for the global minimum of BiB$_6^-$, as well as the VDE$_1$ for Iso1 and Iso2, are calculated at two different levels of theory, as shown in Table 4-4. Higher VDEs at the TD-DFT level for the $C_1$ 2D global minimum are given in Table 4-1, where they are compared with the experimental data.

4-4.2. BiB$_7^-$

The global minimum of BiB$_7^-$ is a doublet $C_{2v}$ ($^2A_2$) planar structure with the Bi atom bonded to the periphery of a hexagonal B$_7$ cluster (Figure 3\4-4B). The B$_7$ motif is similar to the global minimum of the bare B$_7$ except that the latter is only quasi-planar. The valence MOs of the global minimum are shown in Figure S3 (Supporting Information in the original paper). The HOMO–SOMO (beta MOs) gap was computed to be 2.6 eV, and the SOMO–LUMO gap (alpha MOs) was 3.2 eV. The next low-lying isomer (Iso1) is 15.1 kcal/mol higher in energy at the CCSD(T) level ($C_{2v}$, $^2B_1$, Figure 4-4B), and its structure is similar to the global minimum except that the B$_7$ moiety undergoes some in-plane distortions. In fact, Iso1 can be viewed as replacing a B atom with the Bi atom on the
periphery of the $B_8^{-}$ cluster. $^{58}$ Clearly, the insertion of the Bi atom is too disruptive to the B–B bonding, resulting in a much higher energy Iso1. The second low-lying isomer has an elongated double-chain structure, similar to the global minimum of BiB$_6^{-}$, but it is significantly higher in energy in comparison to the $C_{2v}$ global minimum. The computed ADE and VDE$_1$ for the global minimum and the VDE$_1$ for Iso1 of BiB$_7^{-}$ at both PBE0 and CCSD(T) are also given in Table 4-4. The higher VDEs of the global minimum at the TD-DFT level are compared with the experimental data in Table 4-2.

4-4.3. BiB$_8^{-}$

The global minimum of BiB$_8^{-}$ consists of a $B_8$ wheel and a Bi atom bonded to its edge with $C_{2v}$ symmetry (Figure 4-4C). The $B_8$ motif is similar to the global minimum of the bare $B_8$ cluster. $^{58}$ The valence MOs for the global minimum are shown in Figure S4 (Supporting Information in the original paper). The HOMO–LUMO gap was computed to be 2.37 eV. The first low-lying isomer (Iso1) is a 3D bipyramidal structure with a triplet state and $C_{6v}$ symmetry. It is 13.7 kcal/mol higher in energy than the planar global minimum at the PBE0 level and 18.2 kcal/mol higher at the CCSD(T) level. The second low-lying isomer is a triplet $C_3$ structure with the Bi atom bent out of the $B_8$ plane. Another 3D bipyramidal structure (Iso3) is close in energy to Iso2. The computed ADE and VDE$_1$ for the global minimum as well as the computed VDE$_1$ for the three low-lying isomers of BiB$_8^{-}$ are also given in Table 4-4. The higher VDEs of the global minimum at the TD-DFT level are compared with the experimental data in Table 4-3.
4-4.4. **Neutral BiBₙ (n = 6–8)**

We also performed global minimum searches for neutral BiBₙ (n = 6–8), as shown in Figure 4-5. The potential energy surfaces of the neutral clusters are found to be quite different from those of the anions. While the global minimum of neutral BiB₆ is similar to that of the anion, the Iso1 and Iso2 of the neutral are not present as low-lying isomers in the anion (Figure 4-4). More remarkably, the global minima of BiB₇ and BiB₈ are 3D half-sandwich type structures, in which the B₇ and B₈ motifs are similar to the global minima of the respective bare clusters. The planar global minimum structures of the anions become Iso1 for both neutral BiB₇ and BiB₈. It is interesting to see that detachment of a single electron can significantly alter the relative stability of the different isomers of these clusters. The coordinates of the global minima of the BiBₙ⁻ (n = 6–8) anions and the BiBₙ neutrals at the PBE0 level are given in Tables S1–S6 (see Supporting Information in the original paper).

4-5. **Discussion**

4-5.1. **Comparison between Experiment and Theory**

The experimental PES data are essential for the verification and determination of the global minima and low-lying isomers of size-selected clusters. The computed ADE/VDE₁ for the global minima of BiBₙ⁻ (n = 6–8) and VDE₁ for low-lying isomers are compared with the experimental results in Table 4-4. The calculated VDEs for all the detachment channels of the global minima within the experimentally observed spectral range are compared with the PES data in Tables 4-1, 4-2, 4-3 and indicated in Figures 4-1, 4-2, 4-3.
4-5.1.1  BiB₆⁻

The calculated ADE/VDE₁ of 2.34/2.53 eV for the global minimum of BiB₆⁻ at the CCSD(T) level agrees well with the experimental data of 2.46/2.62 eV, while the values calculated at the PBE0 level (2.15/2.29 eV) are underestimated (Table 4-4). Iso1 is almost degenerate with the global minimum at the PBE0 level, though it is higher in energy by 8.8 kcal/mol at the CCSD(T) level. The calculated VDE₁ for Iso1 is 2.07 eV at the CCSD(T) level. There are no discernible PES signals in the low binding energy range, which rules out the presence of Iso1 in the cluster beam. The 3D Iso2 is 5.0 kcal/mol higher in energy than the global minimum, but it becomes degenerate with the global minimum at the CCSD(T) level. The computed VDE₁ of Iso2 is 3.02 eV at the CCSD(T) level. Careful examination of the photoelectron spectrum of BiB₆⁻ (Figure 4-1) indicates very weak signals around ~3.3 eV between bands X and A. This weak feature could suggest the presence of Iso2 in the cluster beam as a minor component.

The calculated VDEs at the PBE0 level for higher binding energy detachment channels of the C₁ global minimum are given in Table 4-1 and marked in Figure 4-1 by the vertical bars. The first PES band (X) is due to detachment of an electron from the HOMO (27a), which is an in-plane σ MO on the B₆ moiety (Figure S2, Supporting Information in the original paper). The removal of an electron from the 27a orbital results in a structural change from the quasi-planar anion (C₁) to a perfect planar neutral BiB₆ (Cₛ). The spectral width of band X is consistent with the geometry change between the ground state of the anion and that of the neutral. Electron detachment from the HOMO−1 (26a) gives a computed VDE of 3.78 eV, in good agreement with the measured VDE of band A at 3.65 eV. The 26a orbital is a π MO (Figure S2, Supporting Information in the original paper),
consistent with the observed vibrational progression, which is likely due to a symmetric B–B vibrational mode. Electron detachment from the HOMO–2 (25a) results in a theoretical VDE of 4.20 eV, again in good agreement with the measured VDE of band B at 4.26 eV. The 25a orbital is an in-plane σ MO, involving in B–B bonding and Bi–B bonding. Significant structural changes are expected upon detachment of a 25a electron, consistent with the broad B band in the photoelectron spectrum (Figure 4-1). The theoretical results for the elongated C1 structure are in excellent agreement with the experimental observations, providing considerable credence for it to be the global minimum of BiB6−.

4-5.1.2 BiB7

The computed ADE/VDE1 for the global minimum of BiB7− are 2.75/3.18 eV at the CCSD(T) level (Table 4-4). Even though the computed ADE seems to be underestimated in comparison to the experimental value (3.03 eV), the computed VDE1 is in good agreement with the experimental value of 3.21 eV. The calculated VDE1 of 2.83 eV for Iso1 at the CCSD(T) level is in good agreement with the minor feature at 2.84 eV. Higher binding energy detachment features from the minor isomer are likely buried in the spectral features of the global minimum.

As shown in Figure 4-5, the global minimum of neutral BiB7 is a half-sandwich 3D structure, and it cannot be reached from photodetachment of the planar anion global minimum. The final states of the photodetachment should be those involving Iso1 of neutral BiB7 (Figure 4-5B), which is a 2D structure but nonplanar. The substantial geometry change from the global minimum of BiB7− to Iso1 of BiB7 is consistent with the
broad spectral width of band X (Figure 4-2). Band X is derived from electron detachment of the 2a_2 SOMO (Figure S3, Supporting Information in the original paper), which is a bonding π orbital. As will be shown below, the removal of the π electron in the 2a_2 orbital makes the neutral 2D BiB_7 an antiaromatic system, consistent with the large geometry change and the fact that it is no longer the global minimum on the neutral potential energy surface. The next detachment channel takes place from the 4b_1 HOMO, which gives rise to a high-spin (^3B_1) and a low-spin (^1B_1) final state. The calculated VDEs for these two final states, 3.52 and 3.90 eV (Table 4-2), are in good agreement with the measured VDEs of band A (3.42 eV) and band B (3.81 eV). Detachment from the 9b_2 HOMO–1 also results in a high-spin (^3B_2) and a low-spin (^1B_2) final state. The calculated VDE for the ^3B_2 final state (3.63 eV) is consistent with the unresolved shoulder at ~3.5 eV of the A band, whereas that for the ^1B_2 (4.07 eV) agrees well with band C (4.04 eV). Finally, the detachment from the 15a_1 HOMO–2 leads to two final states with different spins (^3A_1 and ^1A_1) and similar VDEs (4.46 and 4.48 eV), which are in good accord with the experimental VDEs of band D at 4.39 eV and band E at 4.47 eV, respectively. Hence, the congested photoelectron spectrum of BiB_7^- is a direct consequence of the open-shell nature of its global minimum. The good agreement between experiment and theory provides strong evidence for the C_{2v} (^2A_2) global minimum of BiB_7^-.

Even though Iso1 is a relatively high energy isomer for BiB_7^-, it is apparently present as a minor component experimentally. The geometry of the global minimum and that of Iso1 are in fact very similar. The major difference is the much larger separation between the two B atoms that are bonded to the Bi atom or the B–Bi–B bond angle in Iso1.
As shown in Figure S3 (Supporting Information in the original paper), the SOMO (2a$_2$) of the global minimum is a $\pi$ orbital on the B$_7$ moiety, while the HOMO (4b$_1$) is a $\pi$ orbital involving B–Bi–B bonding. Iso1 can be viewed as a consequence of promoting an electron from the 4b$_1$ orbital to the 2a$_1$ orbital, thus weakening the B–Bi–B bond and resulting in a large B–Bi–B bond angle.

4.5.1.3 BiB$_8^-$

The calculated ADE/VDE$_1$ for the global minimum of BiB$_8^-$ are 3.13/3.19 eV at the CCSD(T) level of theory (Table 4-4), in excellent agreement with the experimental values of 3.07/3.13 eV. The global minimum of neutral BiB$_8$ is also a 3D half-sandwich type structure similar to that of BiB$_7$, except that the Bi atom is off center and only interacts with part of the B$_8$ plane (Figure 4-5C). Iso1 of BiB$_8$ is similar to the global minimum of BiB$_8^-$ and should be the final state of photodetachment from the 2a$_2$ HOMO (Figure S4, Supporting Information in the original paper). There is little structure change between the $C_{2v}$ BiB$_8^-$ global minimum and the $C_{2v}$ Iso1 of BiB$_8$, consistent with the sharp X band observed in the photoelectron spectrum (Figure 4-3). The next detachment channel from the 10b$_2$ HOMO–1 gives a computed VDE of 3.78 eV, in good agreement with the broad band A at 3.64 eV (Table 4-3). The 10b$_2$ orbital is an in-plane $\sigma$ MO. Electron detachment from this orbital is expected to induce structural changes in the B$_8$ moiety, consistent with the broad band A. The next detachment channel is from the 4b$_1$ HOMO–2 with a computed VDE of 4.10 eV, in excellent agreement with the measured VDE of band B at 4.18 eV. The 4b$_1$ orbital is a $\pi$ MO. Electron detachment from the 4b$_1$ orbital is expected to activate the totally symmetric mode involving the Bi atom, in agreement with the simple vibrational
progression observed for band B. Overall, the theoretical results are in excellent agreement with the experimental data, confirming the closed-shell planar $C_{2v}$ global minimum of BiB$_8^-$. The lowest-lying isomer of BiB$_8^-$ is a 3D structure with a triplet state and $C_{6v}$ symmetry (Figure 4-5C). The computed VDE$_1$ for the $C_{6v}$ isomer is 3.78 eV (Table 4-4), which would be buried under band A of the global minimum (Figure 4-3) if it were present in the cluster beam. Iso2 of BiB$_8^-$ is also a triplet state with $C_s$ symmetry. The calculated VDE$_1$ of 2.74 eV at the CCSD(T) level is in good agreement with the weak PES feature at $\sim$2.7 eV in the photoelectron spectrum of BiB$_8^-$ (Table 4-4). However, Iso3, which is close in energy to Iso2, also gives a computed VDE$_1$ (2.88 eV) that could correspond to the weak feature at $\sim$2.7 eV. Regardless, the low binding energy feature in the spectrum of BiB$_8^-$ (Figure 4-3) is very weak, and the minor isomer in the cluster beam is almost negligible, in accord with their relatively high energies (Figure 4-5C).

4-5.2. *Chemical Bonding in BiB$_n^- (n = 6–8)*

Because of the relativistic effects, the $6s^2$ electrons of Bi are significantly stabilized and do not actively participate in chemical bonding. Thus, only the 6p orbitals are involved in bonding in Bi compounds without sp hybridization. A $6s^2$ lone pair is found in all Bi–B binary clusters reported previously. We have analyzed the bonding in BiB$_n^- (n = 6–8)$ using AdNDP, as shown in Figures 4-6, 4-7, 4-8, respectively. A $6s^2$ lone pair is found in each case, whereas the 6p$_x$ and 6p$_y$ orbitals form two Bi–B $\sigma$ bonds and the 6p$_z$ orbital participates in $\pi$ bonding with the B$_n$ moiety.
4.5.2.1 BiB$_6^-$

The AdNDP results for BiB$_6^-$ are shown in Figure 4-6. In addition to the expected 1c–2e 6s$^2$ lone pair on Bi, we found seven 2c–2e σ bonds (five B–B and two Bi–B bonds) on the periphery of the 2D BiB$_6^-$ cluster, two 3c–2e delocalized σ bonds, and two delocalized π bonds. Each of the delocalized σ and π systems fulfills the 4N electron counting rule for antiaromaticity, making BiB$_6^-$ doubly antiaromatic. The elongated shape and nonplanarity of BiB$_6^-$ are consistent with the double antiaromaticity.

4.5.2.2 BiB$_7^-$

The AdNDP results for the global minimum of BiB$_7^-$ (Figure 4-7) reveal the expected 6s$^2$ lone pair on Bi, seven 2c–2e peripheral σ bonds (five B–B and two Bi–B bonds), three delocalized σ bonds, and three delocalized π bonds. However, one of the π bonds is a single-electron bond because BiB$_7^-$ is open-shell. The six delocalized σ electrons render BiB$_7^-$ σ aromatic. Even though there are only five delocalized π electrons, BiB$_7^-$ should still be considered π aromatic on the basis of its planarity. Upon removing the SOMO π electron in BiB$_7^-$, the resulting BiB$_7$ neutral becomes antiaromatic, consistent with its out-of-plane distortion (Iso1, Figure 4-5B). The relatively large electron binding energy of BiB$_7^-$ is also consistent with the π aromatic interpretation. The ADE of BiB$_7^-$ is almost the same as that of BiB$_8^-$ (Table 4-4), both derived from removing a π electron (SOMO for BiB$_7^-$ and HOMO for BiB$_7^-$). Adding an electron to BiB$_7^-$ would make a perfectly doubly aromatic BiB$_7^{2-}$ species. However, removing a π electron from BiB$_7^{2-}$ probably weakens the π aromaticity in BiB$_7^-$ but does not seem to destroy it. This
is also confirmed by the electron detachment from the $\pi$ HOMO of BiB$_8\textsuperscript{−}$. There is little structural change in the resulting BiB$_8$ neutral (Iso1 in Figure 4-5C).

**4-5.2.3 BiB$_8$**

The bonding picture of BiB$_8\textsuperscript{−}$ is similar to that of BiB$_7\textsuperscript{−}$ but more straightforward because it is a closed-shell system. The AdNDP analyses (Figure 4-8) reveal the 6s$^2$ lone pair of the Bi atom, eight 2c–2e peripheral $\sigma$ bonds (six B–B and two Bi–B bonds), three delocalized $\sigma$ bonds, and three delocalized $\pi$ bonds. Each of the delocalized $\sigma$ and $\pi$ systems satisfies the $4N + 2$ Hückel rule for aromaticity, rendering BiB$_8\textsuperscript{−}$ doubly aromatic. The double aromaticity in BiB$_8\textsuperscript{−}$ is reminiscent of that in the bare closed-shell B$_8\textsuperscript{2−}$ system. In fact, the B$_8$ moiety in BiB$_8\textsuperscript{−}$ is similar to the bare boron cluster with little structural distortion.

**4-5.3. Chemical Bonding in the Global Minima of Neutral BiB$_7$ and BiB$_8$**

In all the global minimum planar structures of BiB$_n$ (n = 6–8), the Bi atom can be viewed as a trivalent “big nitrogen”, engaging in covalent bonding with the planar boron moiety by using its three 6p orbitals while the 6s$^2$ electrons are inert and remain as a lone pair. In each case, Bi forms two localized Bi–B 2c–2e $\sigma$ bonds by using its 6p$_x$ and 6p$_y$ orbitals and participates in multicenter $\pi$-bonding with its 6p$_z$ orbital. The large atomic radius of the Bi atom hinders its insertion into the periphery of the planar boron clusters, in contrast to that observed in carbon- or Al-doped boron clusters. Thus, in all cases the Bi atom is side-bonded to the planar boron moiety with relatively small perturbation to their structures compared to the respective bare boron clusters. However, except for neutral BiB$_6$, the global minima of neutral BiB$_7$ and BiB$_8$ become 3D half-sandwich-type
structures, while the planar structures derived from the anions become higher energy isomers, as shown in Figure 4-5. In these cases, the electronic stability and aromaticity of the respective boron clusters dictate the structures and stability of neutral BiB\(_7\) and BiB\(_8\), in which the metallic bonding property of Bi is revealed.

### 4-5.3.1 Half-Sandwich BiB\(_7\)

The global minimum of neutral BiB\(_7\) is closed-shell with a \(C_{6v}(^1A_1)\) half-sandwich structure (Figure 4-5B). As shown in Figure 4-9, chemical bonding analyses using AdNDP reveal that the \(C_{6v}\) BiB\(_7\) possesses a \(6s^2\) lone pair, six \(2c\text{--}2e\) \(\sigma\) bonds on the periphery of the B\(_7\) moiety, three delocalized \(\sigma\) bonds, and three delocalized \(\pi\) bonds. The global minimum of B\(_7^-\) is a triplet with two unpaired electrons and a \(C_{6v}\) structure.\(^{57}\) The closed-shell B\(_7^{3-}\) species is known to be doubly aromatic and forms half-sandwich type clusters, first observed in PrB\(_7\) and recently in B\(_7\)–B–BO\(^-\).\(^{22,23}\) It has been used to design several binary clusters computationally.\(^{66\text{--}68}\) Thus, the stability of the \(C_{6v}\) BiB\(_7\) is a consequence of the high stability of the doubly aromatic B\(_7^{3-}\) species; the three 6p electrons participate in the \(\pi\) bonding with the B\(_7\) moiety to fulfill the \(\pi\) aromaticity. Thus, the \(C_{6v}\) BiB\(_7\) can be viewed as \([\eta^7\text{-}B_7^{3-}][\text{Bi}^{3+}]\), where the metallic bonding property of Bi is manifested.

Electron detachment from the planar global minimum of the BiB\(_7^-\) anion and subsequent optimization of the resulting neutral BiB\(_7\) give the low-lying neutral \(C_s\) isomer, which is 16.3 kcal/mol higher in energy than the \(C_{6v}\) global minimum (Figure 4-5). While the \(C_s\) structure is still \(\sigma\)-aromatic, it becomes \(\pi\)-antiaromatic because the electron is detached from the \(\pi\) SOMO, leaving only four electrons in the closed-shell neutral. The out-of-plane distortion of the \(C_s\) BiB\(_7\) isomer is consistent with the \(\pi\) antiaromaticity. Both
the extraordinary stability of the aromatic $C_{6v}$ structure and the antiaromaticity of the $C_5$ structure results in the large energy separation (16.3 kcal/mol) between the two structures of neutral BiB$_7$.

4-5.3.2 Half-Sandwich BiB$_8$

The global minimum of neutral BiB$_8$ is a half-sandwich-like structure with $C_5$ symmetry, in which the Bi atom is off-center and only interacts with part of the B$_8$ plane (Figure 4-5C). The AdNDP bonding analysis reveals a $6s^2$ lone pair, a single $6p$ electron, seven $2c$–$2e$ $\sigma$ bonds on the periphery of the B$_8$ moiety, three delocalized $\sigma$ bonds, and three delocalized $\pi$ bonds, as shown in Figure 4-10. The two delocalized $\sigma$ and $\pi$ systems make BiB$_8$ doubly aromatic. Neutral B$_8$ is known to be doubly aromatic with a triplet state and $D_{7h}$ symmetry, whereas the closed-shell B$_8^{2-}$ is also doubly aromatic and highly stable. Thus, similar to the $C_{6v}$ BiB$_7$, it is the highly stable doubly aromatic B$_8^{2-}$ ligand that favors the half-sandwich-like structure for BiB$_8$, which can be viewed as $[\eta^5\text{B}_8^{2-}][\text{Bi}^{2+}]$ (Figure 4-5C). Thus, the Bi atom transfers two electrons to the B$_8$ moiety to fulfill its double aromaticity, leaving it in a rare oxidation state of $+II$.

Electron detachment from the $C_{2v}$ global minimum of the BiB$_8^-$ anion and subsequent reoptimization result in the low-lying isomer of neutral BiB$_8$ (Iso1, Figure 4-5C), which has little structure distortion relative to the anion. Apparently, the removal of a $\pi$ electron from BiB$_8^-$ (HOMO, Figure S5, Supporting Information in the original paper) may have weakened its aromaticity but does not destroy it, similar to the five-$\pi$-electron situation in the planar global minimum of BiB$_7^-$. The lingering aromaticity in the five-electron $C_{2v}$ BiB$_8$ can also be glimpsed by the fact that it is only 5.6 kcal/mol higher in
energy than the half-sandwich-like global minimum. This observation also indirectly confirms the \( \pi \) aromaticity in the five-\( \pi \)-electron global minimum of \( \text{BiB}_7^- \) and the antiaromatic behavior of the corresponding neutral \( \text{BiB}_7 \), which is 16.3 kcal/mol higher in energy than the half-sandwich global minimum of \( \text{BiB}_7 \).

4-6. Conclusions

We report a combined photoelectron spectroscopy and theoretical study of a series of Bi-doped boron clusters, \( \text{BiB}_n^- \) (\( n = 6–8 \)). Well-resolved photoelectron spectra are obtained for all three clusters and are used to understand their structures and bonding. All three clusters are found to be planar with the Bi atom side-bonded to the boron cluster moiety. The global minimum of \( \text{BiB}_6^- \) has an elongated double-chain boron motif with a terminal Bi atom, consistent with its double antiaromaticity. The global minima of \( \text{BiB}_7^- \) and \( \text{BiB}_8^- \) consist of a wheel-like boron motif with the Bi atom bonded to its edge, and both are doubly aromatic. The Bi atom engages in covalent bonding by using its three 6p orbitals with the planar boron moieties, forming two Bi–B \( \sigma \) bonds with the 6p\(_x\) and 6p\(_y\) orbitals while the 6p\(_z\) orbital participates in delocalized \( \pi \) bonding. In the \( \text{BiB}_n \) neutrals, \( \text{BiB}_6 \) has a planar global minimum similar to its anion, but the global minima of both \( \text{BiB}_7 \) and \( \text{BiB}_8 \) are found to have half-sandwich-type 3D structures as a result of the high stability of the doubly aromatic \( C_{6v} \text{B}_7^3^- \) and \( D_{7h} \text{B}_8^2^- \) species, where the Bi atom primarily engages in ionic bonding.

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### Tables and Figures

Table 4-1. Experimental VDEs and Comparison with the Calculated Values for the Global Minimum of $BiB_6^-$.  

<table>
<thead>
<tr>
<th>Band</th>
<th>VDE (exp.)</th>
<th>Final State and Electron Configuration</th>
<th>VDE (theo.) PBE0/aug-cc-pVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>2.62 ± 0.03</td>
<td>$^2A {\ldots (25a)^2(26a)^2(27a)^1 }$</td>
<td>2.29</td>
</tr>
<tr>
<td>A</td>
<td>3.65 ± 0.02</td>
<td>$^2A {\ldots (25a)^2(26a)^1(27a)^2 }$</td>
<td>3.78</td>
</tr>
<tr>
<td>B</td>
<td>4.26 ± 0.03</td>
<td>$^2A {\ldots (25a)^1(26a)^2(27a)^2 }$</td>
<td>4.20</td>
</tr>
</tbody>
</table>
Table 4-2. The experimental VDEs and comparison with the calculated values for the global minimum of BiB$_7$.

<table>
<thead>
<tr>
<th>Band</th>
<th>VDE (exp.)</th>
<th>Final State and Electron Configuration</th>
<th>VDE (theo.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>PBE0/aug-cc-pVTZ</td>
</tr>
<tr>
<td>X</td>
<td>3.21 ± 0.03</td>
<td>$^1A_2 {\ldots(15a_1)^2(9b_2)^2(4b_1)^2(2a_2)^0}$</td>
<td>3.33</td>
</tr>
<tr>
<td>A</td>
<td>3.42 ± 0.03</td>
<td>$^3B_1 {\ldots(15a_1)^2(9b_2)^2(4b_1)^1(2a_2)^1}$</td>
<td>3.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sim$3.5$^a$ $^3B_2 {\ldots(15a_1)^2(9b_2)^1(4b_1)^2(2a_2)^1}$</td>
<td>3.63</td>
</tr>
<tr>
<td>B</td>
<td>3.81 ± 0.02</td>
<td>$^1B_1 {\ldots(15a_1)^2(9b_2)^2(4b_1)^1(2a_2)^1}$</td>
<td>3.90</td>
</tr>
<tr>
<td>C</td>
<td>4.04 ± 0.03</td>
<td>$^1B_2 {\ldots(15a_1)^2(9b_2)^1(4b_1)^2(2a_2)^1}$</td>
<td>4.07</td>
</tr>
<tr>
<td>D</td>
<td>4.39 ± 0.02</td>
<td>$^3A_1 {\ldots(15a_1)^1(9b_2)^2(4b_1)^2(2a_2)^1}$</td>
<td>4.46</td>
</tr>
<tr>
<td>E</td>
<td>4.47 ± 0.02</td>
<td>$^1A_1 {\ldots(15a_1)^1(9b_2)^2(4b_1)^2(2a_2)^1}$</td>
<td>4.48</td>
</tr>
</tbody>
</table>

$^a$The unresolved shoulder of band A (see Figure 3-2).

Table 4-3. The experimental VDEs and comparison with the calculated values for the global minimum of BiB$_8$.

<table>
<thead>
<tr>
<th>Band</th>
<th>VDE (exp.)</th>
<th>Final State and Electron Configuration</th>
<th>VDE (theo.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>PBE0/aug-cc-pVTZ</td>
</tr>
<tr>
<td>X</td>
<td>3.13 ± 0.02</td>
<td>$^2A_2 {\ldots(4b_1)^2(10b_2)^2(2a_2)^1}$</td>
<td>3.01</td>
</tr>
<tr>
<td>A</td>
<td>3.64 ± 0.03</td>
<td>$^2B_2 {\ldots(4b_1)^2(10b_2)^1(2a_2)^2}$</td>
<td>3.78</td>
</tr>
<tr>
<td>B</td>
<td>4.18 ± 0.02</td>
<td>$^2B_1 {\ldots(4b_1)^1(10b_2)^2(2a_2)^2}$</td>
<td>4.10</td>
</tr>
</tbody>
</table>
Table 4-4. Comparison of the experimental ADE and VDE\(_1\) with calculated values at the PBE0/aug-cc-pVTZ and CCSD(T)/ def2-TZVP levels of theory for the global minima (GM) of BiB\(_n^-\) (\(n = 6–8\)) and the VDE\(_1\) for low-lying isomers.

<table>
<thead>
<tr>
<th>Final state</th>
<th>ADE (theo)</th>
<th>VDE(_1) (theo)</th>
<th>ADE (exp)</th>
<th>VDE(_1) (exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiB(_6^-), (C_1) (GM)</td>
<td>2A</td>
<td>2.15</td>
<td>2.34</td>
<td>2.29</td>
</tr>
<tr>
<td>(C_s) (Iso1)</td>
<td>2A(^\prime)</td>
<td>2.21</td>
<td>2.07</td>
<td></td>
</tr>
<tr>
<td>(C_2) (Iso2)</td>
<td>2B(^2)</td>
<td>2.61</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>BiB(<em>7^-), (C</em>{2v}) (GM)</td>
<td>1A(^1)</td>
<td>2.86</td>
<td>2.75</td>
<td>3.33</td>
</tr>
<tr>
<td>(C_2) (Iso1)</td>
<td>1B(^2)</td>
<td>2.77</td>
<td>2.83</td>
<td>2.71</td>
</tr>
<tr>
<td>BiB(<em>8^-), (C</em>{2v}) (GM)</td>
<td>2A(^2)</td>
<td>2.94</td>
<td>3.13</td>
<td>3.01</td>
</tr>
<tr>
<td>(C_6) (Iso1)</td>
<td>2E(^1)</td>
<td>3.65</td>
<td>3.78</td>
<td></td>
</tr>
<tr>
<td>(C_s) (Iso2)</td>
<td>2A(^\prime)</td>
<td>2.78</td>
<td>2.74</td>
<td>~2.7(^a)</td>
</tr>
<tr>
<td>(C_s) (Iso3)</td>
<td>2A(^\prime)</td>
<td>2.78</td>
<td>2.88</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The weak low-binding energy feature in Figure 3-3.
Figure 4-1. Photoelectron spectrum of BiB₅⁻ at 266 nm (4.661 eV). The vertical bars correspond to computed VDEs at the PBE0/aug-cc-pVTZ level of theory.

Figure 4-2. Photoelectron spectrum of BiB₇⁻ at 266 nm (4.661 eV). The vertical bars correspond to computed VDEs at the PBE0/aug-cc-pVTZ level of theory. The longer bars correspond to transitions to triplet final states; the shorter bars correspond to transitions to singlet final states.
Figure 4-3. Photoelectron spectrum of BiB$_5^-$ at 266 nm (4.661 eV). The vertical bars correspond to computed VDEs at the PBE0/aug-cc-pVTZ level of theory.

Figure 4-4. Global minima and low-lying isomers of (A) BiB$_6^-$, (B) BiB$_7^-$, and (C) BiB$_8^-$.
Relative energies are given in kcal/mol at the PBE0/aug-cc-pVTZ + ZPE level and the CCSD(T)/def2-TZVP level [in brackets].
Figure 4-5. Low-lying isomers of (A) BiB₆, (B) BiB₇, and (C) BiB₈. Relative energies are given in kcal/mol at the PBE0/aug-cc-pVTZ + ZPE level of theory.

Figure 4-6. AdNDP bonding analysis for BiB₆⁻. ON stands for occupation number.
Figure 4-7. AdNDP bonding analysis of BiB\textsubscript{7}\textsuperscript{−}. ON stands for occupation number.

Figure 4-8. AdNDP bonding analysis of BiB\textsubscript{8}\textsuperscript{−}. ON stands for occupation number.
Figure 4-9. AdNDP bonding analysis for the half-sandwich global minimum of neutral BiB$_7$. ON stands for the occupation number.

Figure 4-10. AdNDP bonding analysis for the half-sandwich global minimum of neutral BiB$_8$. ON stands for the occupation number.
CHAPTER 5

DOUBLE σ-AROMATICITY IN A PLANAR ZINC-DOPED GOLD CLUSTER: Au₉Zn⁻¹

Abstract

The strong relativistic effects result in many interesting chemical and physical properties for gold and gold compounds. One of the most surprising findings has been that small gold clusters prefer planar structures. Dopants can be used to tune the electronic and structural properties of gold nanoclusters. Here we report an experimental and theoretical investigation of a Zn-doped gold cluster, Au₉Zn⁻¹. Photoelectron spectroscopy reveals that Au₉Zn⁻¹ is a highly stable electronic system with an electron binding energy of 4.27 eV. Quantum chemical studies show that the global minimum of Au₉Zn⁻¹ has a D₃h structure with a closed-shell electron configuration (¹A₁'), which can be viewed as replacing the central Au atom by Zn in the open-shell parent Au₁₀⁻ cluster. The high electronic stability of Au₉Zn⁻¹ is corroborated by its extremely large HOMO–LUMO gap of 3.3 eV. Chemical bonding analyses revealed that the D₃h Au₉Zn⁻¹ are bonded by two sets of delocalized σ bonds, giving rise to double σ aromaticity and its remarkable stability. Two planar low-lying isomers are also observed, corresponding to a similar triangular structure with the Zn atom on the edge and another one with one of the corner Au atoms moved to the edge of the triangle.

5-1. Introduction

Since it was first proposed to rationalize the apparent stability of cyclopropane,\textsuperscript{1} the concept of $\sigma$-aromaticity has been used to explain the bonding in a wide variety of chemical systems.\textsuperscript{2–28} It has been particularly valuable to understand the bonding and stability of the all-metal aromatic and antiaromatic systems\textsuperscript{29–44} and boron clusters.\textsuperscript{45–60} Gold clusters have received tremendous attention over the past 2 decades,\textsuperscript{61–65} because of the discovery of catalytic effects by gold nanoparticles.\textsuperscript{66,67} One of the most surprising findings is that negatively charged gold clusters (Au$_n^-$) can be planar up to Au$_{12}^-$.\textsuperscript{68–70} The planarity has been generally understood to be due to the strong relativistic effects that can induce 6s–5d hybridization.\textsuperscript{71–75} The Au$_6^-$ cluster was in fact first proposed to be a $D_{6h}$ ring based on the observation of a single vibrational progression in photodetachment spectroscopy.\textsuperscript{76} A subsequent theoretical calculation found that the global minimum of Au$_6^-$ was a triangle with $D_{3h}$ symmetry,\textsuperscript{77} which was confirmed by joint experimental and theoretical investigations.\textsuperscript{68,78} Photoelectron spectroscopy of Au$_6^-$ revealed that the neutral Au$_6$ cluster is an exceptionally stable electronic system with a large HOMO–LUMO gap.\textsuperscript{76,79} The high stability of the Au$_6$ cluster with six valence electrons was confirmed by the isoelectronic Au$_5$Zn$^+$ cluster, which was found to exhibit $\sigma$-aromaticity.\textsuperscript{80} $\sigma$-aromaticity was also found in the planar Au$_6$Y$^-$ cluster with 10 valence electrons.\textsuperscript{81} However, chemical bonding in the larger planar gold clusters has not been examined. An interesting question is the following: Is $\sigma$-aromaticity a general bonding feature for all the planar gold clusters?

The Au$_{10}^-$ cluster is interesting, and its global minimum also has a $D_{3h}$ triangular structure.\textsuperscript{68,78} Photoelectron spectroscopy (PES) of Au$_{10}^-$ showed the presence of minor isomers with lower electron binding energies and the main isomer with a very high electron
binding energy. Theoretical calculations confirmed that the global minimum of \( \text{Au}_{10}^- \) is the \( D_{3h} \) structure with a high electron binding energy, while two other lowing-lying planar isomers with lower symmetries (\( D_{2h} \) and \( C_{2h} \)) have lower electron binding energies in agreement with the experimental observation. It was subsequently shown that the global minimum \( D_{3h} \) \( \text{Au}_{10}^- \) was inert toward \( \text{O}_2 \), but the lower symmetry \( D_{2h} \) and \( C_{2h} \) isomers were reactive with \( \text{O}_2 \) and could be titrated out of the cluster beam. The high binding energy of the \( D_{3h} \) global minimum was due to the fact that neutral \( \text{Au}_{10} \) is open shell with two unpaired electrons occupying a doubly degenerate HOMO, similar to that of the \( \text{Au}_{16} \) cage cluster. Thus, both \( \text{Au}_{10}^- \) and \( \text{Au}_{16}^- \) are doublets with one unpaired electron and unusually high electron binding energies, which explained their inertness toward \( \text{O}_2 \) whereas all other even sized \( \text{Au}_n^- \) clusters between \( n = 2 \)–\( 20 \) are highly reactive with \( \text{O}_2 \). The open shell nature of the \( \text{Au}_{16}^- \) cluster was confirmed by doping a monovalent atom inside the \( \text{Au}_{16} \) cage, \( \text{M@Au}_{16}^- \).

For \( \text{Au}_{10}^- \) on the other hand, substitution of an Au atom by a divalent atom, such as Zn, should create a closed shell \( \text{Au}_9\text{Zn}^- \) with similar bonding properties as the parent if the \( D_{3h} \) symmetry can be maintained. Small Zn-doped clusters, \( \text{Au}_n\text{Zn}^- \) (\( n < 7 \)), have been studied experimentally and the Zn atom was shown not to change the planarity of the parent \( \text{Au}_{n+1}^- \) clusters in this size regime. \( \text{Cu} \) and \( \text{Ag} \) atoms have been shown to simply substitute an Au atom of the \( \text{Au}_{10}^- \) parent in the \( \text{Au}_9\text{Cu}^- \) and \( \text{Au}_9\text{Ag}^- \) doped clusters, whereas \( \text{Y} \)-doping has been shown to result in a 3D structure for \( \text{Au}_9\text{Y} \). A previous computational study showed that \( \text{Au}_9\text{Zn}^- \) maintained the triangular structure of \( \text{Au}_{10}^- \) with a closed-shell configuration and a lower \( C_s \) symmetry (\( ^1\text{A}' \)). The objective of the current work is to investigate the geometrical and electronic structure of \( \text{Au}_9\text{Zn}^- \) and
assess if σ-aromaticity plays a role in its chemical bonding using a joint PES and relativistic quantum chemical study.

Well-resolved photoelectron spectra are obtained for Au$_9$Zn$^-$ at two photon energies and are used to verify the obtained structures from the theoretical calculations. The electron affinity (EA) of Au$_9$Zn is measured to be extremely high (4.27 eV). In addition, minor isomers with lower electron binding energies are also observed. Global minimum structural searches reveal that the triangular closed-shell $D_{3h}$ cluster with a central Zn atom is the most stable structure with two lower symmetry low-lying planar isomers. The calculated high binding energy and the simulated photoelectron spectrum of the closed-shell $D_{3h}$ global minimum are in good agreement with the experimental data. The $D_{3h}$ Au$_9$Zn$^-$ is found to be an extremely stable electronic system with a large HOMO–LUMO gap. Chemical bonding analyses show that the $D_{3h}$ Au$_9$Zn$^-$ consists of two delocalized σ systems: three seven-center–two-electron (7c–2e) bonds describing the bonding between the Zn atom and its six nearest Au atoms; and three 3c–2e bonds at the three corners of the $D_{3h}$ structure. Thus, the Au$_9$Zn$^-$ cluster can be viewed to be doubly σ-aromatic.

5-2. Methods

5-2.1. Photoelectron Spectroscopy

The experiment was conducted using a magnetic-bottle PES apparatus equipped with a laser-vaporization supersonic cluster source, details of which have been published elsewhere.$^{54,92}$ The Au$_9$Zn$^-$ clusters were produced by laser vaporization of a disk target prepared by mixing powders of Au and Zn (Au/Zn molar ratio: 6/1). The laser-induced
plasma was cooled by a high pressure He carrier gas seeded with 5% Ar, initiating nucleation and cluster formation. The nascent clusters were then entrained by the carrier gas and underwent a supersonic expansion to produce a cold cluster beam. After passing a skimmer, negatively charged clusters were extracted perpendicularly from the collimated cluster beam and analyzed using time-of-flight mass spectrometry. The Au$_9$Zn$^-$ clusters of interest were mass-selected and decelerated before photodetachment. Two photon energies were used in the current experiment: 266 nm (4.661 eV) from a Nd:YAG laser and 193 nm (6.424 eV) from an ArF excimer laser. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The photoelectron kinetic energy ($E_k$) was calibrated using the known spectrum of Bi$^-$. The resolution of the magnetic-bottle photoelectron analyzer was $\Delta E_k/E_k \approx 2.5\%$, that is, around 25 meV for electrons with 1 eV kinetic energy.

5-2.2. Computational Details

The theoretical studies were conducted using both density functional theory (DFT) and wave function theory (WFT) methods. Global minimum searches were performed using the AFFCK code, and geometry optimizations were done at the PBE0/LANL2DZ level of theory as implemented in Gaussian-16. The AFFCK code is an efficient global optimization method through the introduction of an intermediate step where structures are optimized using a classical force field generated on the fly within the algorithm. About 7000 initial structures were generated and optimized at the PBE0 level of theory. Both singlet and triplet spin states were tested for each generated structure. Then, the lowest energy isomers were reoptimized at higher levels of DFT and WFT, i.e., PBE0/def2-TZVP,
PBE0/aug-cc-pVTZ, and CCSD(T)/def2-TZVP//PBE0/def2-TZVP. Additionally, the relative order of isomers was tested using scalar relativistic corrections at the PBE0/ZORA-def2-TZVP level as implemented in the ORCA package. Corrections for the relativistic effects did not change the relative order of the isomers. Only structures with the singlet spin state were present in low-lying isomers. The closed-shell singlet character of the global minimum was supported by the wave function stability test (stable = opt) and the determinant coefficients in CASSCF(8,8)/def2-TZVP calculations. We also conducted global minimum searches using the TGMin code and obtained similar low-lying isomers as the AFFCK searches. The TGMin code is based on a constrained basin-hopping algorithm and the generation of structures is based on point group symmetries and random perturbations. Both planar and three-dimensional (3D) isomers were considered via a comprehensive study of structures with various point group symmetries.

Electronic structure, Kohn–Sham molecular orbital (MO) energy-level correlation diagram, the vertical detachment energies (VDE) and spectral simulations were performed using the DFT method as implemented in ADF 2016. The generalized gradient approximation (GGA) with the hybrid PBE0 exchange-correlation functional were used, together with the TZ2P Slater basis sets. Frozen core approximations were applied to the inner shells $[1s^2 2p^6]$ for the Zn atom and $[1s^2 4d^{10}]$ for the Au atoms. The scalar relativistic (SR) and spin–orbit (SO) coupling effects were taken into account using the zero-order-regular approximation (ZORA). The first vertical detachment energy (VDE$_1$) was calculated as the energy difference between the neutral and anionic ground state at the optimized anion geometry. Higher binding energy detachment channels and the spectral simulations were calculated by considering the SO effects via the generalized Koopmans
theorem (GKT), which could qualitatively account for the trend and ordering of VDEs as reported previously. Chemical bonding was analyzed using the adaptive natural density partitioning (AdNDP) approach developed by Zubarev and Boldyrev, at the PBE0/LANL2DZ level of theory as implemented in Gaussian-16.

5-3. Results

5-3.1. Experimental Results

The photoelectron spectra of Au$_9$Zn$^-$ at 266 and 193 nm are shown in Figure 5-1. The 266 nm spectrum (Figure 5-1a) displays two well-resolved PES bands X and A with VDEs at 4.36 and 4.53 eV, respectively. The adiabatic detachment energy (ADE) of band X is estimated from its onset to be 4.27 eV, which represents the EA of the corresponding neutral Au$_9$Zn. Eight more well-resolved PES bands are observed in the 193 nm spectrum (Figure 5-1b), labeled from B to I. The VDEs of all the observed PES bands are given in Table S1 (Supporting Information in the original paper), where they are compared with the theoretical results to be discussed below. Two weak bands X' and X'' are also observed on the lower binding energy side at 3.17 and 3.90 eV, respectively. The relative intensities of these features are reduced in the 193 nm spectrum, suggesting that they are likely due to contributions from low-lying isomers of Au$_9$Zn$^-$.

5-3.2. Theoretical Results

The structures found within 20 kcal/mol of the global minimum are shown in Figure S1 (Supporting Information in the original paper). The first three low-lying isomers are all closed-shell planar structures, as displayed in Figure 5-2. The lowest energy structure of
Au₉Zn⁻ was found to be planar with $D_{3h}$ symmetry at different levels of theory. It is a triangular structure with the Zn atom at the center; its detailed bond lengths are depicted in Figure S2 (Supporting Information in the original paper). The second low-lying isomer (Iso1) is similar to the global minimum with the Zn atom on the edge of the triangle; it is 10.7 kcal/mol higher in energy than the $D_{3h}$ structure at the CCSD(T) level. The third isomer (Iso2) can be described as moving one of the apex Au atoms of the $D_{3h}$ structure to the opposite edge. Iso1 and Iso2 are basically positional isomers of the $D_{3h}$ global minimum with the displacement of one atom.

Because of the stability of the planar structures, there are large energy barriers between the different isomers despite the apparent similarity of these structures. We searched for the transformation between Iso2 and the global minimum, as shown in Figure S3 (Supporting Information in the original paper), where a barrier of 20.1 kcal/mol was found from Iso2 to the $D_{3h}$ structure. As will be shown below, the large energy barriers are important to understand the observation of Iso1 and Iso2 in our experiment despite their relatively high energies above the global minimum.

5-4. Discussion

5-4.1. Confirmation of the Global Minimum of Au₉Zn⁻

To confirm the global minimum of Au₉Zn⁻, we have calculated the first VDE ($VDE_1$) for the top three lowest energy isomers, as compared with the experimental data in Table 5-1. The $VDE_1$ computed for the $D_{3h}$ global minimum, 4.42 eV at the PBE0 level or 4.28 eV at the CCSD(T) level, is in excellent agreement with the VDE of the X band at 4.36 eV.
The theoretical values for the VDE of Iso1 and Iso2 are in good agreement with those measured for the weak peaks X’ and X”, respectively.

We also computed the higher VDEs of the $D_{3h}$ structure using the GKT approach, as compared with the experimental data in Table S1 (Supporting Information in the original paper). The higher VDEs were computed by adding the first VDE from the CCSD(T)/def2-TZVP calculations to the excitation energies computed for the neutral Au$_9$Zn. A simulated spectrum was obtained by fitting the VDEs with unit area Gaussian functions of 0.02 eV width, as compared with the 193 nm spectrum in Figure 5-3. The simulated spectrum almost perfectly reproduces the experimental spectral features.

The first PES band X represents the transition from the ground state of the $D_{3h}$ Au$_9$Zn$^-$ to that of the corresponding neutral compound, due to electron detachment from the HOMO (34e’, Figures 5-4 and 5-5). Because of the strong spin–orbit coupling, removal of an electron from the doubly degenerate 34e’ orbitals results in two detachment channels corresponding to peaks X and A, as shown in Table S1 (Supporting Information in the original paper). The calculated VDEs of 4.28 and 4.41 eV are in good agreement with the experimental VDEs for peaks X (4.36 eV) and A (4.53 eV), respectively. The next detachment channel is from the 20a$_{1}'$ orbital with a calculated VDE of 4.67 eV, in excellent agreement with the VDE of peak B (4.67 eV). The 34e’ and 20a$_{1}'$ orbitals are mainly composed of the Au 6s atomic orbitals (AOs), as shown in the energy-level correlation diagram (Figure 5-4) and the MOs in Figure 5-5. Following an energy gap, higher detachment channels are mainly derived from the Au 5d-dominated orbitals or 6s–5d hybrid orbitals (Figure 5-4 and Figure S4). All the calculated VDEs are in good agreement with the observed features (Table S1). The overall excellent agreement between the
simulated and the observed spectrum, as shown in Figure 5-3, provides unequivocal evidence for the \( D_{3h} \) structure as the global minimum of \( \text{Au}_9\text{Zn}^- \).

The good agreement between the computed VDE of the higher energy isomers, Iso1 and Iso2, and the weak peaks \( \chi' \) and \( \chi'' \) (Table 5-1) suggests that they were present experimentally. However, Iso1 and Iso2 are 10.7 and 13.3 kcal/mol higher in energy than the global minimum, respectively, at the CCSD(T)/def2-TZVP level (Figure 5-1). These isomers were likely kinetically trapped once they were formed during the cluster growth because the large energy barriers separating them from the global minimum (Figure S3).

5-4.2. Chemical Bonding in the \( D_{3h} \) \( \text{Au}_9\text{Zn}^- \)

The global minimum \( D_{3h} \) \( \text{Au}_9\text{Zn}^- \) consists of a central Zn atom, three apex or corner Au atoms (Au\(_a\)) and six Au atoms at the edge sites (Au\(_e\)). The large electron binding energy of \( \text{Au}_9\text{Zn}^- \) (ADE, 4.27 eV; VDE, 4.36 eV) indicates that it is an extremely stable electronic system. The high electronic stability of \( D_{3h} \) \( \text{Au}_9\text{Zn}^- \) is borne out from the MO analysis shown in Figure 5-4, which indicates a large HOMO–LUMO energy gap of 3.3 eV at the PBE/def2-TZVP level. The \( D_{3h} \) structure of \( \text{Au}_9\text{Zn}^- \) is essentially the same as the parent \( D_{3h} \) \( \text{Au}_{10}^- \), which is an open-shell system with an unpaired electron.\(^{82}\) Substitution of the central Au atom by Zn in the \( D_{3h} \) \( \text{Au}_{10}^- \) cluster resulted in the stable closed-shell \( D_{3h} \) \( \text{Au}_9\text{Zn}^- \) with 12 valence electrons, a magic number in the 2D jellium model.\(^{87}\)

As can be seen from Figure 5-5, the pattern of the 34\( \varepsilon' \) and 20\( a_1' \) orbitals are reminiscent of a typical \( \sigma \)-aromatic system with \( 4n + 2 \) (\( n = 1 \)) electrons, as discussed for the triangular \( \text{Au}_6 \) cluster\(^{108}\) and several isoelectronic doped \( \text{Au}_6 \) clusters.\(^{80,81,87}\) As indicated in Figure 5-4, significant 6s–5d hybridization occurs, primarily involving the
28e′ and 17a1′ orbitals on the Au93– framework. To understand the structure and chemical bonding of Au9Zn− in more detail, we performed AdNDP analyses. Because of the d10-configuration of Zn and Au, we have 100 out of 112 valence electrons localized as lone pairs with occupation numbers (ONs) of 1.99 |e|. Out of the remaining 12 electrons, the AdNDP results revealed three 3c–2e σ bonds formed at the apex sites by one Auₐ atoms and two adjacent Auₑ atoms, as shown in Figure 5-6. The other three 7c–2e σ bonds describe the bonding of Zn with the six Au atoms in its first coordination shell. In fact, these three delocalized σ bonds are reminiscent of those in Au₆.¹⁰⁸

Inasmuch as the localization of canonical MOs are not unique, we found that the three 7c–2e bonds can also be further represented by three 3c–2e bonds, as shown in Figure S5 (Supporting Information in the original paper). However, the ONs of the three 3c–2e bonds are much lower (1.75 |e|), which suggests that the 7c–2e representation better describes the bonding situation in Au₉Zn−. The three 7c–2e bonds also display more vividly the σ aromaticity. Thus, the D₃h Au₉Zn− cluster can be viewed to possess two σ aromatic systems, one describing the bonding between Zn and its six nearest neighbors and a second σ system describing the bonding of the three corner Au atoms with the central Zn@Au₆ unit. The double σ aromaticity underlies the extremely high stability of the D₃h Au₉Zn− cluster. The parent D₃h Au₁₀ cluster with two unpaired electrons²⁸ should be considered a doubly σ Baird aromatic system for triplet states.⁴⁴,¹⁰⁹ The deviation of the ONs from 2 is an indication of the s–d hybridization. The larger ONs of the three 3c–2e bonds suggests they are primarily from the three 6s-based MOs shown in Figure 5-5. The larger deviation of the 7c–2e bonds from 2 indicates they are from MOs of significant s–d
hybridization. The strong s–d hybridization, due to the relativistic effects of gold, is a major reason for the planarity of small gold clusters.\(^{71-75}\)

5-5. Conclusions

We report a photoelectron spectroscopy and theoretical study of the Au\(_9\)Zn\(^-\) cluster. The photoelectron spectra revealed well-resolved spectral features, as well as evidence of two low-lying isomers. The global minimum of Au\(_9\)Zn\(^-\) was found to have a planar \(D_{3h}\) structure with a central Zn atom. Two planar low-lying isomers were found due to the displacements of one atom from the \(D_{3h}\) global minimum. The electron affinity of the \(D_{3h}\) Au\(_9\)Zn\(^-\) cluster was measured to be 4.27 eV, which is extremely high and indicates Au\(_9\)Zn\(^-\) is a very stable electronic system. The high electronic stability of the \(D_{3h}\) Au\(_9\)Zn\(^-\) is consistent with its large HOMO–LUMO gap of 3.3 eV computed at the PBE0 level. Chemical bonding analyses showed that the \(D_{3h}\) Au\(_9\)Zn\(^-\) cluster possesses two delocalized \(\sigma\) systems, one consisting of three 3c–2e bonds at the three corners and another consisting of Zn and its first coordination shell. The double \(\sigma\)-aromaticity further underlies the high stability of the \(D_{3h}\) Au\(_9\)Zn\(^-\).

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**Tables and Figures**

Table 5-1. Comparison of the experimental and calculated VDE₁ for the global minimum $D_{3h}$ structure, and the two low-lying isomers, Iso1 and Iso2, of Au₆Zn⁻.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Electron Configuration</th>
<th>VDE₁ (exp.)</th>
<th>VDE₁ (theo.) PBE0/def2-TZVP</th>
<th>VDE₁ (theo.) CCSD(T)/def2-TZVP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{3h}$</td>
<td>$(a'')^2(e'')^3(e')^0$</td>
<td>4.36</td>
<td>4.42</td>
<td>4.28</td>
</tr>
<tr>
<td>Iso1, $C_s$</td>
<td>$(a')^2(a')^1(a')^0$</td>
<td>3.90</td>
<td>3.77</td>
<td>3.83</td>
</tr>
<tr>
<td>Iso2, $C_{2v}$</td>
<td>$(a)^2(a)^1(a)^0$</td>
<td>3.17</td>
<td>3.38</td>
<td>3.37</td>
</tr>
</tbody>
</table>
Figure 5-1. Photoelectron spectroscopy of Au$_9$Zn$^-$ at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV).

Figure 5-2. Global minimum (GM) and low-lying isomers of Au$_9$Zn$^-$ and their relative energies. All energies are in kcal/mol at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP, PBE0/def2-TZVP (in parentheses), and PBE0/TZ2P (in brackets) levels.
Figure 5-3. Comparison of the simulated spectrum for the global minimum of $D_{3h} \text{Au}_9\text{Zn}^-$ with the experimental spectrum at 193 nm. The simulated spectrum is obtained via the GKT approach at the PBE0/TZ2P SO-ZORA level.

Figure 5-4. Kohn–Sham MO correlation diagram between Zn$^{2+}$ and Au$^{3+}$ for $D_{3h} \text{Au}_9\text{Zn}^-$ at the PBE0/TZ2P SR-ZORA level via the ADF program. The energy levels in magenta, blue, red, and green denotes to the MOs derived from 4s(Zn), 3d(Zn), 6s(Au), and 5d(Au) AOs, respectively. Electrons on the occupied MOs are represented by dots.
Figure 5-5. Contour plots of the 6s-based HOMO (34e') and HOMO–1 (20a_1') of the $D_{3h}$ Au$_9$Zn$^-$ at the PBE0/TZ2P SR-ZORA level via the ADF program.

Figure 5-6. AdNDP bonding patterns of $D_{3h}$ Au$_9$Zn$^-$. ON is the occupation number.
CHAPTER 6
HYDRATED SULFATE CLUSTERS SO₄²⁻(H₂O)ₙ (n = 1–40): CHARGE DISTRIBUTION THROUGH SOLVATION SHELLS AND STABILIZATION¹

Abstract

Investigations of inorganic anion SO₄²⁻ interactions with water are crucial for understanding the chemistry of its aqueous solutions. It is known that the isolated SO₄²⁻ dianion is unstable, and three H₂O molecules are required for its stabilization. In the current work, we report our computational study of hydrated sulfate clusters SO₄²⁻(H₂O)ₙ (n = 1–40) in order to understand the nature of stabilization of this important anion by water molecules. We showed that the most significant charge transfer from dianion SO₄²⁻ to H₂O takes place at a number of H₂O molecules n ≤ 7. The SO₄²⁻ directly donates its charge only to the first solvation shell and surprisingly, a small amount of electron density of 0.15|e| is enough to be transferred in order to stabilize the dianion. Upon further addition of H₂O molecules, we found that the cage effect played an essential role at n ≤ 12, where the first solvation shell closes. During this process, SO₄²⁻ continues to lose density up to 0.25|e| at n = 12. From this point, additional water molecules do not take any significant amount of electron density from the dianion. These results can help in development of understanding how other solvent molecules could stabilize the SO₄²⁻ anion as well as other multicharged unstable anions.

6-1. Introduction

Hydrates of the sulfate dianion $\text{SO}_4^{2-}$ play a significant role in chemistry and biochemistry where they appear as units of solutions and molten substances. This textbook compound occurs in drinking water, soils, and atmospheric aerosols.\(^1\) While sulfate aggregates participate in earth processes such as cloud formation,\(^2\) hydrated sulfate minerals were even detected on the Martian surface\(^3\) meaning sulfate ubiquity through the solar system. Moreover, sulfate dianion is also known as strong kosmotropic molecule in terms of Hofmeister series.\(^4\) Because of the strong intramolecular Coulomb repulsion of the two excess charges, an isolated sulfate dianion was shown to be unstable,\(^5\)\(^–\)\(^7\) whereas it is stabilized in the condensed phase by solvation in solution or counterions in solid. As for the gas phase, Blades and Kebarle\(^6\) observed stable hydrated sulfate clusters with four additional water molecules. Then, Wang and co-authors made a game changing discovery revealing that only three water molecules are necessary for sulfate dianion stabilization.\(^7\) Further study was continued in series of recent experimental and theoretical works on the structure and stability of the solvated sulfate dianion.\(^8\)\(^–\)\(^24\)

These intriguing systems deserved much attention in the scientific community and, no doubt, they bear interesting chemical and physical properties, and many of them are not studied yet. In the present work, we report our computational study of charge distribution in $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ ($n = 1$–$40$) clusters. We show that the most significant charge transfer takes place at $n = <7$. Though even above this value, $\text{SO}_4^{2-}$ still donates a certain amount of the charge to water molecules; such transfer is not so intense, and the cage effect is mostly responsible for further stabilization. It is well known that the sulfate dianion becomes stable
only at $n = 3$. However, we performed calculations both for $n = 1$ and 2 in order to track how the charge distribution behaves from the quantum mechanical point of view.

6-2. Computational Methods

For $n = 1–3$ $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$, we used the Coalescence Kick procedure to obtain low lying isomers. Coalescence Kick was designed to carry out unbiased machine search of global minimum (GM) on the potential energy surface out of the large set of initial structures. Within this procedure, we used the PBE0 $^{25}$ level of theory and the 6-31+G* basis set. $^{26}$ For $\text{SO}_4^{2-}(\text{H}_2\text{O})$, $\text{SO}_4^{2-}(\text{H}_2\text{O})_2$, and $\text{SO}_4^{2-}(\text{H}_2\text{O})_3$, we searched out of 5000 initial geometries, and then, we selected five lowest lying isomers within 20.0 kcal/mol from GM. In these calculations, we chose water molecules and sulfate as stable subunits and searched for structures where water molecules and sulfate are randomly distributed in a cube. After that, we reoptimized them at the more sophisticated PBE0/aug-cc-pVDZ $^{27}$ level of theory. Relative energies of the lowest isomers were calculated within the PBE0/aug-cc-pVTZ level of theory including zero-point energy correction. The resulting geometries of these three stoichiometries were not surprising: hydrogens of water molecules form double hydrogen bonds with oxygen atoms of the sulfate anion [Figure 6-1].

Geometries of clusters with $n = 4–7$ were taken from the work of Boldyrev and Wang $^{28}$ and co-workers and then reoptimized within the PBE0/aug-cc-pVDZ level of theory. We took geometries of clusters with larger $n = 8–40$ from the comprehensive investigation of Johnston and co-workers. $^{29}$ The overall methodology of obtaining these clusters is described in detail in their work. We also reoptimized these structures at the PBE0/aug-cc-pVDZ level of theory, and no significant changes were observed. After that,
we performed NBO analysis\textsuperscript{30–32} within the PBE0/aug-cc-pVTZ method. This procedure allows us to extract plenty of information from structures including unit charges which are issues of interest in the present work. By means of AdNDP analysis,\textsuperscript{33,34} which is an extension of NBO, we examined the pathway of charge distribution through solvation shells. Additionally, we constructed a classical physics model of SO\textsubscript{4}\textsuperscript{2−} stabilization with the cage effect. We replaced every atom of the water molecule with point charges (positive on hydrogens and negative on oxygens). The values of charges were chosen to reproduce the same dipole moment as a solitary water molecule. Then, vertical detachment energies of such systems were calculated. All calculations mentioned were performed using the Gaussian09 package.\textsuperscript{35}

6-3. Results and Discussion

In Figure 6-2, we present the dependence of the amount of the negative charge located on the sulfate dianion on the number of water molecules in the cluster. We can see that the most intense charge transfer from sulfate to water molecules takes place at \( n \leq 7 \) and even above this number, the charge still decreases until \( n = 10 \) but in a less degree. Intuitively, we expected a hyperbolic further character of this curve, assuming that SO\textsubscript{4}\textsuperscript{2−} will donate less and less charge to additional water molecules. However, the results were much more surprising than we initially guessed. Clusters with \( n = 11, 12, \) and \( 13 \) form a plateau which is higher than neighboring charge values for \( n = 10 \) and \( n = 14 \). After this pretty flat region, we can observe charge decreasing in range \( n = 14–22 \).
The same curve pattern can be found in Figure 6-3, where we present data on the mean hydrogen bond length between water molecules and sulfate. At $n \geq 8$, these two graphs explicitly correlate with each other.

At the same time, at $n \leq 7$, the charge monotonously goes from the sulfate molecule without any peaks, and a pretty large slope in Figure 6-2 does not correlate with the graph in Figure 6-3. This leads us to the conclusion that the stabilization of the sulfate dianion by charge transfer is the most pronounced at $n \leq 7$ because this molecule donates its charge so willingly in these clusters. Though the charge still transfers from the sulfate to water at some regions on Figure 6-2 for higher $n$, it obviously correlates with the mean hydrogen bond length and is a side effect of the orientation. Based on the NBO analysis, and the well-known fact that three water molecules are necessary for $\text{SO}_4^{2-}$ stabilization, it can be concluded that about $0.15|e|$ should migrate from the dianion in order to make it stable.

After complete reoptimization at the PBE0-D3 \(^{36}\) and B3LYP-D3 \(^{37}\) levels of theory, we can see that this value is independent of the functional used. Inclusion of empiric Grimme’s dispersion correction also did not affect charge distribution. Although local density may depend on the partitioning mechanism, we believe that the time-tested NBO localization scheme is the most suitable for this study. However, the exact value of $0.15|e|$ should be comprehended in a more qualitative way, pointing out that even slight charge transfer makes the $\text{SO}_4^{2-}$ dianion stable. In sum, one may consider this result the following way: delocalization of about $0.15|e|$ within the NBO scheme is needed in order to make the $\text{SO}_4^{2-}$ dianion stable.

Therefore, the so-called cage effect is mostly responsible for further stabilization of bigger clusters and greater $n$ values. In Figure 6-4, we present our classical physics
approximation of sulfate stabilization by the presence of point charges which mimic the solitary water dipole moment. The charge transfer does not occur in such systems.

We consider the stability in terms of vertical detachment energies (VDEs). As it is depicted in Figure 6-4, the cage effect has the most considerable influence on the system at \( n \leq 12 \), where the first solvation shell is closed. Red and blue lines are linear fitting curves for \( n = 0–12 \) and \( n = 13–40 \), respectively. Obviously, there is a noticeable difference in slopes which indicates a decrease in further stabilization rate. Results of calculations including Grimme’s dispersion corrections \(^3^6\) at the PBE0-D3 and B3LYP-D3 \(^3^7\) levels of theory are identical with ones obtained within the PBE0 functional (see the Supporting Information of the original paper).

One more important result was obtained using AdNDP analysis. We examined electron density transfer through the first, second, and third solvation shells in terms of occupation numbers (ONs) using a direct search procedure implemented in the AdNDP program. A comprehensive manual for this procedure can be found in the work of Boldyrev and co-workers. \(^3^8\) We defined the first solvation shell as water molecules which are directly bonded to the \( \text{SO}_4^{2-} \) dianion. The second solvation shell is a set of water molecules which are connected by hydrogen bonds to \( \text{H}_2\text{O} \) molecules from the first solvation shell and are not directly attracted by the sulfate dianion. The third one is defined by water molecules attracted neither by the sulfate dianion nor by the first solvation shell but by water molecules from the second shell. We treated the amount of the donated charge in terms of ON of multicentered bonds in comparison with ON of one-centered lone pair of oxygen. Let us discuss our observations for the \( \text{SO}_4^{2-}(\text{H}_2\text{O})_{18} \) cluster as an example. As for the first shell, three water molecules are attributed to each oxygen atom of sulfate. As for
the second shell, we defined a water molecule attributed to certain oxygen of sulfate if at least two out of three atoms in \( \text{H}_2\text{O} \) are closer to this sulfate oxygen than to the rest of sulfate oxygen atoms. Solvation shells attributed to a selected oxygen atom and the whole cluster are depicted in Figure 6-5. Detailed calculations are placed in the Supporting Information of the original paper.

Since solvation shells are explicitly determined now, we can examine the evolution of electron density distribution through them. In Table 6-1 we present ONs for two valence lone pairs of one selected sulfate oxygen under different calculation conditions:

1. Lone pairs of oxygen without taking into account any water molecules;
2. Lone pairs of oxygen with contribution from water molecules of the first solvation shell attributed to this oxygen (which also can be interpreted as the multicenter bond);
3. Both the first- and the second-attributed solvation shells are taken into account;
4. Lone pairs of oxygen plus the second solvation shell.

Based on data presented in Table 6-1, we can conclude that only the first solvation shell significantly contributes into the ONs. Therefore, the direct \( \text{SO}_4^{2-} \rightarrow \text{H}_2\text{O} \) charge transfer occurs only between the dianion and the first solvation shell. In other words, once the first solvation shell is closed, the residual charge distribution on higher order shells, which is much less in its intensity, takes place as first-to-second and second-to-third solvation shell transitions but not as direct dianion-to-second or dianion-to-third shell transitions. Taking into account this result, and also the fact that the most intense charge transfer takes place at \( n \leq 7 \) and the cage effect plays an important role at \( n \leq 12 \), many important investigations modeling behavior or stability of sulfate in aqueous solutions might be substantially accelerated according to our results.
6-4. Conclusions

The SO$_4^{2-}$ dianion and its water clusters attract a considerable interest of researchers. In the present work, we studied the charge distribution and its effect on stabilization of local water clusters formed by sulfate dianion SO$_4^{2-}$. We showed that the most significant charge transfer takes place in clusters SO$_4^{2-}$(H$_2$O)$_n$ with $n \leq 7$ where the unstable SO$_4^{2-}$ dianion intensively donates its charge to water molecules in order to weaken the Coulomb repulsion of its two extra electrons. Though this compound continues to donate its charge to water in clusters with $n \geq 7$, this transition is not so intense, and the pattern of the charge curve explicitly correlates with the dependence of the mean hydrogen bond length on the number of water molecules at $n \geq 7$. According to NBO analysis, the donation of about 0.15|e| to water molecules is enough to make the dianion stable. However, one should bear in mind that atomic charges are not rigorously determined and may depend on the partition scheme. Therefore, this value can be used as a guide for assessing how many other solvent molecules are necessary for SO$_4^{2-}$ stabilization.

Additionally, we performed calculations of sulfate dianion stability to vertical detachment of the electron. Using the classical physics model in which charge transfer does not occur and water molecules are simulated by point charges, we showed that the cage effect plays an important role in stabilization at $n \leq 12$ and is not significant at larger $n$. AdNDP analysis revealed that the sulfate dianion donates its charge directly and intensively only to the first solvation shell. The further charge distribution (which is not so essential) occurs via shell–shell interactions. We believe that these results could be used as a receipt for biochemical, environmental, and even outer space studies and significantly accelerate them.
References


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\[ \text{SO}_4(\text{H}_2\text{O})_n^{2-} = \text{SO}_4(\text{H}_2\text{O})_{n-1}^{2-} + \text{H}_2\text{O}. \] *J. Phys. Chem. A* **2005**, *109*, 8293–8298.


**Tables and Figures**

Table 6-1. ONs of multi-centered bonds.

<table>
<thead>
<tr>
<th>Occupation numbers</th>
<th>1st lone pair</th>
<th>2nd lone pair</th>
</tr>
</thead>
<tbody>
<tr>
<td>O atom</td>
<td>1.872</td>
<td>1.865</td>
</tr>
<tr>
<td>O atom + attributed 1st solvation shell (Figure 7-5, a)</td>
<td>1.897</td>
<td>1.894</td>
</tr>
<tr>
<td>O atom + attributed 1st solvation shell + attributed 2nd solvation shell (Figure 7-5, b)</td>
<td>1.897</td>
<td>1.894</td>
</tr>
<tr>
<td>O atom + attributed 2nd solvation shell (Figure 5, c)</td>
<td>1.872</td>
<td>1.865</td>
</tr>
</tbody>
</table>
Figure 6-1. $\text{SO}_4^{2-}(\text{H}_2\text{O})$, $\text{SO}_4^{2-}(\text{H}_2\text{O})_2$, and $\text{SO}_4^{2-}(\text{H}_2\text{O})_3$ structures. Hereinafter, S atoms are green, O atoms are red, and H atoms are blue. Dotted lines indicate H bonds.

Figure 6-2. Dependence of the sulfate charge on the water molecule number.

Figure 6-3. Mean hydrogen bond length between water molecules and the sulfate ion, $r_{\text{OH}^{\text{w}}}$, for the putative global minimum structures of $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ clusters as a function of the number of water molecules, $n$. 
Figure 6-4. VDE of system SO$_4^{2-}$ with point charges in respect to the number of modeled water molecules. Red line: linear fitting of $n = 0$–$12$ region. Blue line: linear fitting of $n = 13$–$40$ region.

Figure 6-5. (a) SO$_4^{2-}$(H$_2$O)$_{18}$ cluster; (b) first solvation shell attributed to one oxygen atom; (c) first and the second solvation shell attributed to one oxygen atom.
CHAPTER 7
PERIODIC F-DEFECTS ON THE MgO SURFACE AS POTENTIAL SINGLE-DEFECT CATALYSTS WITH NON-LINEAR OPTICAL PROPERTIES

Abstract

Single-atom catalysis is the ultimate approach in catalysis science which implies the utilization of a catalyst is as efficient as it gets. In this paper we suggest a new type of a single-atom (or single-defect) catalyst – MgO with periodic defects on the (0 0 1) surface – which possesses noticeable non-linear optical properties. Periodicity of these defects leads to the significant extensive increase in the activity of a catalyst by growth of the concentration of active sites.

In this work we showed the presence of diffuse electride-like multicenter bonds inside every periodic F-center. We also discovered that MgO with periodic defects on the surface gains non-linear optical properties due to electride-like polarizable bonds inside every defect. And most importantly, such defective structures are stable up to 1500 K opening wide range of applications even in extreme conditions. We considered both multiple (50% surface defects) and rare defects (12.5% surface defects) which are potential single-defect catalysts similar to ones that are referred as single-atom catalysts.

7-1. Introduction

From the ancient times humanity was driven by the idea that all the Universe is built of diminutive invisible particles and the time completely proved that wild guess. Centuries after we learned how to operate not only molecules but even to work with single atoms. The utilization of atomic precision looks extremely prospective, especially in the field of catalysis because one could not imagine more efficient catalysts than ones in which every atom or almost every is active. Indeed, such species were recently reported, and single-atom catalysts opened a new frontier in the catalytic science [1-10]. Conventional heterogeneous catalysts are essential to many important industrial chemical processes, but their efficiency is extremely low on a per metal atom basis because only active-site atoms on the surface are involved. Therefore, catalysts with single-atom distribution on the surface are extremely needed to maximize atom activity, but design and fabrication of them is challenging. Recent works report [1-10] on the synthesis of single-atom catalysts that consist of only isolated single catalyst atoms anchored to the surfaces of nanocrystallites. Such single-atom catalysts have extremely high efficiency and show excellent stability and high activity.

At the same time, magnesium oxide is a well-known catalyst [11-20] and supporting surface of catalytic nanoparticles [21-27] for many reactions. Highly reactive defect sites at the surface are mostly responsible for the catalytic activity of this metal oxide [28]. Recently Popov et al. [29] showed that F-center defects – defects with oxygen atom missing – contain doubly occupied electron orbital which can be interpreted as 5-centered bond. These excess electrons can be transferred to the particle or molecule making mentioned F-centers promising catalytic sites on the surface. Interestingly, these 5-centered
bonds can be classified as electrides – extraordinary compounds in which electrons are localized in space distinct from atoms and act like anions. There is a number of investigations where electrides were proven to be efficient catalysts and electron conveyors [30-36]. Moreover, electrides are capable of boosting nitrogen dissociation which facilitates the process of ammonia synthesis [30-35]. In addition, many recent theoretical works are devoted to the investigation of molecular electrides, [37-39] and one of them is represented by a defective unit cell of MgO – Mg$_4$O$_3$ [40].

Recently we showed that the Mg$_4$O$_3$ defective unit cell possesses diffuse electride orbital which is responsible for significant non-linear optical (NLO) properties of this molecule. NLO materials attract significant interest because of their wide applications in optical computing, optical communication, laser devices, and dynamic image processing [41-49].

In the present work we would like to focus on catalytic and non-linear properties of MgO crystalline surface (001) with superstructures built out of F-centers containing diffuse electride-like bonds. These bonds consist of electrons coming from Mg atoms and the entire system remains neutral since neutral oxygen atoms are detached from the surface. We made these defects in a periodic fashion with different types of periodicities – multiple and rare. Being periodic, these sites extensively increase the catalytic activity and non-linear optical response of the MgO surface which is of great importance for efficient catalyst utilization and second harmonic generation (SHG).

Using quantum chemistry tools, we managed to show that magnesium oxide with periodic voids missing oxygen atoms on the surface is a stable structure even at the temperature of 1500 K. And most importantly, these voids possess electride-like doubly
occupied diffuse bonds which makes them potential candidates for single-atom catalytic sites. In the science of heterogeneous catalysis, many efforts were devoted toward the downsizing the catalytic sites and one may consider these sites on MgO surface as the smallest possible single-defect catalyst sites (or single electron pair site since there are actually two electrons in every void). At the same time, possessing diffuse polarizable bonds, these sites are responsible for the non-linear optical response. Fast development of modern experimental methods, including individual atom removal techniques, gives us hope that creation of such species is just a matter of time.

7-2. Computational methods

Geometry optimization of the MgO crystalline with periodic F-centers was performed within the DFT approach using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange–correlation functional revised for solids (PBEsol) [48] and the projected augmented wave approach, as implemented in the Vienna Ab-initio Simulation Package (VASP) [50]. The following lattice constants were used for the pristine MgO unit cell (Fig. 7-1): \( a = b = c = 4.16 \, \text{Å} \).

The non-stoichiometric MgO with multiple defects was modeled as 1x1x2.5 (six layers) MgO pristine supercell (Fig. 7-1) with one O atom removed from the surface, i.e., every second oxygen is missing on the surface (Fig. 7-1). For the MgO slab a vacuum gap of 15 Å was added in the z direction to eliminate interactions between cells. In this case, the lattice parameters are \( a = b = 4.16 \, \text{Å}, c = 20 \, \text{Å} \). The Brillouin zone was sampled with a \( 13 \times 13 \times 1 \) \( \Gamma \)-centered Monkhorst-Pack [51] k-point grid.
The non-stoichiometric MgO with rare defects was modeled as $2 \times 2 \times 2.5$ MgO pristine supercell with one O atom removed from the surface, i.e., every eighth oxygen is missing on the surface (Fig. 7-1). The same vacuum gap was added. In this case, the lattice parameters are $a = b = 8.31$ Å, $c = 20$ Å. The Brillouin zone was sampled with a $6 \times 6 \times 1$ Monkhorst-Pack k-point grid.

Large kinetic energy cutoff of 450.0 eV was used alongside with the tight electronic convergence criteria of $10^{-8}$ eV and forces threshold of $10^{-4}$ eV/Å for optimization within quasi-Newton ionic relaxation algorithm. Since MgO is known as insulator, we used Gaussian smearing for determining partial occupancies of orbitals and converged occupation threshold of 0.05.

Periodic NBO [52,53] and SSAdNDP [54-57] calculations were performed using the same parameters within VASP. Periodic NBO, like the standard NBO code, allows the recognition of 1c-2e bonds (lone pairs) and 2c-2e bonds (2-centered 2-electron bonds). SSAdNDP code, which is an extension of original AdNDP [58-63] for solid state calculations, enables the identification of multicenter delocalized chemical bonds (nc-2e, $n > 2$). Both NBO and AdNDP codes work within the concept of occupation numbers (ON), which represent the amount of electron density localized in a certain bond. The closer these values to 2, the more trustworthy bonding picture is. User-Directed Search procedure implemented in SSAdNDP (UD-SSAdNDP) enables solving tricky bonding cases. Guidelines to UD search and comprehensively described examples can be found in supplementary information of the following references [64,65].
We chose the cc-pVTZ [66] basis set for representing the projected PW so, electron density matrix used for SSAdNDP calculations is in precise agreement with the initial PW results.

Phonon spectra (Fig. 7-2) calculations were performed using finite displacements method implemented in Phonopy code [67].

Molecular dynamics (MD) simulations were performed within VASP software using 1 fs time step and 6000 steps. Temperature control was performed using Nose-Hoover method [68].

The work functions were calculated using dipole interaction corrections along z-directions corresponding to the vacuum gap.

The NLO properties of defective MgO surface were explored by ABINIT [69] software within Random-Phase Approximation (RPA) [70].

The electron pair inside the F-center is highly diffuse and, hence, more flexible. Therefore, even weak electric field can cause high polarization which is no longer linear against the applied field. In this work we investigate the second order polarizability which is usually referred as first hyperpolarizability. This property is used, for example, for second harmonic generation when two photons of frequency $\omega$ cause the emission of the photon with frequency $2\omega$.

The optical responses are driven by electron state transitions, excitonic effects, and phonon effects. The electron state transitions have the biggest contribution and, hence, RPA usually gives reasonable picture of NLO spectra. The expressions in Eqs. (46), (49), and (50) in reference [70] give linear and second-order nonlinear susceptibilities within the RPA. Position matrix elements $r_{mn}$ are determined by response wavefunctions which are
computed by density functional perturbation theory [71]. Since LDA and GGA approximations tend to underestimate band gaps [72], we used the G0W0 [73,74] method to calculate defective MgO quasiparticle band structure. The G0W0 corrected gap was used as scissor shift to calculate the nonlinear optical properties. To get reasonable optical spectrum, a large number of bands (280) and dense sampling of k-points (24 × 24 × 1) are used for NLO response calculations. Kinetic energy cutoff of 20 Ha was chosen. To be unbiased on the geometry used, we performed structural optimization within ABINIT as well. The geometry obtained via Broyden-Fletcher-Goldfarb-Shanno optimization algorithm [75] is essentially the same as used in the abovementioned calculations. LDA-PAW pseudopotentials provided by ABINIT database [76,77] were used.

7-3. Results and discussion

7-3.1. Electronic properties

Although the symmetry of a system with multiple defects decreases after the removal of oxygen atom, the lattice still possesses a rotational axis along z direction (4) and reflection planes (m) containing this axis. That is why we did not observe any displacements in comparison with salt structure: Mg-O bond length is 2.08 Å in every layer.

The same situation can be observed in a system with rare defects, though some Mg-O distances differ by the value of 0.07 Å. We consider such differences as negligible and not deserving a special discussion.

To understand the bonding nature of both systems we performed periodic NBO and SSAadNDP analysis. As for multiple defects case, the unit cell contains 12 Mg atoms and
11 O atoms giving us 45 valence pairs in sum. The bonding analysis gave us quite classical picture for 44 of them: they are distributed as s, pₓ, pᵧ and p_z lone pairs (LPs) on oxygen atoms with ONs of 1.77–1.90 |e| supporting the conventional ionic Mg²⁺O²⁻ representation. Using Direct Search implemented in SSAdNDP code we revealed that the remaining valence pair could not be localized in Lewis-like fashion. It is delocalized over five Mg atoms around the surface defect like σ bond with the ON = 1.84 |e| (Fig. 7-3). When including Mg atoms from both 1st and 2nd coordination spheres (9c-2e bond), the ON slightly increases up to 1.90 |e|.

The same technique was used for bonding analysis in slab with rare defects and approximately the same ONs (1.83 |e| for 5c-2e and 1.90 |e| for 9c-2e bonds) were obtained (Fig. 7-3).

Band structure analysis (Fig. 7-4) of slab structures with and without defects revealed that the removal of oxygen atom from the surface induces the noticeably higher in energy band which, in turn, significantly lowers the optical surface band gap from 3.1 to 1.6 eV. However, DFT calculations usually underestimate band gaps. By means of more sophisticated G0W0 approximation we obtained corrected band gap of 5.2 eV for pristine slab and 2.9 eV for the periodically defective slab. The work function decreased from 5.0 (which is quite close to experimental values)[78] to 3.3 eV, according to our calculations. These observations indicate the increase in reactivity of the system upon the removal of every second oxygen from the surface.

Calculation of pristine bulk MgO within the same approach including G0W0 corrections gave band gap of 7.10 eV which by about 10% less than experimental value of 7.77 eV [79], indicating the reliability of our level of theory.
One may set a fair point that these results could be dependent on the functional used. Here we refer to the work of Popov et al. in which they tested PBE [80] and HSE06 [81,82] functionals for the system similar with ours and obtained essentially the same results for both levels of theory.

As we mentioned above, this crystalline with periodic defects could be a promising non-linear optical material and catalyst with single-defect (or single electron pair) sites. Therefore, to make its utilization possible, we must show the structure is stable at least at room temperature. Actually, the results are much more promising: molecular dynamics calculations of multiple defects case indicate that the structure is unchanged at least up to 1500 K which is clearly reflected in the pair correlation function graph (Fig. 7-5). This fact allows the application of defective MgO even in extremely exothermic chemical processes and high-temperature reactors.

7-3.2. Optical properties

First principle calculations have been successfully used to obtain different properties of bulk semiconductors, such as linear and nonlinear optical properties (just to name few [70,83-86]).

In this section we provide calculated optical properties of MgO with multiple defects on the surface. According to LDA-DFT level of theory via ABINIT, the calculated minimum optical surface band gap $E_g = 1.6$ eV. Using G0W0 corrections, we obtained the value of 3.1 eV which is used in optical spectrum calculations by means of scissor shift. Although in this study we are focused on non-linear response, firstly, we suggest taking a brief look at linear susceptibility spectrum for the optical picture to be complete. In Fig. 7-
6. Fig. 7-7 we present imaginary and real parts of complex dielectric functions $\varepsilon_{11}$ and $\varepsilon_{33}$ for MgO slab with multiple defects. We do not perform any detailed assignments of peaks. According to the low energy limit, static dielectric constants $\varepsilon_{1}(0)$ and $\varepsilon_{3}(0)$ are 2.95 and 2.61, respectively. Definitely, the highest peak of $\varepsilon_{11}$ near 3.1 eV comes from transition from the highest valence band (HVB) to the lowest conduction band (LCB) near X k-point which corresponds to optical band gap (3.1 eV). The highest peak of $\varepsilon_{33}$ likely comes from transition between HVB and LCB at $\Gamma$ k-point which is 4.1 eV after being scissor corrected.

Among all tensor components of second-order optical susceptibility, two independent non-zero components $X^{(2)333}(2\omega, \omega, \omega)$ and $X^{(2)311}(2\omega, \omega, \omega)$ are calculated in this work. In Fig. 7-8 we present different contributions to the imaginary part $\text{Im}X^{(2)333}(2\omega, \omega, \omega)$ of $X^{(2)333}(2\omega, \omega, \omega)$. The real part can be obtained using the Kramers–Kronig relations.

As we can see, all components of imaginary part of the second-order susceptibility are vanishing as energy goes to zero. However, starting with ~2 eV we can observe many peaks and significant non-zero absolute values. The $2\omega$ terms start contributing to the total value at energies about $1/2E_g$ and are completely dominating at low energy regions below ~4.2 eV. Though inter and intraband components have opposite signs and partially cancel each other, they result in significant peaks of the absolute value. At the same time, the $1\omega$ contributions become non-zero at energies above $E_g$ and the region between 4.6 eV and 5.2 eV is mostly dominated by $1\omega$ terms. In higher energy region all terms mostly cancel each other resulting in insignificant total values of $\text{Im}X^{(2)333}(2\omega, \omega, \omega)$. More detailed examination of the second-order susceptibility spectrum is complicated due to the unobvious resonances of $2\omega$ and $1\omega$ terms.
Next, we present the frequency-dependent spectrum of the absolute value of
\(X^{(2)333}_{333}(2\omega, \omega, \omega)\) (Fig. 7-9). Although \(|X^{(2)333}(0)|\) is small \((0.04 \times 10^{-7}\) esu) at static frequency limit, the most pronounced NLO properties are in low energy region between 2.0 and 5.2 eV with peaks of magnitude up to \(3.5 \times 10^{-7}\) esu.

Imaginary part of 311 second-order susceptibility tensor component \(\text{Im}X^{(2)311}_{311}(2\omega, \omega, \omega)\) (Fig. 7-10) has \(2\omega\) contributions mostly dominating from 1.0 to 2.8 eV with amplitude significantly higher than in the 333 component resulting in twice higher amplitude of absolute value of imaginary part. Above 5.8 eV all components tend to cancel each other resulting in almost zero absolute values of imaginary part.

The absolute value of 331 second-order susceptibility tensor component \(|X^{(2)311}(2\omega, \omega, \omega)|\) (Fig. 7-11) also has twice higher peak magnitude than \(|X^{(2)333}(2\omega, \omega, \omega)|\). Noticeably, the static limit value is more than twice bigger as well, being \(0.09 \times 10^{-7}\) esu. According to the graph, the most pronounced NLO properties are supposed to be between 1.0 and 6.0 eV.

We also would like to point out that the first- and second-order susceptibilities are inversely dependent on the volume of a crystal \((X^{(2)333}_{333}(2\omega, \omega, \omega) \sim 1/\Omega)\). Since the slab of defective MgO is modelled using big vacuum gap of 15 Å, we expect the real values to be at least twice higher than calculated in this work. Anyway, we believe our calculations qualitatively prove that periodically defective MgO possesses noticeable non-linear properties in low energy region.

The inclusion of excitonic effects and phonon-assisted processes, which are extremely computationally demanding, could somehow change positions and mutual magnitude of peaks, however, it should not significantly change the average magnitude
and the general picture. We believe RPA is completely enough for purposes of this work. Moreover, there is a number of work where RPA calculations are in good agreement with experimental data [83, 86–88].

We believe that modern equipment enables the creation of abovementioned defects at low costs. Besides widely known radiation damage techniques, recently a new method of individual atoms manipulation [89–93] attracts lots of attention giving as a hope of soon fabrication of the designed material.

7-4. Conclusions

Using electronic structure analysis, we showed that a simple textbook compound MgO still may surprise with its structural and electronic properties.

First, let us summarize commonly known facts. Every MgO crystalline naturally has randomly spaced F-centers on its surface resulted from the removal of oxygen atoms. Bonding analysis of these defects reveals doubly occupied 5c-2e bonds in the voids. Such diffuse electron pairs localized in places distinct from atomic positions are known as electride phases of materials and have already found a plenty of applications including catalysts, electron conveyors, and non-linear optics. It is known that MgO is widely-used as a catalyst and supporting surface, and extremely reactive defect sites at the MgO surface are mostly responsible for such high catalytic activity.

In this work, following the abovementioned facts, we proposed the idea of periodic defects on the (001) MgO surface. The periodicity of these defects extensively increases the catalytic activity of species by multiplication of active sites number. Noticeably, such geometry manipulations do not affect the stability of the structure. We studied both
multiple periodic defects (every second oxygen atom is removed from the surface) and rare periodic defects (every eighth oxygen is removed). Phonon spectrum stability tests did not reveal any imaginary frequencies. Moreover, molecular dynamics simulations indicate that the structure with electron pairs on the surface is kept even at the temperature of 1500 K which enables the application of defective MgO in high temperature conditions.

In addition, we showed that MgO crystalline with every second oxygen removed from the surface is a promising material for non-linear optical applications. Using Random-Phase Approximation in the context of DFT, it was predicted that this defective crystal has noticeable non-linear optical properties in low energy region between 1.0 and 6.0 eV. This result indicates that pristine MgO, which has the center of inversion and does not exhibit any nonlinearity, can be tuned by means of defects to be used for second-harmonic generation.

No doubt, up-to-date methods, including radiation damage and individual atom removal techniques, can easily handle the issue of creating the mentioned periodic F-centers on the surface. We refer to these new surface materials as single-defect (F1) catalysts which are similar to what community calls the single-atom catalysts. We hope this approach can be used to design other single-defect catalysts with missing oxygen atoms in oxides of main group and transition metals as well. Many of them may also exhibit NLO properties induced by defects and the loss of the inversion center.

References


Tables and Figures

Figure. 7-1. a: pristine MgO unit cell. b: unit cell of MgO slab with every second surface oxygen atom removed. c: 2x2x1 supercell of slab with the same defect superstructure. d: 1x1x1 supercell slab with every eight surface O removed.

Figure. 7-2. Phonon spectrum of MgO slab with multiple defects.
Figure. 7-3. Left: bonding analysis of MgO slab with multiple defects. Right: bonding analysis of MgO slab with rare defects.

Figure. 7-4. Left: band structure of MgO slab without defects. Right: band structure of MgO with multiple F-defect. Fermi-levels are set as zeroes. In both cases vacuum gap is added in z-direction.
Figure. 7-5. Pair correlation function of MgO slab with multiple defects.

Figure. 7-6. Imaginary and real parts of optical dielectric function $\varepsilon_{\perp}$ of MgO slab with every second oxygen removed from the surface.

Figure. 7-7. Imaginary and real parts of optical dielectric function $\varepsilon_{\parallel}$ of MgO slab with every second oxygen removed from the surface.
Figure 7-8. Calculated $\text{Im}X^{(2)}_{333}(2\omega, \omega, \omega)$ spectra with the intra-$(2\omega)/(1\omega)$ and inter-$(2\omega)/(1\omega)$ band contributions of MgO slab with every second oxygen removed from the surface.

Figure 7-9. Absolute value of the second-order nonlinear susceptibility $X^{(2)}_{333}(2\omega, \omega, \omega)$ of MgO with multiple defects.
Figure. 7-10. Calculated $\text{Im}X^{(2)}_{311} (2\omega, \omega, \omega)$ spectra with the intra-$\text{(2}\omega)/(1\omega)$ and inter-$\text{(2}\omega)/(1\omega)$ band contributions of MgO slab with every second oxygen removed from the surface.

Figure. 7-11. Absolute value of the second-order nonlinear susceptibility $X^{(2)}_{311} (2\omega, \omega, \omega)$ of MgO with multiple defects.
CHAPTER 8

DESIGNING MOLECULAR ELECTRIDES FROM DEFECTIVE UNIT CELLS
OF CUBIC ALKALINE EARTH OXIDES¹

Abstract

Electrides are an unusual class of compounds where electrons are localized in space distinct from atomic positions and behave like anions. This type of localization makes electron density very flexible, thus even a weak electric field causes significant polarization giving rise to nonlinear optical properties. To date, all synthesized electrides are bulk compounds. However, molecular size electrides would have plenty of applications in nanoscience. It is known that cubic halide and oxide crystals possess anion vacancies which are occupied by electron pairs or single electrons. In this work, we propose a strategy for designing molecular electrides as defective unit cells of cubic crystals with a missing anion. We limit our study by the second group of the periodic table and explore the potential energy surface of $X_4O_3$ stoichiometry which corresponds to the defective cell of cubic XO crystal where X stands for Be, Mg, Ca, Sr, and Ba. Defective cell geometry becomes more dominant and nonlinear optical properties become more intense upon transition from lighter to heavier metal. Electride global minima of $Mg_4O_3$, $Ca_4O_3$, $Sr_4O_3$, and $Ba_4O_3$ have no competing isomers which makes them promising structures for synthesis.

8-1. Introduction

Electrides are known as compounds with unique electronic properties. First proposed and synthesized by J. L. Dye, these compounds have electrons localized at the position of a missing anion, thus the electrons become anions by themselves. Not being directly bound to a nucleus, anion-like electrons result in various interesting chemical and physical properties. In 2003, Hosono et al. synthesized the first room-temperature stable electride, and since that time electrides have already found applications in electron emitting devices, electron-injection layers in organic LEDs, chemical reductants, reversible hydrogen storage materials, secondary electron emitters in display panels, and boosting nitrogen dissociation for ammonia synthesis. Recently synthesized by Oganov et al., unprecedented Na2He, a nontrivial crystal with inert helium in its unit cell, exists in the form of an electride. Being diffused, the electrons in electrides are highly polarizable even in the presence of a weak electric field which gives rise to nonlinear optical (NLO) properties which are of great importance in various industrial fields such as lasers, optical computing, optical communication, dynamic image processing, and so forth.

In fact, all synthesized electrides exist as solid-state compounds with weakly bounded interstitial electrons. Despite many theoretical efforts, no electrides were synthesized as isolated molecular systems. However, the existence of molecular electrides would be beneficial for their application to nanoscale. Thus, the aim of this work is to provide a strategy for finding molecular electrides for potential synthesis.

This study is driven by the fact that many ionic crystals with cubic symmetry, such as NaCl, MgO, and so forth, are known to have anionic vacancies, so-called F-centers, which are occupied by electron pairs or single electrons. The electron density in vacancies is very
diffuse and responsible for various crystal properties like color and catalytic activity. As the crystal is ionic, the electrons of cation atoms occupy the AOs of anions to the noble gas limit. In the case of uneven stoichiometry, the electrons of excessive metal atoms simply have nowhere to go, and, in some cases, it is energetically beneficial for them to be localized in the area of a missing anion. Basically, the electron (or pair) starts to play the role of the anion in such systems.

In 2018, Alexandrova and Boldyrev showed by means of AdNDP\textsuperscript{37} that oxygen vacancies in the bulk and on the surface of MgO are occupied by an electron pair.\textsuperscript{38} Later in 2020, Boldyrev and co-workers showed that MgO with periodic F-defects on the surface is a stable structure with NLO properties.\textsuperscript{39} In this study we aim to model the same electronic structure behavior to the molecular-size scale. The simplest unit with diffuse electride-like electron density is the defective $C_3v$ unit cell with $X_4O_3$ stoichiometry where X stands for a metal. Thus, we explored the potential energy surface (PES) of $X_4O_3$ stoichiometry where X is earth alkaline metals except radium. The desired geometry corresponds to a cube with one missing vertex (Figure 8-1) and the electron pair is supposed to localize in this vacancy.

The premise for this research is our previous work where we showed that Mg$_4$O$_3$ has a global minimum (GM) geometry of $C_3v$ crystalline defective unit cell and possesses a diffused electron density which results in pronounced NLO properties.\textsuperscript{40} In this work, we went down along the second group of the periodic table from Be to Ba and showed that defective cell geometry becomes more dominant on PES upon the descent. As shown previously, the $C_3v$ Mg$_4$O$_3$ is a GM with the next low-lying isomer being 9.3 kcal/mol higher. The PES for Ca$_4$O$_3$, Sr$_4$O$_3$, and Ba$_4$O$_3$ is so pure that no isomers are found within a
20 kcal/mol range except the electride structure. This fact potentially eases the synthesis of the four candidates. The electride-attributed properties increase when switching from lighter to heavier metal, that is, the first hyperpolarizability becomes higher and excitation energy lowers upon transition from top to the bottom of the periodic table.

8-2. Computational Methods

All calculations are performed in Gaussian16 package.\textsuperscript{41} The PES exploration is done using AFFCK code\textsuperscript{42} for starting geometries generation and PBE0/def2tzvp\textsuperscript{43,44} level of theory for the optimization. 3000 starting geometries are generated for each stoichiometry with and without reasonable symmetry constraints. More sophisticated level of theory is used for polarizabilities and excitation energies calculations: PBE0/aug-cc-pVTZ-DK\textsuperscript{45,46} with all-electron relativistic basis set and scalar relativistic DKH Hamiltonian.\textsuperscript{47–50} The excitation energies are calculated within TD-DFT\textsuperscript{51} formalism. In the presence of static electric field $F$, the dipole moment of a system $\mu$ can be expanded according to the formula:

$$\mu = \mu_0 + \alpha F + \frac{1}{2} \beta F^2 + \frac{1}{6} \gamma F^3 + \cdots \quad (1)$$

Here, $\alpha$ is static polarizability, $\beta$ is second order polarizability which is responsible for quadratic response to the applied electric field $F$, the so-called first hyperpolarizability, and $\gamma$ is the third order polarizability or second hyperpolarizability. In this work, we estimate the NLO properties of a systems in terms of $\beta$-values. Because of the Kleinman’s symmetry, the static hyperpolarizability tensor $\beta_{ijk}(0; 0, 0)$ can be described by means of just 10 elements rather than 27. Thus, the first hyperpolarizability along the $i$\textsuperscript{th} direction is given by
\[ \beta_i = \beta_{iii} + \beta_{ijj} + \beta_{ikk} \quad (2) \]

and the total quadratic response is

\[ \beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (3) \]

The polarizabilities and first hyperpolarizabilities are obtained using the finite field method at static limit.

Wave functions of all GMs were checked for stability (stable = opt). We use Adaptive Natural Density Partitioning (AdNDP)\(^{37,52}\) approach, developed by D. Zubarev and A. I. Boldyrev, for bonding analysis which was proven to successfully recognize electride-like bonding patterns\(^{39,40}\) and is widely used for deciphering delocalized bonding in inorganic\(^{53-57}\) and metalorganic clusters,\(^{58,59}\) solids,\(^{16,38,39,60-62}\) mechanically trapped systems,\(^{63}\) and even solvated ions.\(^{64}\) AdNDP, electron localization function (ELF),\(^{65}\) and localized molecular orbitals (LOL)\(^{66}\) analyses were performed at PBE-DKH/aug-cc-pVTZ-DK level of theory. ELF and LOL were carried out using Multiwfn package.\(^{67}\)

8-3. Results and Discussion

8-3.1. \(X_4O_3\) Isomers

The consideration of isolated defective unit cell makes sense only when it is a global minimum on PES. Otherwise, it is a waste of computational time to investigate barely stable electrides. In this study, the desired geometry corresponds to \(C_{3v}\) symmetry resembling an \(X_4O_4\) cube with one O removed (Figure 8-1). The interesting trend is observed along the isoelectronic substitution in the second period of the periodic table.

Electride \(C_{3v}\) structure is not a GM on \(Be_4O_3\) PES and lies 42.5 kcal/mol higher than a true GM (Figure 8-2). AdNDP reveals that the planar \(C_{2v}\) GM has a 2c-2e Be–Be bond
(Figure 8-2, left) with bond length 2.06 Å. The ELF thermal plot (Figure 8-2, right) indicates that the electron density of this bond is pretty diffused. However, the absolute value of $\beta_{\text{tot}}$ is pretty modest being 524.6 au, and the excitation energy is extremely high being 5.25 eV. Therefore, this structure is definitely not an electride. It correlates with the fact that beryllium oxide crystallizes in the hexagonal structure unlike MgO, CaO, SrO, and BaO crystals which obey cubic rock salt motif.

Indeed, the $C_{3v}$ electride-like defective cell becomes a GM at Mg$_4$O$_3$ stoichiometry (Figure 8-3) with some other isomers present within 15 kcal/mol range. However, the next low-lying isomer is 9.4 kcal/mol higher and, thus, is unlikely to compete with GM. Further descent along second period results in purer PESs as Ca, Sr, and Ba stoichiometries have only electride GM within 20 kcal/mol range (Figure 8-3). This makes the four structures promising for their synthesis.

8-3.2. Bonding Analysis

The bonding pattern in all $C_{3v}$ structures is expectedly the same and pretty straightforward. Each one has 26 valence electrons ($3 \times 6 = 18$ from oxygens and $4 \times 2 = 8$ from metals). Twenty-four of them are localized as p-lone pairs on oxygens with ONs = 1.95 |e|. Aside from its own LPs, each oxygen additionally attracts two metal valence s-electrons closing its valence shell which results in the ionic bonding. However, there are four metal atoms and just three oxygens. The cherry on top is the two remaining electrons which oxygen cannot accept due to its filled shell. They should be localized with respect to $C_{3v}$ symmetry and a singlet electronic state. AdNDP reveals the two electrons form a highly diffused 3c-2e electride-like bond in the place of missing oxygen (Figure 8-3). The
bond shape clearly indicates that the electron pair is localized in space distinct from atomic positions and thus is expected to be highly polarizable. The shapes of HOMOs (see SI of the original paper, Figure S1) are essentially similar to the 3c-2e bonds which additionally create conditions for electride-like properties.

The ELF analysis further provides the evidence that electron density of the 3c-2e bond is indeed hovering over the molecule in place of the missing anion, being highly diffused, which is a necessary attribute of an electride (Figure 8-4).

As formulated by Matito et al. in their comprehensive review on electrides characterization, the presence of non-nuclear attractors (NNA) is the rarest yet the most salient feature of electrides. However, among the systems under consideration only Ca₄O₃ explicitly features the NNA represented by (3, −3) critical point (CP) in terms of quantum theory of atoms in molecules (QTAIM). Besides, QTAIM failed to locate CPs at Ba atomic positions (even with reduced criteria for gradient-norm and displacement convergences) which is a common problem for heavy atoms.

Dale and Johnson showed that NNA’s localization in inorganic electrides is sometimes complicated due delocalization errors. Moreover, there are non-electride compounds with NNA present. Thus, they proposed ELF and LOL as more versatile topological characterization tools which, however, should be accompanied by some other tests (AdNDP and NLO properties in the present work). Following Dale and Johnson’s findings, we additionally performed LOL analysis which further proved the presence of electron density basin in the vacancy region. The isosurfaces of the molecules (see SI of the original paper, Figure S2) recover essentially the same information as AdNDP and ELF.
8.3.3. Electronic Properties

Being structures with a highly diffused electron pair, electrides possess two main features, namely, large NLO properties and relatively low excitation energies. Let us examine these properties in Figure 8-5 to test if the structures under consideration are true electrides.

Aside from having large absolute values of first hyperpolarizability and low excitation energies (see SI of the original paper, Table S6 for exact values), there is a clear trend in the graph, and the two properties inversely correlate with each other. Walking down from Mg to Ba along the periodic table, the first hyperpolarizability linearly increases accompanied by the decrease of the excitation energy. The values of isotropic polarizabilities \( \langle \alpha \rangle \) (linear response to electric field) compared to \( \beta_{\text{tot}} \) (quadratic response) provide the evidence that nonlinear response is dominant in all systems (see SI of the original paper, Table S6).

Previously, we showed that the oxygen vacancy and the two “excessive” electrons are responsible for the electride-like properties of \( \text{Mg}_4\text{O}_3 \). That is, \( \text{Mg}_4\text{O}_3^+ \), \( \text{Mg}_4\text{O}_3^{2+} \), and cubic \( \text{Mg}_4\text{O}_4 \) possess significantly lower hyperpolarizabilities and higher excitation energies. For the sake of brevity, we omit this analysis for Ca, Sr, and Ba isomers as the trend is clearly expected to be the same.

These results create premise for at least two future investigations. First, defective cells of other ionic crystals with cubic symmetry may be global minima on PES having diffused electron density in the anion vacancy. The first idea that comes to mind is the most famous rock salt NaCl. Looking ahead, we already tested PES of negatively charged singlet \( \text{Na}_4\text{Cl}_3^- \) and the electride structure is not a global minimum on PES. Second, Boldyrev et
al. recently showed that MgO crystalline surface with periodic neutral oxygen vacancies exhibits noticeable NLO properties and is a potential single-atom (more precisely, single electron pair) catalyst.\textsuperscript{39} We expect that cubic CaO, SrO, and BaO crystals also might be suitable for designing such surfaces with periodic defects occupied by an electron pair.

8-4. Conclusion

In this study, we suggest a strategy for the designing molecular electrides as defective unit cells of ionic cubic crystals with a missing anion. We explored the potential energy surface of $X_4O_3$ stoichiometry where $X$ stands for alkali earth metals from Be to Ba. AdNDP, ELF, and LOL were used for topological characterization of electrides. As discussed, electride structures of Mg$_4$O$_3$, Ca$_4$O$_3$, Sr$_4$O$_3$, and Ba$_4$O$_3$ are $C_{3v}$ global minima on their PESs with no competitive isomers. The structures may be described as $X_4O_4$ cubes with one missing oxygen and the electron pair is localized in the vacancy. The purity of PES makes them good candidates for synthesis. As different $X_nO_m$ fragments are likely to coalesce forming solid seeds, special techniques may be utilized for stoichiometry control such as matrix isolation,\textsuperscript{85−89} single atom manipulation spectroscopy,\textsuperscript{90−95} advanced apparatus involving laser beams, and so forth.

The diffuse electron pair in the oxygen vacancy is responsible for noticeable NLO properties. The electride-attributed properties become more pronounced when moving down from Mg to Ba, namely, nonlinear response to the electric field increases and the excitation energy decreases.

None of molecular electrides were synthesized yet. We hope our findings will push their synthesis as they have plenty of potential applications.
8-5. References


(30) Das, P.; Chattaraj, P. K. Electride Characteristics of Some Binuclear Sandwich Complexes of Alkaline Earth Metals, $\text{M}_2(n^5\text{-L})_2$ ($\text{M} = \text{Be}, \text{Mg}; \text{L} = \text{C}_5\text{H}_5^-, \text{N}_5^-, \text{P}_5^-, \text{As}_5^-$). J. Phys. Chem. A 2020, 124, 9801–9810.


Tables and Figures

Figure 8-1. Geometry representation for a potential electride structure derived from a defective unit cell of a cubic ionic crystal. The transparent vertex corresponds to a missing anion. Electrons are expected to be localized in this vacancy.

Figure 8-2. GM of Be₄O₃. Left: AdNDP 2c-2e Be–Be bond, ON = 1.95 |e|. Right: ELF thermal slice in a molecule plane. O atoms are red, Be atoms are white.

Figure 8-3. GM structures and electride-like 3c-2e bonds of X₄O₃ global minima (X = Mg, Ca, Sr, Ba). Side and top orientations. All systems are of C₃v symmetry. ONs of 3c-2e bonds are ≈1.90 |e|. Contour value is 0.041. Color legend: O is red, Mg is green, Ca is yellow, Sr is orange, Ba is blue.
Figure 8-4. Electron localization function slice in M-M-O plane.

Figure 8-5. Total first hyperpolarizability, $\beta_{\text{tot}}$, (blue) and excitation energy (red) graphs.
CHAPTER 9
SUMMARY

At all times, chemists have always sought to create descriptive and predictive theories based on their observations. The emergence of quantum chemistry (QC) changed the way theoretical chemistry works and enabled the systematic analysis of chemical systems at the atomic scale. And now, with today’s computational powers and various theoretical methods, quantum chemistry has become an essential part of chemical science. *Ab initio* techniques greatly assist the exploration of vast chemical space replacing expensive trial-and-error experimental approaches.

QC goals are two-fold. On the one hand, QC serves as an explanatory tool where experimentalists’ vision is limited by a small scale of a process, a short lifetime of a product, or ambiguous experimental data. For example, today it is hard to imagine a report on experimental spectra without any theoretical justification of spectral features. On the other hand, quantum chemistry offers a wide range of predictive capabilities. High accuracy computational results may serve as a guidance for future experiments and for the rational design of new compounds with desired properties.

Thus, the emphasis of this dissertation was also two-fold. First, the dissertation presented joint experimental and theoretical studies on newly synthesized clusters or new theoretical insights into existing chemical systems. Second, predictive power of modern QC methods was used to probe new chemical species with nonlinear optical (NLO) properties. A common thread through the projects presented was a rationalization of size- and composition-dependent properties of clusters and periodic systems based on the
analysis of their electronic structure. Particularly, chemical bonding deciphering was an essential part of electronic structure analysis in each discussed project. The concept of multicenter bonds helped explain various properties in a chemically intuitive manner. The key results from this thesis are summarized below.

Using the concept of multicenter bonds and AdNDP approach, we performed chemical bonding analysis in a MoS$_2$ monolayer. Although MoS$_2$ is one of the most studied materials in the world and the most important member of transition metal dichalcogenides, its complete bonding picture has remained unclear. In addition to expected Mo–S covalent bonds, we found that this material is σ-aromatic. Three Mo atoms inside each hexagonal ring were shown to be carriers of σ-aromatic 3c-2e bonds. Our finding were later experimentally supported by observed high values of $^{95}$Mo chemical shift anisotropy (1025 ppm).\textsuperscript{1}

In a set of three joint experimental and theoretical investigations, we studied stability trends, dopant effects, and chemical bonding in gas phase clusters.

Using theoretical tools, we identified two isomers of IrB$_3$\textsuperscript{−} in a photoelectron spectrum that compete for the global minimum (GM). Bonding analysis showed that the tetrahedral IrB$_3$ isomer involves a significant covalent Ir–B bonding and a weak ionic bonding with charge transfer from B$_3$ to Ir and can be viewed as an Ir–($\eta^3$B$_3$\textsuperscript{+}) complex. This study provided the first example of a boron-to-metal charge-transfer complex and the evidence of a the smallest π-aromatic B$_3$\textsuperscript{+} system coordinated to a negatively charged transition metal, which may be viable for bulk synthesis with suitable ligands.

In another joint experimental and theoretical investigation, we studied stability and electronic structure of BiB$_n$\textsuperscript{−} ($n = 6–8$) clusters. In all the planar GMs of BiB$_n$\textsuperscript{−} ($n = 6–8$),
the Bi atom can be viewed as a trivalent “big nitrogen”, engaging in covalent bonding with the planar boron GMs by using its three 6p orbitals while the 6s² electrons are inert and remain as a lone pair. The large atomic radius of the Bi atom hinders its insertion into the periphery of the planar boron clusters, in contrast to that observed in carbon- or Al-doped boron clusters.²⁻⁶ BiB₇⁻ and BiB₈⁻ are doubly (σ and π) aromatic, whereas BiB₆⁻ is doubly antiaromatic with global antiaromaticity being decomposed into local aromatic sites. Interestingly, π-aromaticity is shared over entire clusters while σ-aromaticity is the attribute of boron fragments. Because of the large disparity in atomic size between B and Bi, bulk bismuth boride is expected to exhibit unique properties.⁷⁻¹¹ However, it has not been synthesized yet. We hope our contribution to the understanding of B-Bi interactions will facilitate the synthesis of this material.

Gold is known to be one of the most inert metals. However, reduced to nanoscale, gold clusters less than 5 nm exhibit surprising structural and electronic properties.¹²⁻²¹ In an effort to further examine dopant effects and peculiar planarity trends in small gold systems, we performed a study on a gold cluster doped with Zn atom. In collaborative research with Lai-Sheng Wang group, we interpreted a photoelectron spectrum and found a dominant GM of the Au₉Zn⁻ cluster. The closed-shell global minimum of Au₉Zn⁻ was found to have a planar D₃h structure with a central Zn atom. The electron binding energy of the D₃h Au₉Zn⁻ was measured to be 4.28 eV, which is extremely high and indicates a very stable electronic system. Interestingly, this binding energy is even higher than the one of the parental open-shell D₃h Au₁₀⁻ cluster which indicates possible dopant-controlled binding energies in small gold systems. The high electronic stability of the global minimum was consistent with its large computed HOMO-LUMO gap of 3.3 eV. Chemical bonding
analyses showed that the $D_{3h}$ Au$_6$Zn$^-$ is doubly $\sigma$-aromatic systems which further underlines its high stability.

The remaining three projects reported purely theoretical investigations. One of them was devoted to the stabilization of a vital sulfate dianion while the other two described theoretical predictions of new species with nonlinear optical properties.

SO$_4^{2-}$ dianion plays an important role in various biological and atmospheric processes. Interestingly, an isolated dianion is electronically unstable and emits one of its electrons. In a solvated form, it needs at least three water molecules to be stabilized. In an attempt to understand the dianion stabilization upon hydration, we systematically studied charge transfer and cage effect in SO$_4^{2-}$(H$_2$O)$_n$ (n = 1–40) clusters. Computational analysis revealed that small amount of electron density (0.15 |e| in NBO scheme) is transferred from the dianion when it is stabilized by three water molecules. SO$_4^{2-}$ directly donates its charge only to the first solvation shell (12 H$_2$O molecules) and the most intense charge transfer occurs upon the addition of the first 7 H$_2$O molecules. We also showed that the cage effect significantly stabilizes the dianion at $n \leq 12$. Thus, the most intense stabilization processes occur only at $n \leq 12$ (the first solvation shell). These results might be used to improve and accelerate various investigations modeling the behavior of sulfate in aqueous solutions.

F-centers are defects in ionic crystals in which an anion vacancy is filled with one or more electrons. These trapped electrons are directly or indirectly responsible for various electric, optical, magnetic, and catalytic properties in MgO crystal. Using electronic structure analysis, we showed that a MgO surface could be configured to contain ionic defects in a periodic fashion which would help utilize F-centers with highest efficiency. Moreover, a high concentration of diffuse pairs on the surface gives rise to nonlinear optical
response at low photon energy regions. Computational analysis revealed that such defective surface is stable up to 1500 K which potentially enables the application of defective MgO in high temperature conditions.

Inspired by the interesting electronic structure of magnesium oxide defects, we tested the viability of isolated defective unit cells of cubic alkaline earth oxides featuring diffuse electron density. We were curious if cubic defects could exist in an isolated form of electrides – compounds where electrons are localized in space distinct from atomic positions and behave like self-contained anions. The desired geometry corresponded to $X_4O_{4-1}$ ($X = \text{Be, Mg, Ca, Sr, Ba}$) cubes with one missing vertex (oxygen) and the electron pair localized in the vacancy. According to our calculations, all but Be oxide defective cubes are dominant GMs on the potential energy surface which correlates with the fact that beryllium oxide crystallizes in the hexagonal structure unlike rock salt MgO, CaO, SrO, and BaO crystals. Electronic structure analysis showed that a highly diffuse electron pair causes noticeable NLO properties which proves these systems are electrides. To date, all synthesized electrides exist as solid-state compounds. However, molecular electrides could potentially have plenty of applications at nanoscale. Thus, we hope our findings may serve as a possible strategy for the design of electrides in a molecular form. As different $X_nO_m$ fragments are likely to coalesce forming solid seeds, special techniques may be needed for stoichiometry control such as matrix isolation,$^{27-31}$ single atom manipulation spectroscopy,$^{32-37}$ or advanced apparatus involving laser beams.
References


12098–12106.


(22) Markham, J. J. F-centers in Alkali Halides, Academic Press, New York, **1966**.


APPENDICES
Appendix A – Permission letters for journal copyright release

α-Aromaticity in the MoS2 Monolayer
Author: Maksim Kulichenko, Alexander I. Boldyrev
Publication: The Journal of Physical Chemistry C
Publisher: American Chemical Society
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Author: Maksim Kulichenko, Wei-Jia Chen, Yang-Yang Zhang, et al
Publication: The Journal of Physical Chemistry A
Publisher: American Chemical Society
Date: Jun 1, 2021

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Author: Maksim Kulichenko, Nikita Fedik, Konstantin V. Bozhenko, et al
Publication: The Journal of Physical Chemistry B
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Date: May 1, 2019

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Author:
Maksim Kulichenko, Nikita Fedik, Dmitry Steglenko, Ruslan M. Minyaev, Vladimir I. Minkin, Alexander I. Boldyrev

Publication: Chemical Physics
Publisher: Elsevier
Date: 1 April 2020

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Designing Molecular Electrides from Defective Unit Cells of Cubic Alkaline Earth Oxides

Author: Maksim Kulichenko, Andrey N. Utensyhev, Konstantin V. Bozhenko
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Advisor: Alexander I. Boldyrev

**B.Sc.** (with Honors) — Moscow State University, Moscow, Russia 2014 — 2018
Department of Fundamental Physical and Chemical Engineering
Major: Applied Mathematics and Physics

EXPERIENCE

**Graduate Contractor** with Los Alamos National Lab 2020 — 2022
Research assistant position at USU funded by Los Alamos National Lab
Research Assistant — Utah State University 2018 — 2022

Research topic: computational chemistry

Summer Internship — Los Alamos National Lab, NM Summer 2020

Internship topic: Development of sampling techniques for machine learning potentials

Internship — Institute of Problems of Chemical Physics of Russian Academy of Sciences 2017 — 2018

Member of a student council — Moscow State University 2014 — 2018

TEACHING EXPERIENCE

CHEM 1225 Chemical Principles Lab II, USU Spring 2019

CHEM 1215 Chemical Principles Lab I, USU Spring 2020

CHEM 1215 Chemical Principles Lab I, USU Fall 2020

Evaluations in range 9-10

PARTICIPATION IN GRANTS

Los Alamos National Laboratory 2021 — 2022

Development of Next Generation Methods for Constructing Machine Learning Based Interatomic Potentials

US National Science Foundation 2018 — 2020

Deciphering Bonding in Excited States, Solvated Species, and Novel 0D, 1D, 2D, and 3D Chemical Systems
AWARDS
Recipient of Increased State Academic Scholarship, Moscow State University 2017
Winner of Universiade “Lomonosov” in physical chemistry MSU, Moscow 2018
Director's Postdoctoral Fellowship, Los Alamos National Laboratory 2022

PEER REVIEW ACTIVITY
Journal of Physical Chemistry C – 1 review
Inorganic Chemistry – 2 review
Theoretical Chemistry Accounts – 1 review

CONFERENCES AND ORAL MESSAGES
Utah State University, Oral Presentation 2021
Topic: Sampling Rare Events with Bias Machine Learning Potentials

Los Alamos National Lab, Lightning Talks, Oral Presentation 2021
Topic: Diversification of ML Datasets via Bias Potentials as Functions of Uncertainty

ACS Meeting, Live Speaker Presentation 2021
Topic: Diversification of ML datasets via “uncertainty” as a bias potential

Utah State University, Oral Presentation 2020
Topic: Diversification of ML Datasets via Bias Potentials as Functions of Uncertainty

Los Alamos National Lab, Lightning Talks, Oral Presentation 2020
Topic: Diversification of ML Datasets via Bias Potentials as Functions of Uncertainty
Utah State University, Oral Presentation 2019

Topic: Charge Distribution and Stabilization of Hydrated Sulfate Clusters SO$_4^{2-}$(H$_2$O)$_n$

ACS National Meeting at San Diego, CA, poster session 2019

Topic: Elusive Electrides. From Solids to Molecules

Utah State University, Oral Presentation 2019

Topic: Electrides

PUBLICATIONS

Citations –160 (Google Scholar)

h-index – 9

1. Inorganic Molecular Electride Mg$_4$O$_3$: Structure, Bonding and Nonlinear Optical Properties

   M. Kulichenko, N. Fedik, K. V. Bozhenko, A. I. Boldyrev


2. Two Names of Stability: Spherical Aromatic or Superatomic Intermetalloid Cluster [Pd$_3$Sn$_8$Bi$_6$]$^{1+}$

   N. Fedik, M. Kulichenko, A. I. Boldyrev

   Chem. Phys., 2019, 522, 134 (IF=2.3, 15 citations)

3. High-Resolution Photoelectron Imaging of IrB$_3$⁻: Observation of a p-Aromatic B3⁺ Ring Coordinated to a Transition Metal


4. Hydrated Sulfate Clusters $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ ($n = 1$–$40$): Charge Distribution Through Solvation Shells and Stabilization

**M. Kulichenko**, N. Fedik, K. V. Bozhenko, A. I. Boldyrev

*J. Phys. Chem. B*, 2019, 123, 18, 4065 (IF=3.0, 24 citations)

5. Expansion of aromaticity magnetic criteria on multi-layer structures. Magnetic response and spherical aromaticity of Matryoshka-like $[\text{Sn@Cu}_{12}@\text{Sn}_{20}]^{12-}$ cluster

**M. Kulichenko**, N. Fedik, A. I. Boldyrev, A. Muñoz-Castro


6. Periodic F-defects on the MgO Surface as Potential Single-Defect Catalysts with Non-Linear Optical Properties

**M. Kulichenko**, N. Fedik, D. Steglenko, R. M. Minyaev, V. I. Minkin, A. I. Boldyrev

*Chem. Phys.*, 2020, 532, 110680 (IF=2.3, 10 citations)

7. Can aromaticity be a kinetic trap? Example of mechanically interlocked aromatic polycatenanes built of cyclo[18]carbon

N. Fedik, **M. Kulichenko**, D. Steglenko, A. I. Boldyrev

*Chem. Commun.*, 2020, 56, 2711-2714 (IF=6.2, 27 citations)

8. $\sigma$-aromaticity in MoS2 monolayer

**M. Kulichenko**, A. I. Boldyrev


9. Bottled spiro-doubly aromatic trinuclear $[\text{Pd}_2\text{Ru}]^+$ complexes


*Chem. Sci.*, 2021, 12, 477-486 (IF=9.8, 10 citations)
10. Double \( \sigma \)-Aromaticity in a Planar Zinc-Doped Gold Cluster: \( \text{Au}_9\text{Zn}^- \)

   **M. Kulichenko**, W.-J. Chen, Y.-Y. Zhang, C.-Q. Xu, J. Li, L.-S. Wang

   *J. Phys. Chem. A*, 2021, 125, 21, 4606 (IF=2.8, 5 citations)

11. Designing Molecular Electrides from Defective Unit Cells of Cubic Alkaline Earth Oxides

   **M. Kulichenko**, A. N. Utenyshev, K. V. Bozhenko

   *J. Phys. Chem. C*, 2021, 125, 17, 9564 (IF=4.1, 2 citations)

12. Spherical aromaticity in inorganic chemistry (Invited chapter)

   **M. Kulichenko**, N. Fedik, N. Tkachenko, Á. Muñoz-Castro, Z.-M. Sun, A. I. Boldyrev

   *Aromaticity - Modern Computational Methods and Applications*, Elsevier, 2021

13. The Rise of Neural Networks for Materials and Chemical Dynamics


   *J. Phys. Chem. Lett.* 2021, 12, 6227 (IF=6.5, 7 citations)

14. Bridging Aromatic/Antiaromatic Units. Recent Advances in Aromaticity and Antiaromaticity in Main-group and Transition-metal Clusters from Bonding and Magnetic analyses Invited review

   N. V. Tkachenko, I. A. Popov, **M. Kulichenko**, N. Fedik, Z.-M. Sun, A. Muñoz-Castro, A. I. Boldyrev


15. Photoelectron Spectroscopy of Size-Selected Bi-B Clusters: \( \text{BiB}_n^- \) (n=6-8)


   *J. Phys. Chem. A*, 2021, 125, 31, 6751 (IF=2.8, 3 citations)