# TRANSITION-METALS AND EXCITED STATES; CHALLENGING APPLICATIONS OF AB INITIO CHEMISTRY

by

## NATHAN JOHN DE YONKER

(Under the Direction of Henry F. Schaefer III)

#### ABSTRACT

Two sets of molecular isomers, the iron monoisocyanide (FeNC) / iron monocyanide (FeCN) pair, and the hydroboron monoxide (HBO) / boron hydroxide (BOH) pair, are investigated with a variety of high-level *ab initio* techniques. The electronic structure of the FeNC and FeCN pair does not easily succumb to the coupled cluster ansatz, even when newly developed correlation-consistent polarized valence iron basis sets and inclusion of perturbative or partial iterative triple excitations are included in the wave function. Due to disparities between the one-electron properties obtained with multireference configuration interaction (MRCI) and coupled cluster methods, the coupled cluster wave function could be considered inapplicable, at least at the currently tractable coupled cluster excitation level.

On the contrary, the accuracy of linear and bent ground state BOH MRCI geometries, dipole moments, and harmonic frequencies are spectacularly poor with a full valence active space, while coupled cluster methods perform well. Using a new variant of the equation-of-motion coupled cluster (EOM-CC) method to include partial triple excitations within excited state wave functions, seven linear and nine bent excited states of HBO and BOH are characterized. Adiabatic and vertical transition energies of low-lying BOH states will guide an

experimental hypothesis that BOH, which has not yet been synthesized in any form, may be a suitable high energy-density material.

INDEX WORDS: *ab initio* quantum chemistry, equation-of-motion coupled cluster, coupled cluster, multireference configuration interaction, transition metals, iron cyanide, FeNC, FeCN, boron hydroxide, BOH, HBO, excited electronic state

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My first course at the University of Michigan, Intro Organic Chemistry, was taught by Prof. Brian P. Coppola. He was recommended multiple times as being the best instructor of this notorious course, having won the Golden Apple U. of M. Teacher of the Year award in 1994. Prof. Coppola's unconventional style won me over, and I not only excelled, but signed on for his (even more notorious) honors Orgo II course. This course, more difficult than some of my graduate curriculum, was one of the most intense academic experiences I have ever had. When it was finished, Prof. Coppola agreed to become my academic advisor even though I was not an honors student. During my five years at U of M, Prof. Coppola was always available to offer academic and emotional assistance. Few college students can ever say that their first university Professor would not only become an outstanding professional influence, but also a friend. Thunderous applause also goes to all of my academic mentors and peers at the University of Michigan especially Prof. Robert R. Sharp, Prof. Dimitri Coucouvanis, Dr. Jeremy C. Miller, Dr. Dell T. Rosa, Dr. Nathaniel J. Schaefle, Prof. Charles R. Cowley, Prof. Megan Aronson, the Funky Monkey Oscillators, and the 2001 SAS members.

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# CHAPTER 1

# AN INFORMAL INTRODUCTION AND A SHORT REVIEW OF ELECTRONIC

STRUCTURE THEORY

## LEARNING TO CRAWL, LEARNING TO WALK, LEARNING TO TYPE

The goal of modern computational technology has endeavored towards "smaller, faster, and cheaper" functionality.<sup>1,2</sup> Since it was coined in 1965, Moore's Law, in which the number of transistors able to be fit on a single integrated circuit doubles every few years, has qualitatively held true.<sup>3</sup> Though Moore's Law is often oversimplified or paraphrased incorrectly for marketing aims,<sup>4,5</sup> it is generally used as a testament of the computer industry's continual growth and the imperturbable decline of computing costs.

Until the 1980's, computational chemistry had been primarily performed on mainframes owned by academic or government institutions, and computing time was shared among many principal scientists. The scientific history of these mainframes and their host research institutions is quite rich.<sup>1,6,7</sup>. Administration and maintenance of such massive electronics was costly at best and the portability, or the flexibility of code to run properly on different computer architectures without substantial modification, of *ab initio* software was non-existent.

The use of mini-computers in computational chemistry was pioneered by Schaefer and Miller at the Lawrence Berkeley Laboratory (LBL) in the late 1970's.<sup>8</sup> Their new Datacraft 6024/4 mini-computer would "sit comfortably in a 10 ft x 12 ft room" and cut the cost of computing time by one-sixth compared to that of the LBL-owned CDC 7600 mainframe. Increasing the visibility of cheaper computational chemistry, the benchmarks of Schaefer and Miller would slowly shift the trend towards research groups purchasing and maintaining their own computational resources.

In July of 1985, Susan Colwell published an article under the direction of Prof. Nicholas C. Handy entitled "Quantum Chemistry on Microcomputers".<sup>9</sup> Loaned a PC XT from IBM, the Handy group modified the CADPAC (Cambridge Analytical Derivatives PACkage) FORTRAN code to run self-consistent field (SCF) energy computations with the IBM PC disk operating system (DOS 2.0). This publication represented the first reported *ab initio* computation on a personal computer. Prof. Handy was confident that "the future was very rosy for computation because of the relatively good time performance on a PC, and the huge reduction in cost." Handy would also soon assist Strure Nordholm on the MICROMOL software package, presumably the first portable *ab initio* microcomputer code.<sup>10</sup>

An IBM PC XT would have also been in the DeYonker household in July 1985, shortly after my seventh birthday. In fact, the IBM PC XT would be the third microcomputer that my family had access to. My father worked for IBM for the majority of his professional career, and had procured personal computers through purchase, testing, or loan for almost my entire cognizant life. While I initially learned some BASIC programming, the microcomputer would serve more as a source of entertainment for most of my childhood. Still, educational and recreational PC software instilled within me a never-ending curiosity towards math, science, and technology. Little would I expect to cross paths with the authors of the "Quantum Chemistry on Microcomputers."

In August 2004, I was invited to attend a conference in honor of Prof. Handy's retirement, dubbed "Molecular Quantum Mechanics: The No-Nonsense Path to Progress". It was spearheaded by the first generation of quantum chemists with PCs at their disposal. Personal interactions with Prof. Handy and many of the elder quantum chemists bolstered my appreciation for having unfettered access to such powerful technology.

As it might forever be a dominant area of *ab initio* development, the topic of electron correlation was frequently discussed at the Handy conference. The research contained in this dissertation is concerned with the electronic correlation problem, but has an unusual focus.

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While popular post-Hartree-Fock methods used to determine electron correlation can be applied with confidence towards well-behaved molecules, these methods can occasionally contradict each other or fail to provide an acceptable level of accuracy for "pathological" systems. Understanding why the standard methods are inappropriate, accepting limitations of current theory, and providing the best possible characterization of these challenging systems is a task that quantum chemists do not often voluntarily undertake.

#### DETERMINATION OF ELECTRONIC STRUCTURE

This summarization of electronic structure methodology is by no means complete, and readers are encouraged to seek historical and technical details in numerous review articles and books.<sup>11-18</sup> Manipulation of the time-independent non-relativistic Schrödinger equation using quantum mechanics based solely on fundamental physical constants has largely followed the same formula since Boys initiated the development of configuration interaction (CI) methods.<sup>19</sup> The Schrödinger equation,

$$\hat{\mathbf{H}} \left| \Psi \right\rangle = \boldsymbol{\mathcal{E}} \left| \Psi \right\rangle \tag{1.1}$$

is an eigenvalue equation dependent on the relative position vectors of the N electrons  $(r_{ij})$  and the M nuclei  $(R_{AB})$  of atomic number Z, as well as the nuclear-electronic distance  $(r_{iA})$ .

By assuming the *N* electrons are traveling in a static nuclear field, the Born-Oppenheimer approximation,<sup>20</sup> or the "clamped-nuclei" approximation is applied. Terms from the Hamiltonian that depended on  $R_{AB}$  are eliminated or held constant, thus allowing separate determination of the nuclear and electronic wave function. The total Hamiltonian operator is now the sum of the electronic Hamiltonian,

$$\hat{\mathbf{H}}_{elec} = -\sum_{i}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{i}^{N} \sum_{A}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$$
(1.2)

whose terms are the electronic kinetic energy, the Coulombic electron-nuclear attraction, and the electronic repulsion, respectively, plus a constant nuclear repulsion term,

$$\sum_{A}^{M} \sum_{B}^{M} \frac{Z_A Z_B}{R_{AB}}.$$
(1.3)

As is well-known, only for small and / or highly constrained many-body systems can Eq. 1.2 be solved exactly, due to the mathematical challenge of determining the inter-electronic distance,  $\sum_{i}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$ .<sup>21-25</sup> The unfortunate underlying truth of quantum chemistry is that it is built upon several layers of approximation. Yet even the simplest approximations of the electronic wave function met with encouraging early success when compared to experimentally known results.<sup>13,26-29</sup> The entire field of quantum chemistry has then thrived with the goal of systematically and rigorously improving the accuracy and efficiency of these approximations.

As a starting point for molecular systems, one can take linear combinations of atomic orbitals (functions describing the radial character of one electron in the component atoms) in order to define molecular orbitals (MOs).<sup>30</sup> Taking the Pauli exclusion principle into account, Slater determinants are written as possible antisymmetrized products of MOs, describing both the spin and spatial distribution of one-electron ( $\chi_a$ ).<sup>13,31,32</sup> In terms of defined finite atomic orbital basis sets for all atoms in the molecular system, one can use chemical intuition to write the Slater determinant as the ground state wave function, resulting in the Hartree-Fock (HF) wave function,

$$\Psi^{HF}(\mathbf{x}_{1}\mathbf{x}_{2}...\mathbf{x}_{n}) = \left| \chi_{a}(\mathbf{x}_{1})\chi_{b}(\mathbf{x}_{2})...\chi_{z}(\mathbf{x}_{n}) \right\rangle.$$
(1.4)

The wave function of Equation 1.4 is computed by diagonalizing a matrix of the HF antisymmetrized MO products,

$$\Psi^{HF} = (N!)^{-1/2} \begin{vmatrix} \chi_a(\mathbf{x}_1) & \chi_b(\mathbf{x}_1) & \dots & \chi_N(\mathbf{x}_1) \\ \chi_a(\mathbf{x}_2) & \chi_b(\mathbf{x}_2) & & \chi_N(\mathbf{x}_2) \\ \vdots & & \ddots & \\ \chi_a(\mathbf{x}_N) & \dots & & \chi_N(\mathbf{x}_N) \end{vmatrix}.$$
(1.5)

The eigenvectors of this matrix can be optimized with the iterative SCF method<sup>26,33</sup> and then operated upon to obtain expectation values for the electronic energy and observable physical quantities of the system at a specified nuclear geometry. Solution of the optimal MO set follows the variational principle,

$$\left\langle \Psi^{HF} \left| \hat{\mathbf{H}} \right| \Psi^{HF} \right\rangle \geq \mathcal{E}_{0}$$
 (1.6)

where the expectation value of the Hamiltonian operating on the HF wave function is an upper bound to the exact electronic energy of the system.

In order to optimize the MOs, they must be represented in a form that can be parameterized. The most computationally elegant depiction of MOs is obtained by expansion of contracted Gaussian-type atomic orbitals (CGTOs).<sup>34,35</sup> The use of a finite CGTO basis set implies that the SCF solution to the wave function is only an approximation of the true infinite basis (also called the "complete basis set") Hartree-Fock wave function.

#### ELECTRON CORRELATION

By employing the HF approximation, the Schrödinger equation is treated as a one-body problem and a vast simplification is built into the electronic structure problem. Of course, the electronic wave function is actually dependent on the motion of all *N*-electrons, and the many-body interactions of all electrons within the system must be included. Though HF theory can essentially recover 95 - 99% of the total energy for a given atomic or molecular system, it is on the scale of the unaccounted energy that chemically significant phenomena such as bonding, vibrational and rotational interactions, molecular isomerization, and electronic excitations occur. In the 1950's, deficiencies of the HF method were already well known and it became prudent to employ a linear combination of a larger set of Slater determinants, inclusive of the HF Slater determinant, and to optimize their relative contributions to the electronic wave function.

Generally termed configuration interaction (CI),<sup>19,34,36</sup> it was proven that if the coefficients of the entire set of Slater determinants were determined, then the time independent, non-relativistic electronic wave function would be exactly solved within the constraints of the chosen finite basis sets. Inclusion of all Slater determinants gives what is called the "full CI" wave function. Löwdin<sup>27</sup> first defined the correlation energy as the difference between the full CI energy expectation value and the HF energy expectation value,

$$\boldsymbol{\mathcal{E}}_{corr} = \boldsymbol{\mathcal{E}}_{full \ CI} - \boldsymbol{\mathcal{E}}_{HF} \,. \tag{1.7}$$

For N electrons, and 2K spin orbitals (basis functions), the number of possible Slater determinants and thus the size of the CI matrix can be determined by,

$$\frac{(2K)!}{N!(2K-N)!},$$
(1.8)

which is computationally feasible for a small (but growing) number of systems. Truncating the full CI wave function and optimizing a smaller set of the most "important" Slater determinants remains the best trade-off of computational tractability and wave function accuracy.

Correlated *ab initio* methods employing a trial molecular wave function are generally divided into three major categories: (1) a many-body perturbation correction to the HF wave function, (2) CI expansions (also including multi-configuration self-consistent field methods),

where a linear excitation operator is applied to generate a range of possible substitutions from the occupied MOs of the HF reference into the unoccupied orbital space,

$$\left|\Psi_{CI}\right\rangle = c_{0}\left|\Psi_{HF}\right\rangle + \sum_{ra}c_{a}^{r}\left|\Psi_{a}^{r}\right\rangle + \sum_{\substack{a < b \\ r < s}}c_{ab}^{rs}\left|\Psi_{ab}^{rs}\right\rangle + \sum_{\substack{a < b < c \\ r < s < t}}c_{abc}^{rst}\left|\Psi_{abc}^{rst}\right\rangle + \cdots,$$
(1.9)

and (3) coupled cluster expansions where products of substituted determinants are incorporated in the exponential "cluster" excitation operators in order to approximate the effects of higherorder substitutions,

$$\Phi_{CC} \equiv e^{\hat{T}} \Psi_{HF} \tag{1.10}$$

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots .$$
(1.11)

A consequence of truncating the CI / CC expansion of the electronic wave function is that two different types of electron correlation emerge. One type is the short-range interaction of electrons in a system, often called the "instantaneous interaction". The antisymmetric nature of the Hartree-Fock wave function subtly accounts for some of this short-range interaction because of the Pauli exclusion principle, as the wave function will become zero (called a "Fermi hole") when two electrons with equivalent spin occupy the same spatial coordinates. However, the positions of electrons with opposite spin do not depend on each other. The instantaneous Coulombic repulsion of electrons with opposite spin can be grossly underestimated. If electrons are allowed to "jump" into unoccupied MOs of higher energy, there is a small, but finite chance that *N*-electrons can occupy the same region of space. By allowing occupation of these MOs (previously unoccupied in the HF approximation) some percentage of this new Slater determinant will contribute to the correlated wave function. It is expected that the kinetic energy of the system will get higher and the potential energy of the system will lower dramatically when two electrons are about to "collide". It is the Virial Theorem that dictates an overall lowering of the electronic energy when considering electron correlation, as the electronic potential energy is proportional to double the kinetic energy,

$$-2T(\chi) = V(\chi) \tag{1.12}.$$

To summarize, inclusion of excited determinants (configurations) and the instantaneous interaction of electrons within them describes the electron dynamics. Our terminology is combined to conclude that the configuration interaction is solved for in order to recover the "dynamical correlation" of electrons in the system.

Sinanoğlu<sup>37</sup> first proposed the second type of electron correlation, when multiple Slater determinants strongly contribute to the wave function, sometimes approaching or containing degeneracy with the zeroth-order HF approximation. This can occur in situations when one is trying to characterize bond-breaking, geometries near transition-states, molecules containing atoms with near-degenerate atomic orbitals, or excited electronic states. This effect is known as long-range correlation, often called "nondynamical" or "static" correlation. Atoms or molecules containing significant nondynamical correlation are often referred to as "multireference" systems.

## CHALLENGING SYSTEMS

Highly developed since the humble beginnings as a hypothesis of Sinanoğlu<sup>38</sup> and its first implementations in modern form by Čížek and Paldus,<sup>39-41</sup> coupled cluster algorithms are generally regarded as recovering the most dynamical correlation energy for the computational time required, while also adhering to the notion of wave function "size consistency".<sup>42</sup> The most useful forms of the coupled cluster equations are the coupled cluster singles and doubles (CCSD)

equations first derived by Purvis and Bartlett,<sup>43</sup> and the perturbative triples correction [CCSD(T)] formalized by Raghavachari *et al.*<sup>44</sup> Due to its success, speed, and accuracy level, the CCSD(T) method has often been dubbed the "gold-standard" of *ab initio* quantum chemistry. Interested readers are recommended more complete reviews of coupled cluster theory and applications.<sup>17,45-47</sup>

As the coupled cluster expansion eventually reaches the full CI limit of the exact wave function, it has been shown that single-reference dynamically-correlated coupled cluster methods can also indirectly account for some nondynamical correlation when a high enough excitation level is utilized. An excellent example of this has been studies of ozone, a rather pesky multireference molecule.<sup>48-53</sup> A transition-metal complex with multiple-bonded ligand species may present even larger dynamical and nondynamical correlation effects. Contrary to ozone, the coupled cluster wave function may fail in such a situation, even when using large basis sets and high orders of reference wave function excitation. A method that explicitly determines both dynamical and nondynamical correlation such as multireference configuration interaction (MRCI) must be employed.<sup>12,15,54</sup> However, for very difficult systems, the amount of dynamical correlation recovered by MRCI methods might not be nearly enough to accurately quantify excitation energies and spectroscopic properties. An example of this situation is presented; the isomeric pair of iron monoisocyanide and iron monocyanide (FeNC / FeCN).

Coupled cluster methods perform quite well in characterizing ground and excited electronic states of hydroboron monoxide and boron hydroxide (HBO / BOH). General quantum chemical intuition would lead one to believe that the ground states of this molecular pair would also be accurately described by the MRCI methods. Surprisingly, the MRCI wave functions of BOH and HBO are severely affected by active space problems, and a careful, non-"black box"

approach must be taken in order to unravel the mysteries of this deceptively complex system using multireference methods.

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# CHAPTER 2

# LOW-LYING ELECTRONIC STATES OF FENC AND FECN: A THEORETICAL JOURNEY INTO ISOMERIZATION AND QUARTET/SEXTET COMPETITION<sup>1</sup>

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## ABSTRACT

With several levels of multireference and restricted open-shell single-reference electronic structure theory, optimum structures, relative energetics, and spectroscopic properties of the lowlying  ${}^{6}\Delta, {}^{4}\Delta, {}^{4}\Pi, {}^{6}\Pi$ , and  ${}^{4}\Sigma^{-}$  states of linear FeNC and FeCN have been investigated using five contracted Gaussian basis sets ranging from Fe[10s8p3d], C/N[4s2p1d] to Fe[6s8p6d3f2g1h], C/N[6s5p4d3f2g]. Based on cc-pVQZ MRCISD+Q results appended with core correlation and relativistic corrections, we propose the relative energies:  $T_{\rm e}({\rm FeNC})$ ,  ${}^{6}\Delta(0) < {}^{6}\Pi(2300 {\rm ~cm}^{-1}) < {}^{4}\Delta$  $(2700 \text{ cm}^{-1}) < {}^{4}\Pi (4200 \text{ cm}^{-1}) < {}^{4}\Sigma^{-}; \text{ and } T_{e}(\text{FeCN}), {}^{6}\Delta (0) < {}^{6}\Pi (1800 \text{ cm}^{-1}) < {}^{4}\Delta (2500 \text{ cm}^{-1}) < {}^{6}\Omega (0) < {}^{6}\Pi (1800 \text{ cm}^{-1}) < {}^{6}\Omega (0) < {}^{6}\Omega (0) < {}^{6}\Pi (1800 \text{ cm}^{-1}) < {}^{6}\Omega (0) < {}^{6}\Omega (0) < {}^{6}\Pi (1800 \text{ cm}^{-1}) < {}^{6}\Omega (0) < {}^{6}\Omega (0) < {}^{6}\Pi (0) < {}^{6}\Omega (0) <$  ${}^{4}\Pi$  (2900 cm<sup>-1</sup>) <  ${}^{4}\Sigma^{-}$ . The  ${}^{4}\Delta$  and  ${}^{4}\Pi$  states have massive multireference character, arising mostly from  $11\sigma \rightarrow 12\sigma$  promotions, whereas the sextet states are dominated by single electronic configurations. The single-reference CCSDT-3 method appears to significantly overshoot the stabilization of the quartet states provided by both static and dynamic correlation. The  ${}^{4,6}\Delta$  and  $^{4,6}\Pi$  states of both isomers are rather ionic, and all have dipole moments near 5 D. On the ground  $^{6}\Delta$  surface, FeNC is predicted to lie 0.6 kcal mol<sup>-1</sup> below FeCN, and the classical barrier for isocyanide/cyanide isomerization is about 8 kcal mol<sup>-1</sup>. Our data support the recent spectroscopic characterization by Lei and Dagdigian [J. Chem. Phys. 114, 2137 (2000)] of linear  $^{6}\Delta$  FeNC as the first experimentally observed transition-metal monoisocyanide. Their assignments for the ground term symbol, isotopomeric rotational constants, and the Fe-N  $\omega_3$  stretching frequency are confirmed; however, we find rather different structural parameters for <sup>6</sup> $\Delta$  FeNC:  $r_{e}$ (Fe-N) = 1.940 Å and r(N-C) = 1.182 Å at the cc-pVQZ MRCISD+Q level. Our results also reveal that the observed band of FeNC originating at 27 236 cm<sup>-1</sup> should have an analog in FeCN near 24 700 cm<sup>-1</sup> of almost equal intensity. Therefore, both thermodynamic stability and absorption intensity factors favor the eventual observation of FeCN via a  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  transition in the near-UV.

## **INTRODUCTION**

The electronic structure of small polyatomic molecules (M-X) containing a transition metal (M) and a common ligand (X) is of broad chemical interest. Theoretical studies of such molecules can provide general insight about metal-ligand bonding interactions and may greatly increase the chemical knowledge available for larger poly-ligand systems. Poly-ligand metal-cyanides are a prevalent class of compounds. The  $[Fe(CN)_6]^{2^2,4^-}$  ions, classic examples of low-spin octahedral complexes, are commonly referred to as "Prussian Blues," and are useful for removing or identifying toxins in animals, humans, and plants.<sup>1,2</sup> The Fe-CN bond is also thought to influence bioinorganic synthesis<sup>3</sup> and hemeprotein chemistry.<sup>4</sup> Observations of monocyanides and monoisocyanides in the interstellar medium using radio-frequency spectroscopy,<sup>5,6</sup> as well as terrestrial characterizations using laser fluorescence excitation or laser induced fluorescence spectroscopy,<sup>7-12</sup> have provided many opportunities to experimentally study the structure of the metal-cyanide and metal-isocyanide bonds.

Due to the rather isotropic electronic charge distribution of the CN<sup>-</sup>/NC<sup>-</sup> ligand, the bonding within alkali-metal monocyanide/isocyanide molecules is often "polytopic",<sup>13</sup> meaning that the metal-ligand interaction is quite ionic and nondirectional. This characteristic allows the metal atom to orbit the CN<sup>-</sup> ligand on a flat potential energy surface at moderate temperatures. From an alternative dynamical perspective, if the metal atom is massive, the ligand executes facile internal rotation. The equilibrium structure of such polytopic compounds is often controversial.<sup>14-16</sup> Two alkali-metal cyanide/isocyanide pairs (NaCN/NaNC and KCN/KNC) exhibit a "T-shaped" equilibrium structure.<sup>16,17</sup> In the case of lithium and the alkaline earth metals, the linear isocyanide isomer is the equilibrium geometry, but slight vibrational excitation

allows these molecules to tunnel through low-energy internal rotation barriers, as experimentally and theoretically observed with MgNC, BeNC, CaNC, and SrNC, and also with AlNC.<sup>11,13,18-23</sup> A few molecules, such as CuCN and NiCN, have been theoretically predicted or spectroscopically characterized to have a cyanide global minimum.<sup>24,25</sup>

In the interstellar medium, iron is one of the ten most<sup>26</sup> cosmically abundant atoms, and it is expected that a vast number of novel iron-containing compounds will be discovered. Terrestrial production of FeNC was recently achieved by Lei and Dagdigian,<sup>7</sup> and substantiated with high-resolution fluorescence excitation spectroscopy, which indicated the linear isocyanide to be the most stable species. According to analysis of rotational-resolved lines near the 360 nm region, Lei and Dagdigian reported a linear  $^{6}\Delta$  ground electronic state indicated by a  $\Omega' = 7/2 \leftarrow$  $\Omega''=9/2$  transition attributed to a  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  electronic excitation, believed identical to that of FeF and FeCl. Assuming that FeNC has a similar spin-orbit coupling constant to the FeF and FeCl high-spin ground states ( $A = -78.15 \text{ cm}^{-1}$  and  $-75.88 \text{ cm}^{-1}$ , respectively), the observed rotational constants were fit using the Hund's case (a) coupling scheme to obtain the bond distances of the ground state. The Fe-N and N-C bond lengths were reported to be  $2.01 \pm 0.05$  Å and  $1.03 \pm 0.08$ Å, respectively. Lei and Dagdigian do not comment on this unusual C-N bond length, which is 0.1 Å shorter than any C-N bond length observed theoretically or experimentally. A linear leastsquares fit to an observed (00v<sub>3</sub>) vibrational progression up to  $v_3 = 7$  yielded an  $\omega_3$  Fe-N harmonic vibrational stretching frequency of 464 cm<sup>-1</sup>, but no statistically significant  $\omega_{e}x_{e}$  value.

Since iron is a d<sup>6</sup> element, there are many possibilities of both high-spin and low-spin electronic configurations for polyatomic molecules with an iron center.<sup>27</sup> Many of these states have potential energy surfaces that are very low-lying in energy near the ground state. The reasoning for an Fe-X molecule to have a high- or low-spin ground state is not simplistic,

beginning with the case of the simplest iron molecule, FeH, where the ground state is thought to be  ${}^{4}\Delta$ , although other nearly isoenergetic candidates exist.<sup>28,29</sup> Comparisons of FeCN/FeNC to FeH will be discussed in detail in later sections. An excellent review by Harrison<sup>30</sup> recently summarized the complexity of the electronic structure of Fe-X diatomics. Sophisticated levels of theory that include a multireference valence description to describe nondynamical correlation (also known as static correlation), high orders of electronic excitation to describe dynamical correlation, and large basis sets are necessary to ensure the relative energies of the ground state with respect to low-lying excited states are accurately determined.

To add to the understanding of cyanide/isocyanide bonding, *ab initio* studies of transition metal CN/NC compounds have been undertaken in our laboratory to determine how the ionic/covalent nature of the metal-ligand bond affects the stability of the cyanide versus the isocyanide isomer. In this paper, equilibrium geometries, harmonic frequencies, and electronic excitation energies of FeNC and FeCN are compared to those found in the experimental work of Lei and Dagdigian.<sup>7</sup> New basis sets and highly-correlated methods are used in order to determine the barrier height for internal rotation and relative energetics of various electronic states.

## THEORETICAL METHODS

Five basis sets were utilized in this study of FeNC/FeCN.<sup>31</sup> The first is of double-zeta quality and is a combination of the Fe(14s11p6d/10s8p3d) Wachters set<sup>32</sup> and the Huzinaga-Dunning (9s4p1d/4s2p1d) basis<sup>33</sup> for the C and N atoms. In their study of FeH, Sodupe et al.<sup>34</sup> stress the importance of including f polarization functions to properly describe the energy difference between the ground state and low-lying excited states of iron-containing compounds.

Accordingly, the next basis set used for FeCN/FeNC was the Roos augmented double-zeta ANO basis set<sup>35,36</sup> for all three atoms [Fe(21s15p10d6f/6s5p4d2f), C/N(14s9p4d/4s3p2d)]. A second ANO basis set developed at NASA Ames<sup>37,38</sup> was also implemented, which is not only of triplezeta quality, but also includes g functions for iron (21s15p10d6f4g/7s6p4d3f2g), and f and g functions for carbon and nitrogen (13s8p6d4f2g/5s4p3d2f1g). Triple- and quadruple-zeta correlation-consistent polarized valence (cc-pVXZ) basis sets very recently developed for iron by Ricca and Bauschlicher<sup>39</sup> are new, high-quality basis sets developed for iron-containing molecules. These basis sets were conjoined with augmented correlation-consistent basis sets<sup>40</sup> for the lighter atoms in order to describe any anionic character of the NC/CN ligand. The ccpVTZ/aug-cc-pVTZ basis has Fe(20s15p10d2f1g/6s8p6d2f1g) and C/N(11s6p3d2f/5s4p3d2f), the cc-pVQZ/aug-cc-pVQZ basis has Fe(20s15p10d3f2g1h/6s8p6d3f2g1h) and and C/N(13s7p4d3f2g/6s5p4d3f2g). To determine the effects of core-valence interactions, the ccpVTZ basis set was modified in the manner proposed by Ricca and Bauschlicher<sup>39</sup> to create the cc-pCVTZ basis and combined with the standard aug-cc-pCVTZ basis set for C and N.<sup>41</sup>

Full geometry optimizations were performed for all basis sets at the ROHF,  $^{42,43}$  CISD,  $^{44,45}$  CCSD,  $^{46-48}$  and CCSDT-3<sup>49</sup> levels of theory for the lowest-lying states of each applicable term symbol of FeCN/FeNC:  $^{6}\Delta$ ,  $^{6}\Pi$ ,  $^{4}\Delta$ ,  $^{4}\Pi$ , and  $^{4}\Sigma^{-}$ . In general, the correlation treatments included only valence electrons, freezing the 1s MOs of carbon and nitrogen, as well as the 1s, 2s, 2p, 3s, and 3p MOs of Fe. No virtual orbitals were frozen in this study. In computations with the cc-pCVTZ basis set, the 3s and 3p orbitals of iron and the 1s orbitals of C/N were included to gauge core correlation effects.

When investigating the multireference character of the molecules, state-averaged (SA) CASSCF geometry optimizations were performed with a 13 electron/12 MO active space.<sup>50,51</sup>

This active space includes all valence orbitals except the low-lying 2s orbitals of carbon and nitrogen, whose omission greatly reduced computation time. Internally contracted multireference CI<sup>52</sup> was also performed using SA-CASSCF optimized MOs. Appendix Table A.1 gives the leading CI coefficients (0.10 cutoff) of the four electronic states for both isomers that were studied using multireference CI methods. These coefficients remained similar amongst basis sets. All configuration state functions (CSFs) contained in the SA-CASSCF wavefunction with CI coefficients greater than 0.02 in magnitude were used as references in internally-contracted MR-CISD computations. Equilibrium geometries were also optimized upon the multireference Davidson corrected energy (MRCISD+Q).<sup>53</sup> For the quartet states and sextet states, the MRCI computations employed 21-22 and 8 reference configurations, respectively. Quartet states had approximately 25-460 million uncontracted configurations contracted by one order of magnitude, while the sextet states had 16-325 million uncontracted configurations contracted one order of magnitude using the Wachters/DZP basis set and two orders of magnitude with cc-pVQZ. The sum of the squares of the reference configuration coefficients was between 0.993 and 0.997 in the final MRCI wavefunctions. The Psi 2.0.8,<sup>54</sup> ACES II,<sup>55</sup> and MOLPRO<sup>56,57</sup> software packages were all extensively used in this study.

Scalar relativistic corrections for relative energies were carried out by computing oneelectron mass-velocity and Darwin first-order perturbation terms,<sup>58-60</sup> principally via MOLPRO at the valence MRCISD level with the fully uncontracted cc-pVQZ/aug-cc-pVQZ basis set. Comparative single-reference relativistic results were obtained via ACES II at the all-electron level with the cc-pVQZ/aug-cc-pVQZ basis, kept contracted due to program limitations.

## **RESULTS AND DISCUSSION**

The primary valence configurations for the five electronic states of FeNC/FeCN studied here are compiled in Table 2.1, along with  $C_{\infty v}$  and  $C_{2v}$  state designations. In Tables 2.2 (FeNC) and 2.3 (FeCN), ROHF geometries, harmonic vibrational frequencies, and dipole moments are collected for various states. Tables 2.4 (FeNC) and 2.5 (FeCN) show relative energies, geometries, and harmonic vibrational frequencies using the largest basis sets and correlated wavefunctions. Figure 2.1a and 2.1b depict equilibrium geometries for the two lowest-lying states (<sup>4</sup> $\Delta$  and <sup>6</sup> $\Delta$ ) at various levels of theory.

#### EQUILIBRIUM GEOMETRIES

For FeNC, the ROHF geometries exhibit Fe-N distances in a relatively narrow 1.967-2.007 Å range, and with larger basis sets the ordering of r(Fe-N) values is  ${}^{4}\Delta < {}^{4}\Sigma^{-} < {}^{6}\Delta < {}^{4}\Pi < {}^{6}\Pi$ . The corresponding N-C bond lengths lie in the 1.150-1.166 Å interval, with the quartet states displaying r(N-C) values shorter than in the sextet states by roughly 0.002 Å. For FeCN, the ROHF metal-ligand (Fe-C) distances, with a range of 2.037-2.120 Å, are longer and more dispersed than for FeNC, and the order of bond lengths among the states is quite different:  ${}^{4}\Sigma^{-} < ({}^{4}\Delta, {}^{4}\Pi) < ({}^{6}\Delta, {}^{6}\Pi)$ . The larger metal-ligand separations are accompanied by r(C-N) values that are in a similar 1.134-1.150 Å interval compared to the isocyanide isomer. In contrast to FeNC, the C-N distances of the quartet cyanide states are longer than those of the sextet states. The Badger's Rule correlation of decreasing bond distances with increasing stretching frequencies is generally but not inviolately found among the ROHF results. The real bending frequencies in

Tables 2.2 and 2.3 give a preliminary indication that all low-lying states of FeNC and FeCN have linear equilibrium geometries.

As shown in Figure 2.1, Tables 2.4, 2.5, and Appendix A.2, methods which include dynamic correlation result in substantial Fe-C/Fe-N bond shortening, particularly for the quartet states. For quartet states, FeNC has r(Fe-N) distances of 1.869 - 1.896 Å, and FeCN has r(Fe-C) distances of 1.925 - 1.980 Å. FeNC sextet states have an r(Fe-N) range of 1.928 - 1.956 Å, and FeCN sextet states have an r(Fe-C) range of 2.031 - 2.055 Å. The order of Fe-N bond lengths for FeNC is  ${}^{4}\Delta < {}^{4}\Pi < {}^{6}\Delta < {}^{6}\Pi$ , and the Fe-C bond lengths order as  ${}^{4}\Pi < {}^{4}\Delta < {}^{6}\Pi < {}^{6}\Delta$ . Thus, dynamic correlation changes the ROHF ordering of metal-ligand distances among electronic states. Examining r(C-N) for FeNC states, the ROHF bond distance ordering remains  ${}^{4}\Pi < {}^{4}\Delta < {}^{6}\Pi < {}^{6}\Delta$  at dynamically correlated levels of theory. However, for FeCN, the correlated r(C-N) values are more tightly clustered and reordered  $({}^{4}\Delta < {}^{6}\Delta < {}^{6}\Pi < {}^{4}\Pi)$  compared to their ROHF counterparts. Clearly, as a possible measure of metal-ligand charge transfer and  $\pi$  backbonding, r(C-N) for the two isomers displays very subtle effects that require a more in depth study. The cc-pVQZ MRCISD+Q results show agreement of Fe-C/Fe-N bond lengths with CCSD to 0.008 Å for the  $\Delta$  states. The inclusion of core-valence effects does not significantly change equilibrium geometries.

The equilibrium geometries agree with the trend that the cyanides typically have an M-C bond length that is 0.1 Å longer than the isocyanide M-N bond. Our C-N bond distances for FeNC/FeCN are in full accord with the 1.14-1.19 Å range of bond distances in other metal cyanide and/or isocyanide studies,<sup>61,62</sup> as well as various results for the bond length of CN<sup>-</sup> anion, including the latest theoretical MRCISD+Q value (1.183 Å),<sup>63</sup> our cc-pVQZ CCSDT-3 prediction (1.181 Å), and a fitted  $r_e(CN^-)$  of 1.177 Å from a photoelectron spectroscopy study.<sup>64</sup>

The experimental value<sup>7</sup> of  $1.03 \pm 0.08$  Å ascribed to linear <sup>6</sup> $\Delta$  FeNC is far shorter than any known C-N bond distance and is most likely due to the large uncertainties in B<sub>0</sub> when analyzing the results of laser excitation fluorescence spectra. Our theoretical results [ $r_e$ (N-C) = 1.183 Å with cc-pVQZ CCSDT-3 and 1.182 Å with cc-pVQZ MR-CISD+Q] are barely within twice the error interval of experiment. Our best Fe-N (cc-pVQZ MRCISD+Q) bond length of 1.93 Å is also in significant disagreement with the 2.01 ± 0.05 Å value of Lei and Dagdigian. The two isomers have very large Fe-C/Fe-N bond distances compared to those of diatomic Fe-C ( $r_e = 1.58$  Å)<sup>65,66</sup> and Fe-N ( $r_e = 1.57$  Å), <sup>67,68</sup> since strong multiple Fe-X bonding is not present within the cyanide and isocyanide isomers. In the initial study of the cc-pV*XZ* basis sets for Fe, Ricca and Bauschlicher<sup>39</sup> compare FeCO geometries to observed rotational spectra.<sup>69</sup> Their CCSD(T) results for X = 3.5 show Fe-C and C-O bond lengths within 0.02 Å and 0.005 Å of experiment, respectively. We expect similar accuracy of our results, highlighting strong disagreement with the experimental geometry of <sup>6</sup> $\Delta$  FeNC.

Carbon-13 isotopic substitution on FeNC agrees well with experiment, giving an average shift in the rotational constant of 0.062 cm<sup>-1</sup> for our results compared to 0.060 cm<sup>-1</sup> in Ref. 7. Validating Lei and Dagdigian's characterization of the isocyanide isomer, the <sup>13</sup>C-substituted cyanide isomer shows a lessening of  $B_e$  of 0.0013 cm<sup>-1</sup>. The FeCN isotopic substitution is expected to have less of an effect on the rotational constants because the substituted atom is closer to the molecular center of mass.

# TRANSITION STATE GEOMETRIES ON THE $^6\!\Delta$ SURFACE

The transition state for a  ${}^{6}\Delta$  surface isomerization representing rotation of the iron atom around the CN ligand is shown in Figure 2.1c. The energetics for this isomerization are shown in Table 2.6. The Fe-C-N angle is sensitive to the level of theory, but the true value is apparently near 90°. The Fe-C bond length is elongated less than 0.05 Å from the FeCN minimum (cf. Figures 2.1a and 2.1b), and is much shorter than the Fe-N distance, giving an "L-shaped" structure. At the ccpVQZ CASSCF optimized geometry, the Fe-C distance is 2.148 Å and the Fe-N distance is 2.411 Å. Only for Cu has a theoretical transition-metal CN/NC transition state geometry been reported thus far, by Boldyrev et al.<sup>62</sup> At the MP2 6-311+G\* level, their study shows a Cu-N bond 0.7 Å shorter than the Cu-C bond.

#### **DIPOLE MOMENTS**

All electronic states of FeNC and FeCN have large dipole moments. With the single-reference correlated methods, the  $\mu$  values for the sextet states lie in the 4-5 Debye range. The corresponding dipole moments for the quartet state are at least 2 D higher, with this gap decreasing substantially as the dynamical electron correlation treatment is extended from CISD to CCSD. It is striking that after inclusion of nondynamical correlation, the quartet dipole moments are lowered so much that they become essentially the same as their sextet counterparts. In the CASSCF computations, the dipole moments of the <sup>4,6</sup> $\Pi$  and <sup>4,6</sup> $\Delta$  states for both FeCN and FeNC cluster in the 4.87-5.84 D range, while the MRCISD values for the <sup>4,6</sup> $\Delta$  states are uniformly smaller by roughly 0.5 D. This trend can be understood from the contour plots shown
in Figure 2.2 of the  $11\sigma(^4\Delta)$  and  $12\sigma(^6\Delta)$  ROHF molecular orbitals of FeCN. Clearly,  $11\sigma \rightarrow 12\sigma$  promotions shift electron density to the Fe atom and in turn lower the magnitude of the dipole moment. The corresponding orbitals of FeNC are of similar nature, leading to the same effect on  $\mu$ . The single-reference description of the quartet states has a  $(11\sigma)^2(12\sigma)^0$  configuration, and the ROHF dipole moments exceed 9 D. However, these states have prodigious multireference character (Appendix Table A.1), and the most important excited configurations involve single or double  $12\sigma$  occupation, which serves to reduce the dipole moment to near 5 D. The sextet states are dominated in zeroth-order by a triplet-coupled  $(11\sigma)^1(12\sigma^1)$  configuration and thus have  $\mu$  near 5 D. Mulliken partial charge analysis at the cc-pVQZ MRCISD level gives partial positive charges on Fe of 0.73-0.78 for quartet states and 1.08-1.14 for sextet states. One conclusion to be drawn from assessment of the dipole moment data for FeNC and FeCN is that the single-reference correlation methods overestimate the ionic character of the quartet states and may thus be dubious in their predictions of quartet/sextet energy differences.

## VIBRATIONAL FREQUENCIES

The only vibrational frequency assigned by experiment for FeNC/FeCN is for the Fe-N stretching mode of the  ${}^{6}\Delta$  state of the isocyanide isomer. As previously mentioned, a fit to an observed (00v<sub>3</sub>) progression gave the harmonic frequency  $\omega_3$ (FeNC) = 464 cm<sup>-1</sup>.<sup>7</sup> With larger basis sets, the ROHF method gives harmonic frequencies of 470-475 cm<sup>-1</sup>. The valence correlation treatments contract the Fe-N bonds significantly, but the corresponding vibrational frequency predictions are only slightly higher, 488-494 cm<sup>-1</sup>. The inclusion of Fe outer core correlation yields  $\omega_3$ (FeNC) = 475 cm<sup>-1</sup> with cc-pCVTZ CCSD, in excellent agreement with

experiment. By comparison, the same level of theory gives  $\omega_3$ (FeCN) = 417 cm<sup>-1</sup> for the <sup>6</sup> $\Delta$  state of the cyanide isomer. Thus, our predictions for the metal-ligand stretching vibrations favor the experimental assignment of the observed frequency to the isocyanide species. For FeNC, the <sup>4</sup> $\Delta$  – <sup>6</sup> $\Delta$  difference for  $\omega_3$  is about +10 cm<sup>-1</sup> with coupled cluster methods, but when the quartet states are given a proper multireference correlation treatment (MRCISD+Q), the difference becomes –83 cm<sup>-1</sup>, enough to clearly distinguish the IR spectra of these two states.

For the C-N stretching mode ( $\omega_1$ ), the cyanide frequencies are 84-165 cm<sup>-1</sup> higher than their isocyanide counterparts for all states and across all levels of theory and are shown in Tables 2.2 – 2.5. With the correlated methods, the  $\omega_1$  values for the <sup>4,6</sup> $\Delta$  and <sup>4,6</sup> $\Pi$  states of each isomer cluster in narrow intervals of less than 15 cm<sup>-1</sup>, making it difficult to distinguish amongst these states on this basis. Lei and Dagdigian<sup>7</sup> proposed  $\omega_1$ (FeNC) = 2200 cm<sup>-1</sup> as a rough estimate based on frequencies of other M-NC compounds. Except at the cc-pVTZ CCSDT-3 level, our values for  $\omega_1$ (FeNC, <sup>6</sup> $\Delta$ ) vary between 2135 and 2145 cm<sup>-1</sup>. For isolated CN<sup>-</sup>,  $\omega_c$  is 2052 and 2072 cm<sup>-1</sup> with cc-pVQZ MRCISD+Q and cc-pVTZ CCSDT-3, respectively, as compared to 2035 cm<sup>-1</sup> from a photoelectron spectroscopy experiment.<sup>64</sup> Adopting the cc-pVQZ MRCISD+Q predictions, this calibration suggests that  $\omega_1$ (FeNC, <sup>6</sup> $\Delta$ ) should be near 2120 cm<sup>-1</sup>, somewhat lower than the estimate of Ref. 7.

The computation of bending frequencies for FeNC/FeCN is complicated by the necessity of retaining the correct root structure of the electronic Hamiltonian, of accounting for Renner-Teller splitting, of overcoming convergence difficulties for the reference wave functions, and lastly, of averting variational collapse as the symmetry of the molecule is lowered to  $C_s$ . At the ROHF level, the energetic ordering of electronic states is  ${}^{6}\Delta ({}^{6}A', {}^{6}A'') < {}^{6}\Pi (2 {}^{6}A', 2 {}^{6}A'') < {}^{4}\Pi ({}^{4}A', {}^{4}A'') < {}^{4}\Delta (2 {}^{4}A', 2 {}^{4}A'')$ , so that upon bending distortions, the only states not subject to

variational collapse are the A' and A'' components of the  ${}^{6}\Delta$  and  ${}^{4}\Pi$  states. For these states, coupled cluster  $\omega_2$  values may be computed by finite difference techniques, and selected results are reported in Tables 2.4 and 2.5. Because the bending frequencies of the  ${}^{6}\Delta$  and  ${}^{4}\Pi$  are real, they can be positively assigned to have a linear geometry at correlated levels of theory. Full resolution of this issue is deferred for later studies that might invoke CASSCF analytic second derivatives, MRCISD finite differences methods, or EOM-CC techniques,<sup>70,71</sup> for example.

## ADIABATIC EXCITATION ENERGIES IN THE IR REGION

Numerous studies of FeH have determined that the relative energies of various electronic states are not similar between Hartree-Fock and correlated levels of theory. Early Hartree Fock calculations initially determined the ground state of FeH to be first  ${}^{4}\Sigma^{-72}$  and then  ${}^{6}\Delta$ .<sup>73</sup> More than a decade passed before the ground state of FeH was consistently shown with both experimental<sup>74</sup> and high-level theoretical methods<sup>28,75,76</sup> to actually be  ${}^{4}\Delta$ . When larger basis sets, static correlation, and dynamic correlation were included, far more correlation energy for the lower spin quartet states was recovered. With high enough levels of theory, the X  ${}^{4}\Delta$  energy eclipses that of the HF ground state a  ${}^{6}\Delta$ . Theoretical and experimental studies of the high-spin molecules FeCl<sup>77</sup> and FeF<sup>78</sup> determined that while dynamical correlation is a large factor in energy state ordering, it is not likely to switch the configuration of the ground state between uncorrelated and correlated levels of theory. Lei and Dagdigian<sup>7</sup> predict that the spin-orbit couplings of FeNC/CN more closely match those of the iron-halogens, one of the factors of validating the  ${}^{6}\Delta$  ground state. To ascertain if FeNC/FeCN behaves more like low-spin FeH or high-spin FeF/FeCl, it is imperative to determine how correlated wavefunctions alter the energy splitting between high spin and low spin configurations.

The most notable problem in predicting relative energies of the low-lying states of FeNC/FeCN is that the sextet states are dominated by single configurations, while the quartet states have large multireference character, as detailed in Appendix Table A.1. When singlereference CCSD theory is applied to the  ${}^{4}\Delta$  and  ${}^{4}\Pi$  states, extraordinarily large  $T_{1}$  amplitudes result for the  $11\sigma \rightarrow 12\sigma$  excitations, precisely those seen above which reduce the dipole moments. In contrast, for both isomers no  $T_1$  coefficient exceeds 0.06 for the  $^6\Delta$  and  $^6\Pi$  states at any level of theory. As a specific case, the Wachters/DZP CCSD wavefunction for the  ${}^{4}\Delta$  state of FeCN shows a maximum  $T_1$  amplitude of 0.96 and 9 different  $T_1$  amplitudes over 0.06. The Wachters/DZP CCSDT-3 method fares even worse, giving for example, FeNC  $^4\Delta$  and  $^4\Pi$ maximum amplitudes of 1.70 and 1.61, with 18 and 14  $T_1$ 's over 0.06, respectively! For quartet states, we find that the largest  $T_1$  amplitudes, as well as the number of amplitudes over 0.06, decrease significantly with increasing basis set size, but are as still as large as 0.50 at the ccpVQZ CCSDT-3 level. The large  $T_1$  amplitudes for the quartet states signal enormous orbital relaxation effects from the ROHF reference, and are consistent with the presence of competing electronic configurations, as seen in the CASSCF CI coefficients of Appendix Table A.1. Not surprisingly, our attempts to determine full CCSDT wavefunctions were crippled by severe convergence problems. Given these manifestations of multireference character, the popular CCSD(T) method<sup>79-81</sup> should not be relied upon for FeNC/FeCN quartet states, because it should not be expected that connected triple excitations in these types of systems can be adequately treated by perturbation theory. Regarding the various CCSDT-n iterative partial triples methods, a recent study by He et al.<sup>82</sup> concluded that CCSDT-1b may overestimate the contribution of triple excitations, and we found that CCSDT-4 suffers from the same convergence problems as CCSDT. Therefore, we have used the CCSDT-3 method to gauge the effect of connected triple excitations. In this study, we do gain valuable information on relative energetics from analysis of coupled cluster results, but greater weight must be placed on the multireference configuration interaction predictions.

In Tables 2.7 and 2.8, theoretical results are collected for the adiabatic excitations energies of the low-lying states of FeNC and FeCN. Variations with level of theory of the  ${}^{6}\Delta - {}^{4}\Delta$  excitation energies obtained with the cc-pVQZ basis set are plotted in Figure 2.3. For the methods that do not include dynamical electron correlation, the excitation energies depend only weakly on basis set. Specifically, in Tables 2.7 and 2.8, the range of  $T_{e}$  values across basis sets is generally less than 350 cm<sup>-1</sup> for ROHF and 150 cm<sup>-1</sup> for CASSCF. The ROHF ordering of electronic states for both isomers is  ${}^{6}\Delta < {}^{6}\Pi < {}^{4}\Delta < {}^{4}\Sigma^{-}$ , with  ${}^{4}\Delta$  over 20 000 and 18 000 cm<sup>-1</sup> above  ${}^{6}\Delta$  for FeNC and FeCN, respectively. Improving the zeroth-order description with the CASSCF method gives the ordering  ${}^{6}\Delta < {}^{6}\Pi < {}^{4}\Delta < {}^{4}\Pi$  for both isomers, now with  ${}^{4}\Delta$  lowered to about 6400 and 6200 cm<sup>-1</sup> above  ${}^{6}\Delta$  FeNC and FeCN, respectively.

As expected, the dynamically correlated  $T_e$  predictions do display significant basis set dependence, as the addition of higher angular momentum functions slowly accounts for shortrange electron-electron cusp behavior.<sup>83-89</sup> The effect is largest for quartet states, where differential correlation effects with the ground <sup>6</sup> $\Delta$  state are greatest and valence basis set augmentation steadily lowers the excitation energies. For example, at the CCSD level,  $T_e(^4\Delta)$  for FeCN is lowered from 3372 cm<sup>-1</sup> with Wachters/DZP to 2260 cm<sup>-1</sup> with cc-pVTZ, and then finally to 2050 cm<sup>-1</sup> with cc-pVQZ. However, comparison of cc-pVTZ and cc-pCVTZ valence correlation results shows that improved flexibility in the core/valence region raises the quartet excitation energies by 100-250 cm<sup>-1</sup>. As shown in Fig. 3, both the ROHF  $\rightarrow$  CISD  $\rightarrow$  CCSD  $\rightarrow$  CCSDT-3 and CASSCF  $\rightarrow$  MRCISD  $\rightarrow$  MRCISD+Q correlation series exhibit monotonic reductions in the  ${}^{4}\Delta \leftarrow {}^{6}\Delta$  excitation energy of FeNC and FeCN. In fact, such correlation trends are seen in all of the  $T_{e}$  results in Tables 2.7 and 2.8. Using smaller basis sets, CCSDT-1b  ${}^{6}\Delta - {}^{4}\Delta$  energy splittings were within 115 cm<sup>-1</sup> of the CCSDT-3 results; with the larger basis sets, we find the CCSD(T) method to give excitation energies intermediate between CCSD and CCSDT-3.<sup>90</sup>

With the dipole moment and  $T_1$  amplitude discussions in mind, predicting the valence, nonrelativistic *ab initio* limits of the relative energies of low-lying states of FeNC and FeCN is treacherous. For the <sup>6</sup> $\Pi$  state, there is excellent agreement among the best coupled cluster and MRCI results in Tables 2.7 and 2.8:  $T_{\rm e}(^{6}\Pi) = 2450 \pm 50 \text{ cm}^{-1}$  for FeNC and 1750  $\pm 100 \text{ cm}^{-1}$  for FeCN. The data suggest that extrapolation to the complete basis set (CBS) limit would bring little change to the relative energy. In contrast, for  $T_{\rm e}(^{6}\Delta)$  the CCSDT-3 values are lower than their MRCISD+Q counterparts by about 2800 cm<sup>-1</sup> and 4000 cm<sup>-1</sup> for FeNC and FeCN, respectively. With a faulty ROHF quartet reference wave function, devoid of important static correlation, the CCSDT-3 scheme apparently *overshoots* the stabilization of the <sup>4</sup> $\Delta$  state. On the other hand, the <sup>6</sup> $\Delta$  – <sup>4</sup> $\Delta$  separation for FeH reveals that the cc-pVQZ MRCISD+Q method probably *underestimates* the stability of the quartet states by 800-1600 cm<sup>-1</sup>.<sup>28,75</sup> Thus we believe that in the non-relativistic, valence limit  $T_{\rm e}(^{4}\Delta) = 3000 \pm 1200 \text{ cm}^{-1}$  for both FeNC and FeCN, with the cyanide excitation being lower by a few hundred cm<sup>-1</sup>.

Core correlation and relativistic corrections to the  $T_e$  values are listed in Tables 2.7 and 2.8 and plotted in Fig. 3. The effect of correlating the Fe (3s, 3p) and C/N (1s) electrons, at the size-extensive cc-pCVTZ CCSD level, is to decrease the energy separation from the  $^6\Delta$  ground

state by 508 (612) and 845 (876) cm<sup>-1</sup> for the  ${}^{4}\Delta$  and  ${}^{4}\Pi$  states of FeNC (FeCN), respectively. The corresponding shifts in the  ${}^{6}\Pi - {}^{6}\Delta$  separations are less than 100 cm<sup>-1</sup>.

With regard to the relativistic corrections, completely different pictures are given by the single-reference CCSD and the multireference CISD computations. In the former case, the  ${}^{4}\Delta$  and  ${}^{4}\Pi$  states of FeNC/FeCN are raised by 1090 to 1990 cm<sup>-1</sup> over the  ${}^{6}\Delta$  ground states, amounts comparable to the magnitude of the analogous relativistic shift (2200 cm<sup>-1</sup>) in the  ${}^{5}D - {}^{5}F$  separation of atomic Fe.<sup>75</sup> We found that the large CCSD corrections obtained with ACES II are broadly confirmed by single-reference ROHF and CISD relativistic computations with MOLPRO. However, when MRCISD computations are executed via MOLPRO, the relativistic effect on the quartet adiabatic excitation energies drops by an order of magnitude, attesting to the dramatic changes static correlation makes on the electron density, as seen above in the dipole moment analysis.

Giving preference to the MRCISD predictions, we conclude that the relativistic shifts in FeNC/FeCN are comparable to the similar correction for the  ${}^{4}\Delta - {}^{6}\Delta$  splitting in FeH.<sup>28</sup> Specifically, relativity increases  $T_{\rm e}$  of the  ${}^{4}\Delta$  state of FeNC(FeCN) by 232 (192) cm<sup>-1</sup> while affecting the  ${}^{6}\Pi - {}^{6}\Delta$  separation by only -22 (-50) cm<sup>-1</sup>. The trends of relativistic effects of  $T_{\rm e}$  values of iron-containing species may be understood on the basis of total s, p, and d Mulliken populations in the various electronic states.<sup>75</sup>

Appending the sizable core correlation and relativistic shifts to the valence, nonrelativistic limits inferred above, we arrive at final estimates for the relative energies:  $T_{\rm e}({\rm FeNC})$ ,  $^{6}\Delta (0) < ^{6}\Pi (2300 \text{ cm}^{-1}) < ^{4}\Delta (2700 \text{ cm}^{-1}) < ^{4}\Pi (4200 \text{ cm}^{-1})$ ; and  $T_{\rm e}({\rm FeCN})$ ,  $^{6}\Delta (0) < ^{6}\Pi (1800 \text{ cm}^{-1}) < ^{4}\Delta (2500 \text{ cm}^{-1}) < ^{4}\Pi (2900 \text{ cm}^{-1})$ . Uncertainties are difficult to reliably assess, but perhaps are as large as  $\pm 1500$  cm<sup>-1</sup> for the quartet states and a few hundred cm<sup>-1</sup> for the  $^{6}\Pi$  states.

### ISOMERIZATION ENERGY AND BARRIER HEIGHT

The data in Table 2.6 address the compelling question of which isomer of FeNC/FeCN is lower in energy, and what is the isocyanide/cyanide interconversion barrier. In the single-reference correlation series, FeCN starts out substantially above FeNC, but the energy gap steadily decreases as the level of theory is improved. For example, with the cc-pVTZ basis, the ROHF, CISD, CCSD, CCSD(T), and CCSDT-3 isomerization energies,  $\Delta E_e(^6\Delta, \text{FeNC} \rightarrow \text{FeCN})$ , are 1819, 856, 413, 251 and 343 cm<sup>-1</sup> in order. Among the basis sets, the range of values is generally less than 100 cm<sup>-1</sup>, but for the correlated methods the NASA ANO set consistently gives outlying predictions 100-150 cm<sup>-1</sup> lower than their cc-pVQZ counterparts. Comparing the cc-pVTZ and cc-pCVTZ valence CCSD treatments suggests that an improved description of the core/valence region may favor the FeCN isomer by around 200 cm<sup>-1</sup>. Interestingly, the multireference correlation series exhibits a reversal of trends, *i.e.*, FeCN starts out substantially below FeNC but is steadily raised as the theoretical method is improved. Specifically, with the cc-pVQZ basis, the CASSCF, MRCISD, and MRCISD+Q isomerization energies are -1258, -509, and -166 cm<sup>-1</sup>, respectively. In summary, both the single- and multireference series predict isomerization energies less than 350 cm<sup>-1</sup> (1 kcal mol<sup>-1</sup>) in magnitude, but in the former case FeNC is lower while in the latter case FeCN is lower. Because the  $^{6}\Delta$  ground states of both isomers are well described in zeroth order by a single electronic configuration (Appendix Table A.1), preference is given here to the rigorously size-extensive coupled cluster results. Based on the cc-pVQZ and cc-pCVTZ CCSDT-3 predictions, we estimate the nonrelativistic, valence limit of  $\Delta E_e(^{6}\Delta, \text{FeNC} \rightarrow \text{FeCN})$  to be 200 ± 150 cm<sup>-1</sup>.

As shown in Table 2.6, the core correlation (+11 cm<sup>-1</sup>) and ZPVE corrections (+89 cm<sup>-1</sup>) do not substantially alter the FeNC/FeCN separation. Similarly to the adiabatic excitation energies, CCSD computations with ACES II predict a substantial relativistic effect (+745 cm<sup>-1</sup>) on the FeNC/FeCN isomerization energy, but the application of MRCISD theory via MOLPRO gives a relativistic shift of only -74 cm<sup>-1</sup>. Giving preference to the MRCISD result, our final prediction becomes  $\Delta E_0(^6\Delta, \text{ FeNC} \rightarrow \text{FeCN}) = 200 + 11 + 89 - 74 \approx 225$  cm<sup>-1</sup> with an uncertainty of perhaps a few hundred wavenumbers.

Several studies<sup>21,24,91</sup> of cyanide/isocyanide pairs have asserted that as the degree of covalency(ionicity) increases the cyanide(isocyanide) isomer becomes more stable and the isomerization barrier is heightened(lowered). As mentioned above, our Mulliken analysis at the cc-pVQZ MRCISD level gives partial charges on Fe of about +1.1 for the ground  $^{6}\Delta$  states of both FeNC and FeCN, revealing that both species are quite ionic. Nonetheless, our work shows that FeNC and FeCN are almost isoenergetic, with the isocyanide lower by about 0.6 kcal mol<sup>-1</sup>. In their study of NiCN, Kingston et al.<sup>24</sup> propose that the cyanide isomer is lower in energy because electron density is better drawn to the peripheral lone-pair nitrogen orbitals than those orbitals of the carbon atom. In FeNC/FeCN there is always greater negative charge on the atom adjacent to Fe, but the nitrogen in FeCN indeed has a -0.4 partial charge while that for the carbon in FeNC is only -0.1. Thus, the same type of charge distribution is present in the iron case as in the nickel case, but this feature is not associated with the existence of a lower-energy iron-cyanide isomer.

From a cc-pVQZ MRCISD+Q single-pont determined on top of the corresponding CASSCF transition state, the FeNC  $\rightarrow$  FeCN classical barrier on the <sup>6</sup> $\Delta$  surface is predicted to be 2775 cm<sup>-1</sup>, or about 8 kcal mol<sup>-1</sup>. While this barrier is large for a polytopic system, it is much smaller than expected for a covalently bonded species. The only available theoretical barrier height for a transition metal cyanide/isocyanide interconversion is 1.8 kcal mol<sup>-1</sup> for CuCN/CuNC at the 6-311+G\* MP2 level,<sup>62</sup> a value much lower than that for FeNC/FeCN. Our FeNC/FeCN barrier height and transition state geometry more closely match that of AlNC/AlCN studied by Ma and co-workers.<sup>20</sup> More information about similar barrier heights needs to be determined before a quantitative model can be made of barrier height/covalency versus directional preference of cyanide/isocyanide pairs of molecules.

# NEAR-UV ${}^{6}\Pi \leftarrow {}^{6}\Delta$ EXCITATION ENERGIES AND TRANSITION INTENSITIES

The experimentally observed band of FeNC starting at 27 236 cm<sup>-1</sup>, which corresponds to an excitation from the  ${}^{6}\Delta$  ground state to a  ${}^{6}\Pi$  state lying in the near-UV region, closely matches analogous excitations in FeCl (28 025 cm<sup>-1</sup>)<sup>92,93</sup> and FeF (30 239 cm<sup>-1</sup>).<sup>94,95</sup> The iron monohalogens have been thoroughly studied experimentally and determined to have high-spin  ${}^{6}\Delta$  ground states. However, the analogous  $e {}^{6}\Pi \leftarrow a {}^{6}\Delta$  excitation for low-spin FeH occurs near 19 000 cm<sup>-1</sup>.<sup>29,96</sup> We investigated electronic excitations of FeNC/FeCN between the ground  ${}^{6}\Delta$  state and the  ${}^{6}\Pi$  state lying in the near-UV region to compare with the experimentally observed transition energy. Table 2.9 shows the theoretical excitation energies of the near-UV  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  bands of FeCN and FeNC along with corresponding excitation energies of other iron-containing compounds. At the cc-pVQZ MRCISD+Q level, the FeNC vertical excitation energy

is 28 224 cm<sup>-1</sup> with an MRCISD square transition dipole matrix element  $|\mu_{fi}|^2$  of 7.330 D<sup>2</sup>. The analogous FeCN vertical excitation energy is found near 25 014 cm<sup>-1</sup> with  $|\mu_{fi}|^2 = 6.074 \text{ D}^2$ . The FeCN square transition dipole matrix element is 83% that of FeNC, indicating that the  ${}^{6}\Pi \leftarrow {}^{6}\Delta$ excitation for FeCN should be almost as intense as that of FeNC. Analyzing MO coefficients of both isomers shows an excitation from the 12 $\sigma$  to  $4\pi$  orbital, essentially an Fe(4p $\leftarrow$ 4s) transition akin to that identified by Lei and Dagdigian.<sup>7</sup> Our predictions of the FeNC  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  excitation are in good agreement with experiment, overestimating the absorption energy by approximately 1000 cm<sup>-1</sup>. Assuming a similar overestimation for the cyanide isomer, the FeCN excitation is expected to occur near 24 000 cm<sup>-1</sup>. Lei and Dagdigian<sup>7</sup> scanned a frequency region between 26 900-29 400 cm<sup>-1</sup> in their initial study, so the FeCN excitation would be out of the range of their experiment. From Table 2.9 and from theoretical transition dipole matrix elements of the excitation, we conclude that both thermodynamic stability and absorption intensity factors favor the eventual observation of an FeCN  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  transition in the near-UV.

### CONCLUSIONS

In this study of FeCN and FeNC, the ROHF, CISD, CCSD, CCSDT-3, CASSCF, MRCISD, and MRCISD+Q methods have been employed with five Fe/C,N basis sets, namely, Wachters/DZP, two ANO basis sets of double- and triple-zeta quality, and the correlation consistent cc-pVTZ/aug-cc-pVTZ and cc-pVQZ/aug-cc-pVQZ sets recently constructed for iron containing molecules. Corrections for core correlation and relativistic effects have also been included. Our principal conclusions are as follows:

(1) Both FeNC and FeCN have  ${}^{6}\Delta$  ground electronic states. Low-lying  ${}^{6}\Pi$ ,  ${}^{4}\Delta$ ,  ${}^{4}\Pi$  states are present in the IR and near-IR regions, with respective  $T_{\rm e}$  values near 2300, 2700, 4200 cm<sup>-1</sup> for FeNC and 1800, 2500, and 2900 cm<sup>-1</sup> for FeCN.

(2) The  ${}^{4,6}\Delta$  and  ${}^{4,6}\Pi$  states of both isomers are quite ionic, with Mulliken partial charges on Fe of 0.73-0.78 for the quartet states and 1.08-1.14 for sextet states. In the final analysis, all of these states have dipole moments near 5 D.

(3) On the ground state surface, FeNC and FeCN are nearly isoenergetic, with the isocyanide isomer lying lower by only 0.6 kcal mol<sup>-1</sup>.

(4) The classical barrier for the FeNC  $\rightarrow$  FeCN isomerization is about 8 kcal mol<sup>-1</sup>, certainly much smaller than anticipated for a covalent system. However, true polytopic species of high ionicity and nondirectionality, such as the monocyanides/isocyanides of alkali earth metals, have barriers of only 0-2 kcal mol<sup>-1</sup>, significantly smaller than for FeNC/FeCN. There is very little data on the isomerization of other transition-metal NC/CN compounds, and studies of the analogs for the 3d<sup>1</sup> to 3d<sup>5</sup> metals are greatly needed before bonding trends can be firmly established.

(5) The  ${}^{4}\Delta$  and  ${}^{4}\Pi$  states of both FeNC and FeCN have striking multireference character, whereas the corresponding sextet states are dominated by single electronic configurations. The additional configurations necessary for a proper zeroth-order decription of the quartet states arise from single and double  $11\sigma \rightarrow 12\sigma$  promotions, which are metal-ligand bonding to antibonding in character. The importance of including these configurations in the quartet reference wave functions is dramatically seen in the computation of the dipole moments, which are otherwise overestimated by 2-4 D.

(6) The recent spectroscopic characterization of linear  ${}^{6}\Delta$  FeNC by Lei and Dagdigian<sup>7</sup> is largely validated by our theoretical work, particularly the assignment of the ground term symbol, the  ${}^{13}$ C shift in the rotational constant, and the Fe-N stretching frequency of 464 cm<sup>-1</sup>. Moreover, our results confirm the essential features of the near-UV  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  excitation on which the experimental analysis was based, including the band origin, the absorption intensity, and the qualitative identification of the excitation as Fe(4p  $\leftarrow$ 4s). However, the empirically derived bond distances,  $r_{e}$ (Fe-N) = 2.01 ± 0.05 Å and  $r_{e}$ (N-C) = 1.03 ± 0.08 Å, are vitiated by theory. The ccpVQZ MRCISD+Q level predicts  $r_{e}$ (Fe-N) = 1.940 Å and  $r_{e}$ (N-C) = 1.182 Å.

(7) Our computations reveal that the observed band of FeNC originating at 27 236 cm<sup>-1</sup> should have an analog in FeCN near 24 000 cm<sup>-1</sup> with a square transition dipole moment less than 20% smaller. This  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  FeCN band is out of range of the XeCl excimer dye laser apparatus used in the experiments of Ref. 7, giving one explanation for why only FeNC was observed. Because FeCN lies less than 1 kcal mol<sup>-1</sup> above FeNC, it should be possible to overcome Boltzmann factors and obtain sufficient intensity to observe FeCN via its  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  transition in the near-UV.

Finally, the gross differences in electronic structure of the quartet vs. sextet states, as well as the isocyanide vs. cyanide isomers, make it particularly difficult to obtain converged *ab initio* predictions for the recalcitrant FeNC/FeCN system. For the quartet states, single-reference coupled cluster methods including connected triple excitations appear to underestimate the energy relative to the  $^{6}\Delta$  ground state, or have severe convergence problems. In contrast, calibrations on FeH suggest that the MRCISD wavefunctions computed here are missing significant dynamical correlation that lowers the relative energies of the FeNC/FeCN quartet states. The application of more advanced, multireference coupled-cluster methods and open-shell

*ab initio* theory would be helpful to refine our best predictions and elucidate the approach to the full CI limit in these model systems. Though many advances are needed in production-level *ab initio* theory to completely unravel the mysteries of transition-metal containing compounds, this study shows the progress of computational chemistry in attacking such difficult systems.

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Table 2.1: Predominant valence electronic configurations of five low-lying electronic states of FeNC and FeCN.

$C_{\infty v}$	$C_{2v}^{a}$	Configuration
$^{6}\Delta$	$A_1, A_2$	$[core]^{b} 8\sigma^{2}9\sigma^{2}3\pi^{4}10\sigma^{2}11\sigma^{1}4\pi^{2}1\delta^{3}12\sigma^{1}$
<sup>6</sup> Π	$B_{1}, B_{2}$	$[\text{core}]8\sigma^29\sigma^23\pi^410\sigma^211\sigma^14\pi^31\delta^212\sigma^1$
$^{4}\Delta$	$A_1, A_2$	$[\text{core}]8\sigma^29\sigma^23\pi^410\sigma^211\sigma^24\pi^21\delta^3$
$^{4}\Pi$	$B_{1}, B_{2}$	$[\text{core}]8\sigma^29\sigma^23\pi^410\sigma^211\sigma^24\pi^31\delta^2$
$^{4}\Sigma^{-}$	$A_2$	$[\text{core}]8\sigma^29\sigma^23\pi^410\sigma^211\sigma^14\pi^21\delta^4$

<sup>a</sup>The first irreducible representation listed is that used in our electronic structure computations unless a state-averaged CASSCF was performed, whereupon the two states were weighted 50/50. <sup>b</sup>Core is represented by [core] =  $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4$ .

Electronic State	Energy	r(Fe-N)	r(N-C)	μ	$\omega_l(\sigma)$	$\omega_2(\pi)^b$	$\omega_3(\sigma)$
Wachters/DZP - Fe[1	0s8p3d], C/N[4s2p	01d]		•	•	•	
<sup>4</sup> Σ <sup>-</sup>	-1354.656636	1.9677	1.1619	9.177	2319	258°	395
$^{4}\Delta$	-1354.672023	1.9677	1.1619	9.000	2349	379 <sup>c</sup>	427
<sup>4</sup> П	-1354.672422	1.9791	1.1622	9.101	2348	190(145)	434
$\Pi^{6}$	-1354.752339	1.9933	1.1645	5.289	2333	191(186) <sup>c</sup>	464
$^{6}\Delta$	-1354.764850	2.0074	1.1659	4.995	2321	206	450
Roos DZ ANO - Fe[6	55p4d2f], C/N[4s3	[p2d]					
4Σ-	-1354.713935	1.9792	1.1548	9.047	2337		418
$^{4}\Delta$	-1354.728965	1.9763	1.1557	8.963	2330		416
<sup>4</sup> Π	-1354.729836	1.9914	1.1551	9.101	2336	92	418
<sup>6</sup> П	-1354.808299	1.9980	1.1571	5.211	2332		452
$^{6}\Delta$	-1354.820701	1.9806	1.1576	4.688	2319	116	472
NASA ANO - Fe[7s6	p4d3f2g], C/N[5s4	lp3d2f1g]					
$4\Sigma^{-}$	-1354.720483	1.9785	1.1506	8.984	2334		419
$^{4}\Delta$	-1354.735017	1.9713	1.1515	9.080	2326		417
<sup>4</sup> П	-1354.735728	1.9881	1.1507	9.037	2332		423
П <sup>9</sup>	-1354.815005	1.9963	1.1530	5.242	2318		455
$^{6}\Delta$	-1354.827143	1.9785	1.1537	4.736	2314		474
cc-pVTZ / aug-cc-pV	TZ - Fe[6s8p6d2f]	lg], C/N[5s4	p3d2f]	•		· · · ·	
<sup>4</sup> Σ <sup>-</sup>	-1354.720155	1.9783	1.1508	9.01	2333		422
$^{4}\Delta$	-1354.729044	1.9706	1.1529	8.92	2318		421
<sup>4</sup> П	-1354.729814	1.9863	1.1523	9.06	2323	98	425
п <sup>9</sup>	-1354.809247	1.9959	1.1544	5.244	2329		426
$^{6}\Delta$	-1354.821510	1.9782	1.1550	4.681	2306	124	475
cc-pVQZ / aug-cc-pV	/QZ - Fe[6s8p6d3f	2g1h], C/N[	6s5p4d3f2g]	-	-		
$^{4}\Delta$	-1354.734921	1.9727	1.1517	8.92	2326	<u> </u>	418
$^{6}\Delta$	-1354.827188	1.9792	1.1538	4.692	2314	124	474
Expt. <sup>d 6</sup> Δ		$2.01\pm0.05$	$1.03\pm0.08$				$464\pm4.2$

Table 2.2: Total energies and physical properties for FeNC at the ROHF level of theory.<sup>a</sup>

<sup>a</sup>Energies are in hartrees, bond distances in Å , dipole moments in D, harmonic

vibrational frequencies in cm<sup>-1</sup>.

 $^{b}$ For the  $\Pi$  electronic states, which exhibit Renner-Teller splitting in the quadratic bending force

constants, each A' component is followed by its A'' counterpart in parenthesis.

<sup>c</sup>Subject to variational collapse; computed by analytic derivative techniques.

<sup>d</sup>Reference 7.

Electronic State	Energy	r(Fe-C)	r(C-N)	μ	$\omega_1(\sigma)$	$\omega_2(\pi)^b$	$\omega_3(\sigma)$
Wachters/DZP - H	Fe[10s8p3d], C/N[4	s2p1d]	• •			• • •	
<sup>4</sup> Σ <sup>-</sup>	-1354.661317	2.0353	1.1500	9.230	2441	210 <sup>c</sup>	394
$^{4}\Delta$	-1354.672733	2.0642	1.1486	9.236	2456	235 <sup>c</sup>	386
<sup>4</sup> П	-1354.674048	2.0686	1.1495	9.364	2447	223(207)	386
<sup>6</sup> П	-1354.746577	2.1196	1.1478	5.707	2463	213(204) <sup>c</sup>	399
$^{6}\Delta$	-1354.756322	2.1193	1.1471	5.359	2470	214	413
Roos DZ ANO - I	Fe[6s5p4d2f], C/N[	[4s3p2d]					
$4\Sigma^{-}$	-1354.718857	2.0411	1.1416	9.305	2449		388
$^{4}\Delta$	-1354.730206	2.0710	1.1403	9.254	2463		379
<sup>4</sup> П	-1354.731762	2.0746	1.1411	9.399	2455	219	381
<sup>6</sup> П	-1354.802856	2.1195	1.1395	5.647	2471		393
$^{6}\Delta$	-1354.812460	2.1187	1.1389	5.287	2479	198	406
NASA ANO - Fe	[7s6p4d3f2g], C/N	[5s4p3d2f1g]					
$4\Sigma^{-}$	-1354.725298	2.0433	1.1372	9.227	2443		387
$^{4}\Delta$	-1354.736183	2.0689	1.1359	9.161	2458		379
<sup>4</sup> П	-1354.737600	2.0739	1.1367	9.308	2454		455
<sup>6</sup> П	-1354.809575	2.1199	1.1352	5.654	2464		395
$^{6}\Delta$	-1354.818913	2.1186	1.1347	5.311	2471	204	408
cc-pVTZ / aug-cc	-pVTZ - Fe[6s8p60	l2f1g], C/N[5s4]	p3d2f]				
$4\Sigma^{-}$	-1354.719230	2.0402	1.1385	9.290	2441		391
$^{4}\Delta$	-1354.730149	2.0676	1.1372	9.241	2455		382
<sup>4</sup> Π	-1354.731585	2.0719	1.1380	9.388	2447	213	384
$\Pi^{6}$	-1354.803725	2.1187	1.1364	5.631	2462		394
$^{6}\Delta$	-1354.813221	2.1177	1.1358	5.279	2470	210	407
cc-pVQZ / aug-cc	-pVQZ - Fe[6s8p6	d3f2g1h], C/N[6]	s5p4d3f2g]				
$^{4}\Delta$	-1354.736036	2.0699	1.1361	9.213	2458		380
$^{6}\Delta$	-1354.818977	2.1186	1.1347	5.263	2472	199	409

Table 2.3: Total energies and physical properties for FeCN at the ROHF level of theory.<sup>a</sup>

<sup>a</sup>Energies are in hartrees, bond distances in Å, dipole moments in D, harmonic vibrational frequencies in cm<sup>-1</sup>.

<sup>b</sup>See footnote b of Table 2.2.

<sup>c</sup>Subject to variational collapse; computed by analytic derivative techniques.

Electronic State	Energy	r(Fe-N)	r(N-C)	Be	$\Delta(B_e^{13}C)$	μ	$\omega_1(\sigma)$	$\omega_2(\pi)$	ω3(σ)
cc-pVQZ / aug-cc	e-pVQZ CISD								
$4\Sigma^{-}$	-1355.255864	1.9161	1.1618	0.145976	0.006328	8.6743			
$^{4}\Delta$	-1354.269043	1.8985	1.1627	0.147887	0.006441	8.5121			
<sup>4</sup> П	-1355.267765	1.9203	1.1621	0.145512	0.006316	8.6871			
$\Pi^{6}$	-1355.296350	1.9586	1.1648	0.141228	0.006098	4.9975			
$^{6}\Delta$	-1355.307876	1.9438	1.1655	0.142739	0.006179	4.4873			
cc-pVQZ / aug-co	e-pVQZ CASSCF								
$^{4}\Delta$	-1354.897260	1.9611	1.1824	0.139795	0.006050	5.3582			
<sup>4</sup> П	-1354.886556	1.9704	1.1820	0.138862	0.006001	5.7234			
<sup>6</sup> П	-1354.913835	2.0066	1.1822	0.135225	0.005813	5.8385			
$^{6}\Delta$	-1354.926577	1.9887	1.1825	0.136980	0.005904	5.3366			
cc-pVQZ / aug-co	e-pVQZ MRCISD								
$^{4}\Delta$	-1355.311606	1.9020	1.1775	0.146444	0.006398	4.8889			
$^{6}\Delta$	-1355.334734	1.9480	1.1783	0.141426	0.006127	4.7868			
cc-pVQZ / aug-co	e-pVQZ MRCISD-	+Q							
$^{4}\Delta$	-1355.357202	1.8844	1.1813	0.148119	0.006483		2171		408
$^{6}\Delta$	-1355.377119	1.9395	1.1819	0.142084	0.006168		2135		491
cc-pVQZ / aug-co	c-pVQZ CCSD								
$4\Sigma^{-}$	-1355.326779	1.8903	1.1725	0.148089	0.006462				
$^{4}\Delta$	-1355.348080	1.8825	1.1741	0.148880	0.006449	6.9814	2153		495
<sup>4</sup> Π	-1355.338984	1.8932	1.1731	0.147733	0.006457	7.8597	2154		465
<sup>6</sup> П	-1355.351508	1.9511	1.1744	0.141367	0.006126	5.0369	2148		473
$^{6}\Delta$	-1355.362780	1.9369	1.1751	0.142833	0.006213	4.3349	2145		488
cc-pCVTZ / aug-	cc-pCVTZ CCSD								
$^{4}\Delta$	-1355.317317	1.8887	1.1767	0.147985	0.006478		2143		487
<sup>4</sup> Π	-1355.307126	1.8978	1.1758	0.147152	0.006432		2144		467
бП	-1355.322135	1.9592	1.1770	0.140358	0.006079		2135		473
$^{6}\Delta$	-1355.333281	1.9446	1.1776	0.141844	0.006157		2137		456
cc-pCVTZ / aug-	cc-pVTZ CCSD (5	frozen cor	e orbitals)						
$^{4}\Delta$	-1355.789401	1.8912	1.1745	0.147866	0.006466	6.7953	2152		482
<sup>4</sup> Π	-1355.781199	1.8963	1.1736	0.147359	0.006438	7.5994	2154		465
<sup>6</sup> П	-1355.791400	1.9562	1.1749	0.140806	0.006097	4.8283	2143		458
<sup>6</sup> Δ	-1355.802917	1.9398	1.1755	0.142500	0.006194	4.5204	2143	118	475
cc-pVQZ / aug-co	pVQZ CCSD(T)								
$^{4}\Delta$	-1355.380342	1.8622	1.1815	0.150648	0.006630				
$^{6}\Delta$	-1355.389455	1.9331	1.1830	0.142704	0.006214				

Table 2.4: Total energies and physical properties for FeNC at correlated levels of theory.<sup>a</sup>

cc-pVTZ / aug-c	c-pVTZ CCSDT-3						
Electronic	Energy	r(Fe-N)	r(N-C)	Be	$\Delta(B_e^{13}C)$	$\mu \omega_1(\sigma)$	$\omega_2(\pi) \omega_3(\sigma)$
$^{4}\Delta$	-1355.344982	1.8694	1.1855	0.149535	0.006588	2070	506
<sup>4</sup> П	-1355.336168	1.8698	1.1850	0.149516	0.006577	2066	485
<sup>6</sup> П	-1355.341899	1.9406	1.1857	0.141731	0.006178	2065	479
$^{6}\Delta$	-1355.353022	1.9284	1.1864	0.142985	0.006245	2064	494
cc-pVQZ / aug-o	cc-pVQZ CCSDT-3						
$^{4}\Delta$	-1355.382504	1.8690	1.1823	0.149805	0.006587		
$^{6}\Delta$	-1355.388939	1.9329	1.1833	0.142704	0.006215		
Expt. ${}^{6}\Delta^{b}$		2.01	1.03	$B_0 = 0.1452$	$\Delta(B_0^{13}C) = 0.006$	•	464
aug-cc-pVQZ M	IRCISD+Q $^{1}\Sigma^{+}$ CN <sup>-</sup>		1.1838			2052	
aug-cc-pVTZ C	$CSDT-3 \ ^{1}\Sigma^{+} CN^{-}$		1.1813			2072	

Table 2.4 (continued): Total energies and physical properties for FeNC at correlated levels of theory.<sup>a</sup>

<sup>a</sup>Energies are in hartrees, bond distances in Å, dipole moments in D, rotational constants and frequencies in cm<sup>-1</sup>. Unless otherwise stated, only the valence electrons were correlated. <sup>b</sup>Reference 7.

Electronic State	Energy	r(Fe-C)	r(C-N)	Be	$\Delta(B_e^{13}C)$	μ	$\omega_1(\sigma)$	$\omega_2(\pi)$	ω <sub>3</sub> (σ)
cc-pVQZ / aug-cc-j	pVQZ CISD								
$4\Sigma^{-}$	-1355.274367	1.9652	1.1498	0.132650	0.001369	8.8121			
$^{4}\Delta$	-1355.274274	1.9834	1.1482	0.131009	0.001339	8.6588			
<sup>4</sup> П	-1355.274731	1.9852	1.1493	0.130773	0.001336	8.8249			
Р <sup>6</sup> П	-1355.295825	2.0598	1.1492	0.124041	0.001396	5.1451			
$^{6}\Delta$	-1355.304257	2.0642	1.1488	0.123658	0.001282	4.7841			
cc-pVQZ / aug-cc-j	pVQZ CASSCF								
$^{4}\Delta$	-1354.904164	2.0767	1.1704	0.121366	0.001295	4.8719			
<sup>4</sup> П	-1354.895887	2.0696	1.1706	0.121949	0.001296	5.1062			
<sup>6</sup> П	-1354.921483	2.1121	1.1713	0.118402	0.001281	5.2877			
$^{6}\Delta$	-1354.932360	2.1090	1.1709	0.118668	0.001282	4.9421			
cc-pVQZ / aug-cc-j	pVQZ MRCISD								
$^{4}\Delta$	-1355.314810	2.0046	1.1638	0.128045	0.001305	4.6376			
$^{6}\Delta$	-1355.337055	2.0613	1.1657	0.122925	0.001283	4.5984			
cc-pVQZ / aug-cc-j	pVQZ MRCISD-	+Q			·	-			
<sup>4</sup> Δ	-1355.359703	1.9796	1.1672	0.130150	0.001334	•	2283		460
$^{6}\Delta$	-1355.377875	2.0506	1.1682	0.123715	0.001307		2271		467
cc-pVQZ / aug-cc-j	pVQZ CCSD								
<sup>4</sup> Σ <sup>-</sup>	-1355.340324	1.9264	1.1619	0.135612	0.001362				
$^{4}\Delta$	-1355.351957	1.9684	1.1596	0.131681	0.001333	7.4413	2251		443
<sup>4</sup> П	-1355.348032	1.9534	1.1607	0.133035	0.001336	7.9598	2238		431
$\Pi^{0}$	-1355.353293	2.0461	1.1602	0.139946	0.001350	5.0011	2245		425
$^{6}\Delta$	-1355.361298	2.0520	1.1598	0.124076	0.001295	4.6359	2250		435
cc-pCVTZ / aug-cc	-pCVTZ CCSD								
$^{4}\Delta$	-1355.321212	1.9745	1.1622	0.130928	0.001317		2240		435
<sup>4</sup> П	-1355.316800	1.9560	1.1633	0.132609	0.001322		2227		425
бП	-1355.324430	2.0563	1.1629	0.123525	0.001289		2237		415
$^{6}\Delta$	-1355.332428	2.0626	1.1625	0.123005	0.001288		2231		405
cc-pCVTZ / aug-cc	-pCVTZ CCSD	(5 frozen	core orbi	itals)					
$^{4}\Delta$	-1355.793859	1.9720	1.1601	0.131300	0.001330	7.2854	2249		432
<sup>4</sup> П	-1355.790380	1.9518	1.1611	0.133157	0.001327	7.8037	2238	237	429
бП	-1355.793664	2.0510	1.1608	0.124107	0.001294	5.0370	2241		406
$^{6}\Delta$	-1355.802017	2.0550	1.1604	0.123755	0.001301	4.6604	2247	184	417
cc-pVQZ / aug-cc-j	pVQZ CCSD(T)								
<sup>4</sup> Δ	-1355.386847	1.9483	1.1680	0.133030	0.001316	• •		-	
$^{6}\Delta$	-1355.388759	2.0455	1.1680	0.124150	0.001285				
cc-pVTZ / aug-cc-p	vQZ CCSDT-3								
<sup>4</sup> Δ	-1355.349347	1.9498	1.1706	0.132704	0.001313		2171		456
$^{4}\Pi$	-1355.345568	1.9247	1.1719	0.135055	0.001323		2154		448
$\Pi^{0}$	-1355.343732	2.0305	1.1712	0.125273	0.001292		2164		423
$^{6}\Delta$	-1355.351457	2.0390	1.1707	0.124517	0.001289		2169		431

Table 2.5: Total energies and physical properties for FeCN at correlated levels of theory.<sup>a</sup>

Table 2.5 (continued): Total energies and physical properties for FeCN at correlated levels of theory.<sup>a</sup>

cc-pVQZ / aug-cc-p	vQZ CCSDT-3								
Electronic State	Energy	r(Fe-C)	r(C-N)	Be	$\Delta(B_e^{13}C)$	μ	$\omega_1(\sigma)$	$\omega_2(\pi)$	ω <sub>3</sub> (σ)
$^{4}\Delta$	-1355.387477	1.9529	1.1674	0.132628	0.001316				
$^{6}\Delta$	-1355.387853	2.0456	1.1676	0.124168	0.001285				

<sup>a</sup>Energies are in hartrees, bond distances in Å, dipole moments in D, rotational constants and frequencies in cm<sup>-1</sup>. Unless otherwise stated, only the valence electrons were correlated.

	$\Delta E_{e}$	Barrier ( $\Delta E_{e}^{\dagger}$ )
	$(^{6}\Delta, \text{FeNC} \rightarrow \text{FeCN})$	$(^{6}\Delta, \text{FeNC} \rightarrow \text{FeCN})$
Wachters/DZP ROHF	1872	4857
Roos DZ ANO ROHF	1809	
NASA ANO ROHF	1806	
cc-pVTZ / aug-cc-pVTZ ROHF	1819	
cc-pVQZ / aug-cc-pVQZ ROHF	1802	4218
Wachters/DZP CISD	810	3595
Roos DZ ANO CISD	807	
NASA ANO CISD	685	
cc-pVTZ / aug-cc-pVTZ CISD	856	
cc-pVQZ / aug-cc-pVQZ CISD	794	
Wachters/DZP CASSCF	-1536	
Roos DZ ANO CASSCF	-1324	
NASA ANO CASSCF	-1269	
cc-pVTZ / aug-cc-pVTZ CASSCF	-1258	
_cc-pVQZ / aug-cc-pVQZ CASSCF	-1269	313
cc-pVQZ / aug-cc-pVQZ MRCISD	-509	
Wachters/DZP MRCISD+Q	-91	
cc-pVQZ / aug-cc-pVQZ MRCISD+Q	-166	2775 <sup>b</sup>
Wachters/DZP CCSD	309	
Roos DZ ANO CCSD	345	
NASA ANO CCSD	194	
cc-pVTZ / aug-cc-pVTZ CCSD	413	
cc-pVQZ / aug-cc-pVQZ CCSD	325	
cc-pCVTZ / aug-cc-pCVTZ CCSD	187	
Wachters/DZP CCSD(T)	200	
Roos DZ ANO CCSD(T)	216	
NASA ANO CCSD(T)	6	
cc-pVTZ / aug-cc-pVTZ CCSD(T)	251	
cc-pVQZ / aug-cc-pVQZ CCSD(T)	153	
Wachters/DZP CCSDT-1b	160	
Roos DZ ANO CCSDT-1b	321	
Wachters/DZP CCSDT-3	362	
Roos DZ ANO CCSDT-3	313	
NASA ANO CCSDT-3	92	
cc-pVTZ / aug-cc-pVTZ CCSDT-3	343	
cc-pVQZ / aug-cc-pVQZ CCSDT-3	238	
Relativistic shift: cc-pVQZ / aug-cc-pVQZ CCSD	+745	
cc-pVQZ / aug-cc-pVQZ MRCISD <sup>c</sup>	-74	
Core correlation shift: cc-pCVTZ / aug-cc-pCVTZ CCSD	+11	
ZPVE shift: cc-pCVTZ / aug-cc-pCVTZ CCSD	+89	

Table 2.6: Isomerization energies (in cm<sup>-1</sup>) of FeNC/FeCN on the  $^{6}\Delta$  surface.<sup>a</sup>

<sup>a</sup>Computed at the optimum geometry for each electronic state and each level of theory, correlating only valence electrons unless otherwise specified. <sup>b</sup>Computed as a single point at the cc-pVQZ / aug-cc-pVQZ CASSCF optimized geometry.

<sup>c</sup>Computed at the cc-pVQZ / aug-cc-pVQZ MRCISD+Q optimum geometry.

	$^{4}\Delta$	<sup>4</sup> Π	$^{6}\Delta$	<sup>6</sup> Π	4Σ-
Wachters/DZP ROHF	20373	20286	0	2746	23750
Roos DZ ANO ROHF	20133	19942	0	2722	23432
NASA ANO ROHF	20220	20063	0	2664	23331
cc-pVTZ / aug-cc-pVTZ ROHF	20294	20125	0	2691	23928
cc-pVQZ / aug-cc-pVQZ ROHF	20251	20085	0	2661	23640
Wachters/DZP CISD	10662	11513	0	2674	14191
Roos DZ ANO CISD	9027	9429	0	2584	12138
NASA ANO CISD	8657	8984	0	2539	9596
cc-pVTZ / aug-cc-pVTZ CISD	8874	9216	0	2545	9755
cc-pVQZ / aug-cc-pVQZ CISD	8523	8800	0	2530	9387
Wachters/DZP CASSCF	6566		0	2798	
Roos DZ ANO CASSCF	6461	8766	0	2771	
NASA ANO CASSCF	6438	8786	0	2800	
cc-pVTZ / aug-cc-pVTZ CASSCF	6459	8813	0	2813	
cc-pVQZ / aug-cc-pVQZ CASSCF	6434	8784	0	2797	
cc-pVQZ / aug-cc-pVQZ MRCISD	5076		0		
Wachters/DZP MRCISD+Q	4718		0	2606	
cc-pVQZ / aug-cc-pVQZ MRCISD+Q	4371		0	2469	
Wachters/DZP CCSD	3910	9309	0	2827	10725
Roos DZ ANO CCSD	3506	5768	0	2527	8720
NASA ANO CCSD	3288	5380	0	2492	8140
cc-pVTZ / aug-cc-pVTZ CCSD	3385	5492	0	2475	8250
cc-pVQZ / aug-cc-pVQZ CCSD	3226	5223	0	2474	7901
cc-pCVTZ / aug-cc-pCVTZ CCSD	3504	5612	0	2446	
Wachters/DZP CCSD(T)		8558	0	2624	
Roos DZ ANO CCSD(T)	2735	4753	0	2507	
NASA ANO CCSD(T)	2089	3992	0	2474	
cc-pVTZ / aug-cc-pVTZ CCSD(T)	2475	4351	0	2436	
cc-pVQZ / aug-cc-pVQZ CCSD(T)	2000		0		
Wachters/DZP CCSDT-1b	3217		0		
Roos DZ ANO CCSDT-1b	1961		0		
Wachters/DZP CCSDT-3	2960	5421	0	2593	
Roos DZ ANO CCSDT-3	1929	4027	0	2513	
NASA ANO CCSDT-3	1471	3446	0	2481	
cc-pVTZ / aug-cc-pVTZ CCSDT-3	1765	3699	0	2441	
cc-pVQZ / aug-cc-pVQZ CCSDT-3	1412		0		

Table 2.7: Adiabatic excitation energies ( $T_e$  in cm<sup>-1</sup>) of FeNC<sup>a</sup>.

Table 2.7 (continued): Adiabatic excitation energies ( $T_e$  in cm<sup>-1</sup>) of FeNC<sup>a</sup>.

	$^{4}\Delta$	4П	$^{6}\Delta$	<sup>6</sup> П	$4\Sigma^{-}$
Relativistic shift:					
cc-pVQZ / aug-cc-pVQZ CCSD	+1417	+1990	0	+437	
cc-pVQZ / aug-cc-pVQZ MRCISD <sup>b</sup>	+232		0	-22	
Core correlation shift:					
cc-pCVTZ / aug-cc-pCVTZ CCSD	-508	-845	0	-82	

<sup>a</sup>Computed at the optimum geometry for each electronic state and each level of theory,

correlating only valence electrons unless otherwise specified.

<sup>b</sup>Computed at the cc-pVQZ / aug-cc-pVQZ MRCISD+Q optimum geometry.

	$^{4}\Delta$	<sup>4</sup> П	$^{6}\Delta$	<sup>6</sup> П	<sup>4</sup> Σ <sup>-</sup>
Wachters/DZP ROHF	18345	18057	0	2139	20851
Roos DZ ANO ROHF	18053	17711	0	2108	20543
NASA ANO ROHF	18157	17846	0	2049	20546
cc-pVTZ / aug-cc-pVTZ ROHF	18232	17917	0	2082	20628
cc-pVQZ / aug-cc-pVQZ ROHF	18203	17888	0	2049	20590
Wachters/DZP CISD	9039	9379	0	2030	11292
Roos DZ ANO CISD	7096	7116	0	1912	9018
NASA ANO CISD	6731	6670	0	1855	8493
cc-pVTZ / aug-cc-pVTZ CISD	6905	6851	0	1869	6890
cc-pVQZ / aug-cc-pVQZ CISD	6581	6480	0	1851	6560
Wachters/DZP CASSCF	6315	8086	0	2404	
Roos DZ ANO CASSCF	6199	7979	0	2367	
NASA ANO CASSCF	6189	8003	0	2388	
cc-pVTZ / aug-cc-pVTZ CASSCF	6223	8044	0	2408	
cc-pVQZ / aug-cc-pVQZ CASSCF	6188	8005	0	2387	
cc-pVQZ / aug-cc-pVQZ MRCISD	4882		0		
Wachters/DZP MRCISD+Q	4358	5330	0	2009	
cc-pVQZ / aug-cc-pVQZ MRCISD+Q	4208	4986	0	1788	
Wachters/DZP CCSD	3372	4938	0	1947	7813
Roos DZ ANO CCSD	2459	3569	0	1826	5471
NASA ANO CCSD	2160	3101	0	1771	4856
cc-pVTZ / aug-cc-pVTZ CCSD	2260	3201	0	1760	4908
cc-pVQZ / aug-cc-pVQZ CCSD	2050	2911	0	1757	4603
cc-pCVTZ / aug-cc-pCVTZ CCSD	2462	3430	0	1755	
Wachters/DZP CCSD(T)	3688	5558	0	1907	
Roos DZ ANO CCSD(T)	1111	2116	0	1786	
NASA ANO CCSD(T)	534	1430	0	1730	
cc-pVTZ / aug-cc-pVTZ CCSD(T)	1685	1685	0	1699	
cc-pVQZ / aug-cc-pVQZ CCSD(T)	445		0		
Wachters/DZP CCSDT-1b	2499		0		
Roos DZ ANO CCSDT-1b	577		0		
Wachters/DZP CCSDT-3	2451	3743	0	1898	
Roos DZ ANO CCSDT-3	690	1712	0	1785	
NASA ANO CCSDT-3	179	1067	0	1728	
cc-pVTZ / aug-cc-pVTZ CCSDT-3	463	1292	0	1695	
cc-pVQZ / aug-cc-pVQZ CCSDT-3	83		0		

Table 2.8: Adiabatic excitation energies ( $T_e$  in cm<sup>-1</sup>) of FeCN<sup>a</sup>.

Table 2.8 (continued): Adiabatic excitation energies ( $T_e$  in cm<sup>-1</sup>) of FeCN<sup>a</sup>.

Relativistic shift:					
cc-pVQZ / aug-cc-pVQZ CCSD	+1090	+1454	0	+276	
cc-pVQZ / aug-cc-pVQZ MRCISD <sup>b</sup>	+192	+67	0	-50	
Core correlation shift:					
cc-pCVTZ / aug-cc-pCVTZ CCSD	-612	-876	0	+79	

<sup>a</sup>Computed at the optimum geometry for each electronic state and each level of theory, correlating valence electrons only, unless otherwise specified.

<sup>b</sup>Computed at the cc-pVQZ / aug-cc-pVQZ MRCISD+Q optimum geometry.

	Theoretical $T_{\rm e}$	Experimental $T_0$	
FeH	18964 <sup>a</sup>	18765 <sup>b</sup>	-
FeF	30290 <sup>c</sup>	30239 <sup>d</sup>	
FeCl	28950 <sup>e</sup>	$28029^{\mathrm{f}}$	
FeCN	25014 <sup>g</sup>		
FeNC	28224 <sup>g</sup>	27236 <sup>h</sup>	
<sup>a</sup> Referen	nce 29, Fe[7s6p4d	2f]/H[5s4p2d] MF	CISD+

Table 2.9: Energies (in cm<sup>-1</sup>) of near-UV  ${}^{6}\Pi \leftarrow {}^{6}\Delta$  electronic excitations in some iron-containing compounds.

<sup>b</sup> Reference 96.

<sup>c</sup> Reference 78, Fe[8s4p1d]/F[3s1p] CISD.

<sup>d</sup> Reference 97.

<sup>e</sup> Reference 93, Fe[8s4p1d]/Cl[5s2p] ROHF.

<sup>f</sup>Reference 77.

<sup>g</sup> Vertical excitation energies from this work, cc-pVQZ / aug-cc-pVQZ MRCISD+Q.

<sup>h</sup> Reference 7.



Figure 2.1a. Equilibrium geometries in Å for the  ${}^{4}\Delta$  states.



Figure 2.1b. Equilibrium geometries in Å for the  $^{6}\Delta$  states.


Figure 2.1c. Equilibrium geometries in Å for the  $^{6}\Delta$  isomerization transition state.





Figure 2.2. Rationalizing dipole moment differences in quartet and sextet states. Orbital contour plots are shown from Wachters/DZP ROHF level.



Figure 2.3. Excitation energies from  ${}^{6}\Delta$  to  ${}^{4}\Delta$  state for FeNC and FeCN using the ccpVQZ basis set.

# CHAPTER 3

# APPLICATION OF EQUATION-OF-MOTION COUPLED CLUSTER METHODS TO LOW-LYING SINGLET AND TRIPLET ELECTRONIC STATES OF HBO AND BOH<sup>1</sup>

<sup>1</sup>N. J. DeYonker, S. Li, Y. Yamaguchi, H. F. Schaefer, T. D. Crawford, R. A. King, and K. A. Peterson. Submitted to *Journal of Chemical Physics*. 3/24/05

# ABSTRACT

Equilibrium structures and physical properties of the  $\tilde{X}^{1}\Sigma^{+}$  linear electronic states, linear excited singlet and triplet electronic states of HBO ( $\tilde{A}^{1}\Sigma^{-}$ ,  $\tilde{B}^{1}\Delta$ ,  $\tilde{a}^{3}\Sigma^{+}$ , and  $\tilde{b}^{3}\Delta$ ) and BOH ( $\tilde{A}^{1}\Sigma^{+}$ ,  $\tilde{B}^{1}\Pi$ , and  $\tilde{b}^{3}\Pi$ ), and their bent counterparts (HBO  $\tilde{a}^{3}A'$ ,  $\tilde{b}^{3}A''$ ,  $\tilde{A}^{1}A''$ ,  $\tilde{B}^{1}A'$  and BOH  $\tilde{X}^{1}A'$ ,  $\tilde{b}^{3}A', \tilde{c}^{3}A'', \tilde{A}^{1}A', \tilde{B}^{1}A', \tilde{c}^{1}A''$  are investigated using excited electronic state *ab initio* equation-of-motion coupled cluster (EOM-CC) methods. A new implementation of open-shell EOM-CC including iterative partial triple excitations (EOM-CC3) was tested. Coupled cluster wave functions with single and double excitations (CCSD), single, double, and iterative partial triple excitations (CC3), and single, double, and full triple excitations (CCSDT) are employed with the correlation consistent quadruple- and quintuple-zeta basis sets. The linear HBO  $\tilde{X}$   $^{1}\Sigma^{+}$ state is predicted to lie 48.3 kcal mol<sup>-1</sup> (2.09 eV) lower in energy than the BOH  $\tilde{X}^{1}\Sigma^{+}$  linear stationary point at the CCSDT level of theory. The CCSDT BOH barrier to linearity is predicted to be 3.7 kcal mol<sup>-1</sup> (0.16 eV). With a harmonic zero-point vibrational energy correction, the HBO  $\tilde{X}^{1}\Sigma^{+}$  - BOH  $\tilde{X}^{1}A'$  energy difference is 45.2 kcal mol<sup>-1</sup> (1.96 eV). The lowest triplet excited electronic state of HBO,  $\tilde{a}^{3}A'$ , has a predicted excitation energy (T<sub>e</sub>) of 115 kcal mol<sup>-1</sup> (4.97 eV) from the HBO ground state minimum, while the lowest bound BOH excited electronic state,  $\tilde{b}^{3}A'$ , has a  $T_{e}$  of 70.2 kcal mol<sup>-1</sup> (3.04 eV) with respect to BOH  $\tilde{X}^{1}A'$ . The  $T_{e}$  values predicted for the lowest singlet excited states are  $\tilde{A}^{1}A'' \leftarrow \tilde{X}^{1}\Sigma^{+} = 139 \text{ kcal mol}^{-1} (6.01 \text{ eV})$  for HBO and  $\tilde{A}^{1}A' \leftarrow \tilde{X}^{1}A' = 102$  kcal mol<sup>-1</sup> (4.42 eV) for BOH. Also for BOH, the triplet vertical transition energies are  $\tilde{b}^{3}A' \leftarrow \tilde{X}^{1}A' = 71.4 \text{ kcal mol}^{-1} (3.10 \text{ eV}) \text{ and } \tilde{c}^{3}A'' \leftarrow \tilde{X}^{1}A' = 87.2$ kcal mol<sup>-1</sup> (3.78 eV).

# INTRODUCTION

Hydroboron monoxide (HBO) is an intermediate or by-product of many reactions involving boron compounds.<sup>1-4</sup> Boron-containing compounds are candidates for fuel additives<sup>5,6</sup> and solid propellants that can increase rocket motor efficiency.<sup>7,8</sup> HBO and its isomer boron hydroxide (BOH) have long been targets of experimental and theoretical studies. In the mid-1960s, HBO was first observed in the trimeric gas phase form, boroxine (H<sub>3</sub>B<sub>3</sub>O<sub>3</sub>), as a product of high-energy<sup>9,10</sup> and combustion reactions.<sup>11</sup> Shortly thereafter, Lory and Porter identified monomeric HBO in an argon matrix and reported its vibrational frequencies.<sup>12</sup>

The first theoretical study on the HBO / BOH system was performed by Thomson and Wishart<sup>13</sup> in 1974. It was concluded from a Mulliken population analysis<sup>14</sup> that HBO has an unusual B-O bond order between two and three, demonstrating an electron-deficient boron center. In 1977, Summers and Tyrrell<sup>15</sup> reported a Hartree-Fock study of isoelectronic 14-electron species, determining the equilibrium geometry of linear BOH to have a higher energy than that of linear HBO. In 1979 Zyubina, Charkin, and Gurvich<sup>16</sup> were the first to analyze a potential energy surface (PES) of the isomerization from HBO to BOH and noted some similarity to the PES for the isoelectronic linear HCN→HNC isomerization.<sup>17</sup> Unlike HCN / HNC, when polarization functions were included in the basis set, a local minimum for bent BOH was discovered at ∠BOH =  $125^{\circ}$  lying 4.1 kcal mol<sup>-1</sup> lower in energy than linear BOH. As such, BOH is an unusual violator of the Walsh-Mulliken qualitative molecular orbital (MO) rules for 14-electron systems.<sup>18-23</sup>

In 1986, the first gas phase detection of monomeric HBO by Hirota's group using the discharge modulation technique renewed interest in the electronic structure of HBO.<sup>24-26</sup> Infrared

and microwave spectroscopy confirmed a linear HBO structure and provided gas-phase vibrational frequencies and rotational spectra. These experimental studies were followed by theoretical papers analyzing linear and bent ground states using correlated methods such as Møller-Plesset perturbation theory,<sup>27-29</sup> coupled cluster,<sup>30</sup> and quadratic configuration interaction.<sup>31-33</sup> These studies predicted the energy difference of the two isomers to be in a range of 44 - 51 kcal mol<sup>-1</sup> and an HBO $\rightarrow$ BOH isomerization reaction barrier height range of 71 - 80 kcal mol<sup>-1</sup>.

In 1995, Gole and Michels<sup>31</sup> provided isomerization PESs for the ground states and lowest <sup>3</sup>A' state of HBO and BOH using quadratic configuration interaction with single and double excitations and a perturbative triples correction [QCISD(T)]. They speculated that if crystalline BOH could be created, it might be able to release considerable energy upon controlled photochemical activation to excited electronic states and subsequent radiative relaxation to ground state HBO. At the  $\angle$ BOH angle of 53.0°, near where the first <sup>3</sup>A' isomerization transition state (TS) is expected to be found, the ground state BOH PES is still fairly shallow. If this system is promoted from ground state BOH to a vibrationally excited level of the first <sup>3</sup>A' state with a photon energy of ~3.7 eV, BOH may be able to undergo facile cyclic interconversion. If BOH is in fact a possible high energy-density material (HEDM),<sup>34-37</sup> the hypothesis of Gole and Michels would be novel.

The 1999 study by Boldyrev and Simons<sup>32</sup> focused on the HBO and BOH cations and not only reported the  $\tilde{X}^{1}\Sigma^{+}$  HBO $\rightarrow \tilde{X}^{2}\Pi$  HBO<sup>+</sup> adiabatic ionization energy of 13.2 eV to be far higher than that of BOH (9.6 eV), but also that BOH<sup>+</sup> had a linear ground state ( $\tilde{X}^{2}\Sigma^{+}$ ) rather different from  $\tilde{X}^{2}\Pi$  HBO<sup>+</sup>. These differences originate from the large energy gap of the  $\pi$ -HOMO /  $\pi$ -LUMO of HBO versus the small  $\sigma$ -HOMO /  $\sigma$ -LUMO energy gap of BOH. A recent (2004) theoretical study conducted by Peng *et al.*<sup>38</sup> recognized the need to use multireference methods to appropriately ascertain the wave functions of HBO / BOH excited electronic states. Energy points on the isomerization PESs were obtained for the first two HBO / BOH triplet states using second-order multireference Brillouin-Wigner perturbation theory (MRBWPT2) and the cc-pVTZ basis sets. Peng reported a ground state isomer energy difference (54.4 kcal mol<sup>-1</sup>) that was 4 kcal mol<sup>-1</sup> higher than those of previous coupled-cluster studies.<sup>30</sup>

Though the singlet-triplet excitations investigated in references 31 and 38 are of a spinforbidden nature, if enough intensity borrowing is available from nearby singlet excited states, the singlet-triplet electronic transition would possess appreciable oscillator strength<sup>39</sup> and the mechanism proposed by Gole and Michels could be possible. While a singlet-singlet BOH electronic transition would have a large oscillator strength, its lifetime would be orders of magnitude shorter than that of a singlet-triplet transition. In this situation, the BOH molecule would likely fluoresce back to its ground state before isomerization towards a strongly exothermic reaction pathway could occur. Although Gole and Michels outline explicit recipes for synthesizing and characterizing BOH,<sup>31</sup> that research has not yet been experimentally realized.

To our knowledge, there are no published reports detailing the isomerization PESs of the HBO and BOH singlet excited electronic states. A more accurate theoretical prediction of excitation energies would validate the possibility of intensity borrowing between the BOH  $\tilde{A}$   ${}^{1}$ A' /  ${}^{3}$ A' states for the proposed HEDM pathway. Our task in this research is to examine some low-lying singlet and triplet excited states of HBO and BOH using excited state coupled cluster techniques.

# ELECTRONIC STRUCTURE CONSIDERATIONS

The electronic configuration of  $\tilde{X}^{1}\Sigma^{+}$  HBO is qualitatively described as

$$[\text{core}] 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 \qquad \tilde{X} \ ^1\Sigma^+, \text{HBO}.$$

The symbol [core] pertains to the occupied 1s-like oxygen and boron orbitals. The ground electronic configuration of the linear BOH molecule is expressed, noting that the  $1\pi$  orbital is lower in energy than the  $5\sigma$  orbital;

$$[\operatorname{core}] 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 \qquad \tilde{X} \ ^1\Sigma^+, \text{BOH.}$$

For the bent ground state of BOH, the occupied  $1\pi$  orbital of linear BOH splits into the 5a' and 1a'' MOs.<sup>40</sup> The 5a' orbital is more stabilized than the 1a'' orbital, a result opposite to the prediction from Walsh diagrams.<sup>18</sup> The bent electronic configuration is expressed as

$$[core](3a')^2(4a')^2(5a')^2(1a'')^2(6a')^2 \quad \tilde{X}^{-1}A'.$$

For linear HBO and BOH, the manifold of singly excited electronic states arises from the following types of electronic excitation,

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a) promotion of a 1\pi electron to one of the antibonding 2\pi orbitals. Six excited electronic states can be derived from these single excitations,
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$$[\operatorname{core}] 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3 2\pi^{-1} \Delta, {}^{1}\Sigma^{-}, {}^{1}\Sigma^{+}, {}^{3}\Delta, {}^{3}\Sigma^{-}, {}^{3}\Sigma^{+},$$

b) promotion of a  $5\sigma$  electron to one of the antibonding  $2\pi$  orbitals. Two excited electronic states can be derived from these excitations,

$$[\operatorname{core}] 3\sigma^2 4\sigma^2 5\sigma 1\pi^4 2\pi \quad {}^{1}\Pi, {}^{3}\Pi,$$

c) promotion of a  $1\pi$  electron to the  $6\sigma$  antibonding MO, whereupon there are two excited electronic states,

 $[\operatorname{core}]3\sigma^2 4\sigma^2 5\sigma^2 1\pi^3 6\sigma^{-1}\Pi, {}^3\Pi,$ 

d) promotion of a  $5\sigma$  electron to the  $6\sigma$  MO, with the following two excited electronic states,

$$[\operatorname{core}] 3\sigma^2 4\sigma^2 5\sigma 1\pi^4 6\sigma \quad {}^{1}\Sigma^{+}, {}^{3}\Sigma^{+}.$$

Thus, there are thirteen unique linear electronic states relevant to this study, including the ground electronic state.

The electronic configuration for the  ${}^{1}\Delta$  state from  $1\pi \rightarrow 2\pi$  excitation in real MO notation requires four Slater determinants. In C<sub>2v</sub> point group symmetry notation, where the linear molecule is in the Cartesian *z*-axis, its A<sub>1</sub> and A<sub>2</sub> components are, in the simplest picture,

$$\begin{bmatrix} \text{core} \end{bmatrix} 3\sigma^2 4\sigma^2 5\sigma^2 \times \begin{bmatrix} (1\pi_x \alpha(1))(2\pi_x \beta(2))1\pi_y^2 - (1\pi_x \beta(1))(2\pi_x \alpha(2))1\pi_y^2 \\ - (1\pi_y \alpha(1))(2\pi_y \beta(2))1\pi_x^2 + (1\pi_y \beta(1))(2\pi_y \alpha(2))1\pi_x^2 \end{bmatrix}^{-1} \Delta (^1A_1), \text{ and}$$

$$\begin{bmatrix} \text{core} \end{bmatrix} 3\sigma^2 4\sigma^2 5\sigma^2 \times \begin{bmatrix} (1\pi_x \alpha(1))(2\pi_y \beta(2)) 1\pi_y^2 - (1\pi_x \beta(1))(2\pi_y \alpha(2)) 1\pi_y^2 \\ + (1\pi_y \alpha(1))(2\pi_x \beta(2)) 1\pi_x^2 - (1\pi_y \beta(1))(2\pi_x \alpha(2)) 1\pi_x^2 \end{bmatrix}^{-1} \Delta (^1A_2).$$

The  ${}^{1}\Sigma^{-}$  excited state requires four Slater determinants for a proper description and is written in terms of real orbitals as

$$[\operatorname{core}] 3\sigma^{2} 4\sigma^{2} 5\sigma^{2} \times [(1\pi_{x}\alpha(1))(2\pi_{y}\beta(2))1\pi_{y}^{2} - (1\pi_{x}\beta(1))(2\pi_{y}\alpha(2))1\pi_{y}^{2} - (1\pi_{y}\alpha(1))(2\pi_{x}\beta(2))1\pi_{x}^{2} + (1\pi_{y}\beta(1))(2\pi_{x}\alpha(2))1\pi_{x}^{2}]^{-1}\Sigma^{-}(^{1}A_{2}).$$

The open-shell  ${}^{1}\Sigma^{+}$  wave function derived from a  $1\pi \rightarrow 2\pi$  excitation is qualitatively described as

$$\begin{bmatrix} \text{core} \end{bmatrix} 3\sigma^2 4\sigma^2 5\sigma^2 \times \begin{bmatrix} (1\pi_x \alpha(1))(2\pi_x \beta(2)) 1\pi_y^2 - (1\pi_x \beta(1))(2\pi_x \alpha(2)) 1\pi_y^2 \\ + (1\pi_y \alpha(1))(2\pi_y \beta(2)) 1\pi_x^2 - (1\pi_y \beta(1))(2\pi_y \alpha(2)) 1\pi_x^2 \end{bmatrix}^{-1} \Sigma^+ ({}^1A_1).$$

The two degenerate components of the  ${}^{3}\Delta$  state are written as

$$[\text{core}] 3\sigma^2 4\sigma^2 5\sigma^2 \times [(1\pi_x \alpha(1))(2\pi_x \alpha(2))1\pi_y^2 - (1\pi_y \alpha(1))(2\pi_y \alpha(2))1\pi_x^2] \quad {}^{3}\Delta ({}^{3}A_1), \text{ and}$$

$$[\text{core}] 3\sigma^2 4\sigma^2 5\sigma^2 \times [(1\pi_x \alpha(1))(2\pi_y \alpha(2))1\pi_y^2 + (1\pi_y \alpha(1))(2\pi_x \alpha(2))1\pi_x^2] \quad {}^{3}\Delta ({}^{3}A_2).$$

The  ${}^{3}\Sigma^{-}$  wave function is

$$[\text{core}] 3\sigma^2 4\sigma^2 5\sigma^2 \times [(1\pi_x \alpha(1))(2\pi_y \alpha(2))1\pi_y^2 - (1\pi_y \alpha(1))(2\pi_x \alpha(2))1\pi_x^2]^{-3} \Sigma^{-}(^{3}A_2).$$

Lastly, the  ${}^{3}\Sigma^{+}$  wave function from  $1\pi \rightarrow 2\pi$  single excitation is

$$[\operatorname{core}]3\sigma^{2}4\sigma^{2}5\sigma^{2} \times [(1\pi_{x}\alpha(1))(2\pi_{x}\alpha(2))1\pi_{y}^{2} + (1\pi_{y}\alpha(1))(2\pi_{y}\alpha(2))1\pi_{x}^{2}] \quad {}^{3}\Sigma^{+}({}^{3}A_{1}).$$

From the  $5\sigma \rightarrow 2\pi$  single excitation, the <sup>1</sup>B<sub>1</sub> component of the following <sup>1</sup> $\Pi$  electronic state wave function can be described as

$$[\operatorname{core}]3\sigma^2 4\sigma^2 1\pi^4 \times [(5\sigma\alpha(1))(2\pi_x\beta(2)) - (5\sigma\beta(1))(2\pi_x\alpha(2))]^{-1}\Pi({}^{1}\mathrm{B}_{1}),$$

and its triplet <sup>3</sup>B<sub>1</sub> counterpart is

$$[\text{core}] 3\sigma^2 4\sigma^2 1\pi^4 (5\sigma\alpha(1))(2\pi_x\alpha(2)) \quad {}^3\Pi ({}^3\text{B}_1).$$

Arising from the  $1\pi \rightarrow 6\sigma$  single excitation, the  ${}^{1}B_{1}$  component of the  ${}^{1}\Pi$  electronic state wave function can be described as

$$[\text{core}]3\sigma^2 4\sigma^2 5\sigma^2 \times [(1\pi_x \alpha(1))(6\sigma\beta(2))1\pi_y^2 - (1\pi_x \beta(1))(6\sigma\alpha(2))1\pi_y^2]^{-1}\Pi (^1\text{B}_1)$$

with the corresponding triplet  ${}^{3}B_{1}$  wave function,

$$[\text{core}] 3\sigma^2 4\sigma^2 5\sigma^2 (1\pi_x \alpha(1)) 1\pi_y^2 (6\sigma\alpha(2))^{-3} \Pi ({}^{3}\text{B}_1).$$

Finally, the wave functions of the two excited states owing to the  $5\sigma \rightarrow 6\sigma$  single excitation are written as

$$[\operatorname{core}] 3\sigma^2 4\sigma^2 1\pi^4 \times [(5\sigma\alpha(1))(6\sigma\beta(2)) - (5\sigma\beta(1))(6\sigma\alpha(2))] {}^{1}\Sigma^{+}({}^{1}A_1) \text{ and}$$
$$[\operatorname{core}] 3\sigma^2 4\sigma^2 1\pi^4 (5\sigma\alpha(1))(6\sigma\alpha(2)) {}^{3}\Sigma^{+}({}^{3}A_1).$$

When the HBO and BOH linear isomers are bent, differences in their electronic structure create separate correspondence between their MOs of  $C_{2v}$  and  $C_s$  point group symmetry.

Translation of the  $C_{\infty v}$  /  $C_{2v}$  MOs of HBO and BOH into  $C_s$  symmetry is shown in Table 3.1 and the wave functions of possible bent singly excited electronic states are listed in Appendix Table B.1.

# THEORETICAL METHODS

For single reference methods, the zeroth-order description of  $\tilde{X}$  <sup>1</sup> $\Sigma^+$  HBO and  $\tilde{X}$  <sup>1</sup> $\Sigma^+$  BOH was obtained using restricted Hartree-Fock (RHF) wave functions. The zeroth-order description of triplet states for coupled cluster references was obtained with unrestricted HF (UHF) wave functions. Ground state dynamical correlation was accounted for using coupled cluster methods<sup>41,42</sup> with single and double excitations (CCSD),<sup>43</sup> single, double, and perturbative partial triple excitations, [CCSD(T)],<sup>44,45</sup> single, double, and iterative partial triple excitations (CC3),<sup>46</sup> and full triple excitations (CCSDT).<sup>47,48</sup> For excited electronic states, we have made use of the equation-of-motion CCSD (EOM-CCSD)<sup>49,50</sup> method as well as the CC3 model, which includes connected triple excitations. Although CC3 excitation energies are usually viewed from a linear-response perspective,<sup>51</sup> we will use the EOM designation for both CCSD and CC3 excited states for the sake of simplicity.

The correlation consistent polarized valence quadruple-zeta (cc-pVQZ) basis sets developed by Dunning and coworkers were used in this study.<sup>52,53</sup> Unless otherwise noted, in all correlated procedures the core 1s-like orbitals of oxygen and boron were frozen. Closed-shell and excited singlet state CC/EOM-CC computations were carried out using ACES II.<sup>54</sup> The open-shell triplet CC3, EOM-CCSD, and EOM-CC3 methods were employed in conjunction

with the PSI 3.2 package.<sup>55</sup> The open-shell implementation of CC3 and EOM-CC3 methods incorporated in PSI 3.2 were recently developed described in Reference 56.

Structural optimizations and vibrational analyses were carried out at each level of theory using finite-differences of energies. For  $\tilde{X} \, {}^{1}\Sigma^{+}$  HBO and  $\tilde{X} \, {}^{1}A'$  BOH, fundamental vibrational frequencies were also determined at the CCSD(T) level of theory (with all electrons correlated due to program requirements) using second-order vibrational perturbation theory with cubic and semi-diagonal quartic force constants computed via finite-differences of analytic second derivatives using the method described by Stanton, Lepreore, and Gauss.<sup>56</sup>

Explicitly for linear HBO, the stationary points of the following electronic states were investigated: the  $\tilde{X}^{1}\Sigma^{+}$  ground state, the  $\tilde{A}^{1}\Sigma^{-}$  state, the  ${}^{1}A_{1}$  component of  $\tilde{B}^{1}\Delta$ , the  $\tilde{a}^{3}\Sigma^{+}$  state, and the  ${}^{3}A_{2}$  component of  $\tilde{b}^{3}\Delta$ , which all arise from the  $1\pi\rightarrow 2\pi$  excitation. For BOH, the electronic states included were the  $\tilde{X}^{1}\Sigma^{+}$  ground state, the  $\tilde{a}^{3}\Sigma^{+}$  and  $\tilde{A}^{1}\Sigma^{+}$  states from the  $5\sigma\rightarrow 6\sigma$  excitation, and the  $\tilde{b}^{3}\Pi$  and  $\tilde{B}^{1}\Pi$  states from the  $5\sigma\rightarrow 2\pi$  excitation. Tables 3.1 and B.1 detail wave functions for the bent counterparts of electronic states under investigation and the state ordering of the bent states will be discussed below. The minima of the highest-lying HBO and BOH excited states characterized are 5.8 eV and 3.2 eV below the ionization potential,<sup>32</sup> respectively. It is not likely that Rydberg excited states exist within these manifolds of electronic states.

#### **RESULTS AND DISCUSSION**

### LINEAR GROUND STATE OF HBO

Total energies, equilibrium geometries, and physical properties of the linear singlet ground electronic states of HBO and BOH are reported in Table 3.2. The equilibrium bond lengths of  $\tilde{X}^{1}\Sigma^{+}$  HBO have been experimentally determined by gas phase microwave spectroscopy to be  $r_{e}(\text{HB}) = 1.1667 \pm 0.0004$  Å and  $r_{e}(\text{BO}) = 1.2007 \pm 0.0001$  Å.<sup>25,26</sup> Coupled cluster methods including triple excitations [CC3, CCSD(T), and CCSDT] reproduce the equilibrium geometry. The CCSD(T)  $r_{e}(\text{BO})$  of 1.2019 Å is only 0.0012 Å longer than the gas phase  $r_{e}(\text{BO})$ . With the boron and oxygen 1s electrons correlated, the CCSD(T) geometries may represent a Pauling point for this electronic state. However, the CC3 and CCSDT methods perform admirably, and we prefer levels of theory with core electrons frozen for the study of excited electronic states.

The CCSDT dipole moment of linear HBO has a magnitude of 2.70 Debye, with direction <sup>+</sup>HBO<sup>-</sup>. The large dipole moment implies a highly polar molecule. The harmonic  $\omega_1(\sigma)$  BH stretching frequencies obtained using the CCSD(T), CC3, and CCSDT methods are 2899, 2885, and 2890 cm<sup>-1</sup>, respectively. In the analysis performed by the Hirota group,<sup>26</sup> the observed fundamental  $v_2(\pi)$  and  $v_3(\sigma)$  frequencies were used as harmonic frequencies in order to estimate the harmonic  $\omega_1(\sigma)$  BH stretching frequency, which may explain their rather low  $\omega_1(\sigma)$  value of 2821 cm<sup>-1</sup>. Using the all-electron CCSD(T) anharmonic correction, the fundamental  $v_1(\sigma)$  frequency is shifted to 2810 cm<sup>-1</sup>, in fair agreement with the more reasonable estimated value of 2849  $\pm$  10 cm<sup>-1</sup> given by Lory and Porter<sup>12</sup> in their IR matrix-isolation experiments. The CCSD(T) fundamental  $v_2(\pi)$  bending frequency of 759 cm<sup>-1</sup> and the  $v_3(\sigma)$  BO stretching frequency of 1831 cm<sup>-1</sup> (computed with all electrons correlated, as noted above) are correct to

within 5 cm<sup>-1</sup> of the respective gas phase fundamental frequencies. However, the inclusion of anharmonicity is seen to raise the bending frequency, a highly unusual effect.

Relative to the full CCSDT result, the triples contribution of the CC3 method to the  $\tilde{X}^{1}\Sigma^{+}$ HBO and  $\tilde{X}^{1}\Sigma^{+}$  BOH total energies are usually overestimated by ~1 kcal mol<sup>-1</sup>. However, CC3 geometries compare very favorably with the experimental and full CCSDT bond lengths, particularly in light of the computational savings offered.<sup>57</sup>

### LINEAR GROUND STATE OF BOH

Table 3.2 shows energetic and geometric data for linear  $\tilde{X}^{1}\Sigma^{+}$  BOH. The CCSDT geometry of  $\tilde{X}^{1}\Sigma^{+}$  BOH is  $r_{e}(BO) = 1.2791$  Å and  $r_{e}(OH) = 0.9493$  Å. The BO distance of  $\tilde{X}^{-1}\Sigma^{+}$  BOH is longer than that of  $\tilde{X}^{-1}\Sigma^{+}$  HBO because of a lessening of  $\pi$ -overlap, and hence a weakening of the multiple bond character. This rather long BO bond is also an indicator of the preference towards a bent BOH minimum.

The CCSDT dipole moment of  $\tilde{X} \, {}^{1}\Sigma^{+}$  BOH is larger than that of  $\tilde{X} \, {}^{1}\Sigma^{+}$  HBO and of the opposite sign,  $\neg$ BOH<sup>+</sup>, with a magnitude of 3.69 D. The O-H  $\omega_{1}(\sigma)$  stretching frequency from the CC3 and CCSDT methods is 4009 and 4018 cm<sup>-1</sup> respectively, and the B-O stretching frequency  $\omega_{3}(\sigma)$  is 1464 and 1473 cm<sup>-1</sup>, respectively. Due to the elongated BO bond length, the  $\omega_{3}(\sigma)$  frequency of  $\tilde{X} \, {}^{1}\Sigma^{+}$  BOH is lower by approximately 360 cm<sup>-1</sup> than the BO stretch of HBO. The bending frequency of  $\tilde{X} \, {}^{1}\Sigma^{+}$  BOH is imaginary, signifying a bent equilibrium geometry for BOH. The imaginary CC3 and CCSDT  $\omega_{2}(\pi)$  harmonic frequencies are 485i and 487i cm<sup>-1</sup>.

The overestimation of the triple excitation contribution to the total energy using the CC3 method is largely cancelled when considering relative energies. With all electrons correlated, the CCSD(T) energy separation between the linear ground states is predicted to be 49.2 kcal mol<sup>-1</sup>. There is little effect due to core-correlation on the harmonic zero-point vibrational energy (ZPVE), and the ZPVE-corrected energy difference between the HBO and BOH linear ground states is predicted to be 48.9 kcal mol<sup>-1</sup> with CC3, and 48.3 kcal mol<sup>-1</sup> with CCSDT. Extension of the basis set to cc-pV5Z (at the CC3 cc-pVQZ geometries) increases the separation by just 0.1 kcal mol<sup>-1</sup>. We are confident that the true energy difference between the linear isomers is near 48 and 49 kcal mol<sup>-1</sup>.

### BENT BOH GROUND STATE

The bent  $\tilde{X}^{1}A'$  BOH equilibrium geometry of the ground state in Table 3.3 has been discussed in a number of theoretical papers.<sup>30,31,38,40</sup> CCSDT bond lengths for the bent BOH  $\tilde{X}^{1}A'$  state increase (compared to the linear structure) due to destabilization of the  $\pi$ -bonding. The CCSDT  $r_e(BO)$  prediction is 1.3051 Å,  $r_e(OH)$  is 0.9617 Å, and  $\angle$ BOH is 121.4°. Harmonic vibrational frequencies are similar to the BOH linear structure and are predicted to be  $\omega_1(a') = 3855$  cm<sup>-1</sup> and  $\omega_2(a') = 1402$  cm<sup>-1</sup>, while the  $\omega_3(a')$  BOH angle bed is predicted to be 619 cm<sup>-1</sup>. The theoretical rovibrational study of HBO / BOH performed by Ha and Makarewicz<sup>29</sup> in 1999 sampled the PES of the  $\tilde{X}^{1}A'$  BOH state and presented evidence that the harmonic approximation will fail due to large amplitude motion of the hydrogen nucleus around the BO bond. Indeed the anharmonic correction to the vibrational frequencies shift the values of the O-H stretching and BOH-angle bending significantly, as the all-electron CCSD(T) level of theory predicts the fundamental  $v_1(a')$  to be 3679 cm<sup>-1</sup>,  $v_2(a')$  to be 1399 cm<sup>-1</sup>, and the bending  $v_3(a')$  to be 563 cm<sup>-1</sup>. The CCSD(T)  $v_2(a')$  and  $v_3(a')$  fundamental vibrational frequencies obtained in our study are larger than the MP2 fundamental vibrational frequencies (of Ha and Makarewicz) by 37 and 57 cm<sup>-1</sup>, respectively.<sup>29</sup> Hopefully the rovibrational parameters fit by Ha and Makarewicz and our improved fundamental vibrational frequencies will assist in the spectroscopic identification of the BOH ground state.

At the CCSDT level of theory, the  $\tilde{X}^{1}A'$  BOH minimum is predicted to be lower in energy than the linear stationary point by 3.7 kcal mol<sup>-1</sup>. With the harmonic ZPVE correction, the energy difference between the  $\tilde{X}^{1}\Sigma^{+}$  HBO and  $\tilde{X}^{1}A'$  BOH ground states is 45.2 kcal mol<sup>-1</sup>. The CCSDT and CC3 methods are again in good agreement for the geometry and energetics, whereas the differences in quantities between CCSDT and CCSD shown in Table 3.3 are somewhat larger. It seems evident that the CC3 method is more reliable than CCSD for the HBO / BOH system, and it is expected that such accuracy can be translated to the EOM-CC3 predictions for the excited electronic states.

#### LINEAR HBO SINGLET EXCITED STATES

Total energies and physical properties of the linear excited states are presented in Table 3.4. The two lowest-lying linear singlet excited states of HBO are the  $\tilde{A} \, {}^{1}\Sigma^{-}$  and  $\tilde{B} \, {}^{1}\Delta$  states, formed from  $1\pi \rightarrow 2\pi$  excitations. As the two states possess the same dominant electronic configuration with different configuration state functions, their relative energies and geometries are similar. For both states, the  $1\pi \rightarrow 2\pi$  excitation greatly increases the B-O bond distance relative to the ground state. At the EOM-CC3 level, the  $\tilde{A} \, {}^{1}\Sigma^{-}$  B-O bond distance is predicted to be 1.4219 Å, and for

the  $\tilde{B}^{-1}\Delta$  state  $r_e(BO)$  to be 1.4276 Å, implying a weak BO bond for both states. Higher in energy, the  $\tilde{B}^{-1}\Delta$  state has the weaker and slightly longer BO bond. Since electrons involved in the  $\pi \rightarrow \pi^*$  excitation of these two states are localized on the boron and oxygen atoms, the EOM-CC3 HB bond distances of the first two singlet excited states remain within 0.003 Å of the  $\tilde{X}^{-1}\Sigma^+$ HBO value of  $r_e(HB)$ . Compared to the EOM-CC3 bond length, the EOM-CCSD method provides a reasonable  $r_e(HB)$  for the HBO singlet excited states, but underestimates  $r_e(BO)$  by nearly 0.03 Å.

The EOM-CCSD dipole moment of the  $\tilde{A}^{-1}\Sigma^{-}$  state is 0.84 D while the dipole moment of the  $\tilde{B}^{-1}\Delta$  state is 0.94 D. Charge localization on the boron atom (compared to the  $\tilde{X}^{-1}\Sigma^{+}$  ground state) reduces the magnitude of the  $\tilde{A}^{-1}\Sigma^{-}$  and  $\tilde{B}^{-1}\Delta$  dipole moments by a factor of three but retains the <sup>+</sup>HBO<sup>-</sup> dipole direction. As the HB bond distance for these two states is in a range similar to the ground state, the EOM-CC3 HB stretching ( $\omega_1$ ) frequency has a similar value; 2882 cm<sup>-1</sup> for the  $\tilde{A}^{-1}\Sigma^{-}$  state and 2880 cm<sup>-1</sup> for the  $\tilde{B}^{-1}\Delta$  state. Inclusion of triple excitations with the EOM-CC3 wave function reduces the value of  $\omega_3(\sigma)$  by more than 100 cm<sup>-1</sup> compared to the EOM-CCSD method, with  $\omega_3(\sigma) = 1095$  cm<sup>-1</sup> for  $\tilde{A}^{-1}\Sigma^{-}$  and 1072 cm<sup>-1</sup> for  $\tilde{B}^{-1}\Delta$ . This trend generally continues among the investigated linear triplet excited states of HBO, as the triple excitations are crucial in the properly describing the weak BO  $\pi$ -bonding. Both excited electronic states have imaginary bending frequencies, 974i and 954i cm<sup>-1</sup>, indicating respective bent equilibrium geometries.

# LINEAR BOH SINGLET EXCITED STATES

Energies, geometries and physical properties of BOH linear excited states are presented in Table 3.5. Preliminary computations of higher-lying  ${}^{1}\Delta$  and  ${}^{1}\Sigma^{-}$  BOH states along with conclusions from the study of the BOH<sup>+</sup> cation<sup>32</sup> imply that the BOH  $\pi \rightarrow \pi^{*}$  excitation is unfavorable and leads to some dissociated excited electronic states. The  $\tilde{A} {}^{1}\Sigma^{+}$  BOH state comes from the 5 $\sigma$  non-bonding B atom lone pair being excited to the 6 $\sigma$  weakly OH antibonding MO, which tightens the BO bonding [ $r_e(BO) = 1.2002$  Å] and creates a weaker OH bond [ $r_e(OH) = 1.4451$  Å]. The EOM-CCSD method performs less well for this excited state, with geometries differing from EOM-CC3 by 0.01 – 0.03 Å. The highly ionic  $\tilde{A} {}^{1}\Sigma^{+}$  excited state contains significant contribution from both single and double  $5\sigma \rightarrow 6\sigma$  substitutions to the reference wave function, and EOM-CCSD fails to adequately describe this multireference character.

The dipole moment of the  $\tilde{A} \, {}^{1}\Sigma^{+}$  state of BOH is 1.465 D at the EOM-CCSD level of theory. Unlike other BOH excited states, the  $\tilde{A} \, {}^{1}\Sigma^{+}$  BOH state has a dipole moment direction of  ${}^{+}BOH^{-}$ . Single and double  $5\sigma \rightarrow 6\sigma$  excitations appear to shift enough charge density to change the direction of the dipole moment. The EOM-CC3 method yields an imaginary bending  $\omega_{2}(\pi)$  frequency of 480i cm<sup>-1</sup>, which implies a bent equilibrium geometry.

The  $\tilde{B}$  <sup>1</sup> $\Pi$  state of BOH mainly involves single excitations from the reference coupled cluster wave function, and thus EOM-CCSD and EOM-CC3 geometries agree more closely. The geometry and two harmonic vibrational stretching frequencies of the  $\tilde{B}$  <sup>1</sup> $\Pi$  state are very similar to those of BOH  $\tilde{X}$  <sup>1</sup> $\Sigma$ <sup>+</sup> ground state. While still large, the EOM-CCSD dipole moment of 2.79 D is smaller in magnitude than that of the BOH  $\tilde{X}$  <sup>1</sup> $\Sigma$ <sup>+</sup> state. The 5 $\sigma$ ->2 $\pi$  excitation shifts charge density from the non-bonding B-atom lone pair to the  $\pi$ -antibonding MOs centered on the boron and oxygen atoms. Therefore, negative charge remains localized on the B and O atoms, and the dipole direction is the same as that for the  $\tilde{X}^{-1}\Sigma^+$  state, namely <sup>-</sup>BOH<sup>+</sup>. The harmonic bending vibrational frequencies for this state show a case (d) Renner-Teller splitting.<sup>58</sup> The a' mode  $\omega_2(\pi)$ has an imaginary frequency of 1443 i cm<sup>-1</sup> and the a'' mode has an imaginary frequency of 640i cm<sup>-1</sup>. Both the <sup>1</sup>A' and <sup>1</sup>A'' components resulting from the linear  $\tilde{B}^{-1}\Pi$  state should have nonlinear equilibrium geometries with the <sup>1</sup>A' stationary point being lower in energy.

#### LINEAR HBO TRIPLET EXCITED STATES

Geometric parameters of the two HBO linear triplet excited states are shown in Table 3.6. Since  $1\pi\rightarrow 2\pi$  excitation enhances BO antibonding and extends  $r_e(BO)$  by approximately 0.2 Å, the geometries of the two linear triplet HBO excited states resemble their singlet counterparts with the same electron configuration. The dipole moments of these two states point in the same direction as the corresponding HBO singlet states, but with smaller magnitudes. The  $\tilde{a}^{3}\Sigma^{+}$  and  $\tilde{b}^{3}\Delta$  harmonic vibrational stretching frequencies are similar, both with respect to each other and to the isoconfigurational linear  $\tilde{A}^{1}\Sigma^{-}$  and  $\tilde{B}^{1}\Delta$  states of HBO. At the EOM-CC3 level of theory, both linear triplet states have imaginary  $\omega_{2}(\pi)$  harmonic frequencies. The  $\tilde{a}^{3}\Sigma^{+}\omega_{2}(\pi)$  bending frequency is 907i cm<sup>-1</sup> and the  $\tilde{b}^{3}\Delta$  value of  $\omega_{2}(\pi)$  is 993i cm<sup>-1</sup>, implying bent equilibrium geometries for both states.

# LINEAR BOH TRIPLET EXCITED STATES

Since the BOH  $\tilde{A}^{1}\Sigma^{+}$  electronic state arising from the  $\sigma \rightarrow \sigma^{*}$  excitation is lower-lying than the  $\tilde{B}^{1}\Pi$  state, it is expected that the triplet state arising from the  $\sigma \rightarrow \sigma^{*}$  HOMO-LUMO excitation will be the lowest-lying excited electronic state of BOH. This excited electronic state does exist; however it dissociates at all levels of theory to the same asymptote (BO  $X^{2}\Sigma^{+}$ radical<sup>59,60</sup> + <sup>2</sup>S H atom) as the BOH ground state. Its bent counterpart, the  $\tilde{a}^{3}A'$  BOH electronic state, also dissociates to BO  $X^{2}\Sigma^{+}$  radical + <sup>2</sup>S H atom. Contrary to the proposed state-ordering of Gole and Michels,<sup>31</sup> consideration of this unbound (dissociative) excited electronic state allows us to label the first bound, linear triplet excited state of BOH as  $\tilde{b}^{3}\Pi$ , arising from the  $5\sigma \rightarrow 2\pi$  excitation.

Geometries, dipole moments, and vibrational harmonic frequencies for the  $\tilde{b}^{3}\Pi$  state are presented in Table 3.5. This electronic state is well described by a single-reference coupled cluster wave function, and higher accuracy is expected with the CC3 method compared to previous studies. Much like the  $\tilde{B}^{1}\Pi$  state, the  $\tilde{b}^{3}\Pi$  state qualitatively resembles the BOH ground state with a slightly extended  $r_e(BO)$  of 1.3142 Å and an  $r_e(OH)$  of 0.9417 Å. Contrary to the discussion of Peng,<sup>38</sup> the first two bent triplet states of BOH connect to the same linear BOH  $\tilde{b}^{3}\Pi$  state. The linear  ${}^{3}B_{1} / {}^{3}B_{2}$  components of this  ${}^{3}\Pi$  state should give identical total energies and geometries when the BOH bond angle is constrained to  $180^{\circ}$ . We suspect use of two different active spaces to describe the  $\tilde{b}^{3}A'$  and  $\tilde{c}^{3}A''$  electronic states by Peng leads to a qualitatively incorrect PES near BOH linearity, providing non-degenerate total energies. The dipole moment of  $\tilde{b}^{3}\Pi$  state has the same sign as the BOH ground state with a value of 2.08 D. Harmonic vibrational frequencies for the BOH  $\tilde{b}^{3}\Pi$  state are similar to those of the BOH  $\tilde{B}^{1}\Pi$  state. Bending frequencies are both imaginary and again show class (d) Renner-Teller splitting, with the a'  $\omega_{2}(\pi)$  component having the larger imaginary frequency. The CC3 frequencies are a'  $\omega_{2}(\pi) = 1122i$  cm<sup>-1</sup> and a''  $\omega_{2}(\pi) = 523i$  cm<sup>-1</sup>. The two bent electronic states should be minima, with the <sup>3</sup>A' stationary point being lower in energy than the <sup>3</sup>A'' state, akin to the BOH  $\tilde{B}^{1}\Pi$  electronic state.

It has been shown that spin contamination affects the quality of open-shell UHF coupled cluster wave functions<sup>61</sup> and that the situation can be exacerbated when investigating open-shell excited states.<sup>62</sup> Szalay and Gauss surveyed a number of systems and found that "well-behaved" reference coupled cluster wave functions led to nearly uncontaminated  $\langle \hat{S}^2 \rangle$  values for excited states.<sup>62</sup> However, to our knowledge the expected lessening of spin contamination with UHF EOM-CC3 (*vis a vis* UHF EOM-CCSD) has not yet been examined. In this investigation, almost all EOM-CC3 triplet excited state wave functions are computed using the closed-shell ground state as a "false-UHF" reference. Therefore the triplet states characterized with this method are exactly spin-adapted and should present no spin contamination. The exceptions to this are the  $\tilde{b}$  <sup>3</sup> $\Pi$  BOH electronic state and the corresponding bent  $\tilde{b}$  <sup>3</sup>A' and  $\tilde{c}$  <sup>3</sup>A'' BOH excited states. For these excited states, our reference  $\langle \hat{S}^2 \rangle$  values of the UHF HBO/BOH linear and bent triplet states are never greater than 2.01, close to the optimal S(S + 1) value of 2.00. Therefore, spin contamination does not appear to be a concern in this study.

# BENT HBO EXCITED STATES

Optimized geometries and harmonic vibrational frequencies for the four bent HBO excited electronic states ( $\tilde{a}^{3}$ A',  $\tilde{b}^{3}$ A'',  $\tilde{A}^{1}$ A'', and  $\tilde{B}^{1}$ A') are reported in Table 3.6. The geometries of the investigated singlet and triplet HBO bent excited states are similar, since they arise from the bending of isoconfigurational excited electronic states. The EOM-CC3  $r_{e}$ (HB) of all four states range from 1.202 – 1.217 Å, which represents a slight elongation from the associated linear states. The  $\tilde{a}^{3}$ A' state is predicted to have the shortest BO bond,  $r_{e} = 1.356$  Å, which is also the case for the corresponding HBO  $\tilde{a}^{3}\Sigma^{+}$  linear structure. Akin to the linear singlet and triplet excited electronic state structures, the EOM-CC3  $r_{e}$ (BO) values for the bent excited states are 0.012 – 0.030 Å longer than those obtained with EOM-CCSD. With a tighter BO bond and a weaker HB bond, the  $\tilde{a}^{3}$ A' state has the smallest ∠HBO of 108.8°.

All harmonic vibrational frequencies for the  $\tilde{a}^{3}A'$ ,  $\tilde{b}^{3}A''$ ,  $\tilde{A}^{1}A''$ , and  $\tilde{B}^{1}A'$  excited states are real, validating the bent structures as minima, and most harmonic vibrational frequencies resemble the values of their linear counterparts. As the  $\tilde{B}^{1}\Delta$  state is higher in energy and possesses a smaller imaginary  $\omega_{2}(\pi)$  frequency than the  $\tilde{A}^{1}\Sigma^{-}$  state, the HBO  $\tilde{A}^{1}A''$  state is formed from the  ${}^{1}A''$  resolution of the  $\tilde{A}^{1}\Sigma^{-}$  state and  $\tilde{B}^{1}A'$  from the  ${}^{1}A'$  component of the  $\tilde{B}^{1}\Delta$ state. The  $\tilde{a}^{3}A'$  state occurs from the  ${}^{3}A'$  resolution of the  $\tilde{a}^{3}\Sigma^{+}$  state and the  $\tilde{b}^{3}A''$  state from the  ${}^{3}A''$  component of the  $\tilde{b}^{3}\Delta$  state.

# BENT BOH EXCITED STATES

Equilibrium geometries and harmonic vibrational frequencies for the characterized bent BOH excited electronic states ( $\tilde{b}^{3}$ A',  $\tilde{c}^{3}$ A'',  $\tilde{A}^{1}$ A',  $\tilde{B}^{1}$ A', and  $\tilde{c}^{1}$ A'') are presented in Table 3.7. The  $\tilde{A}^{1}$ A' state has different geometric parameters than the other characterized BOH excited states, with an EOM-CC3  $r_{e}$ (BO) of 1.243 Å and an  $r_{e}$ (OH) of 1.571 Å, suggesting a very loose OH bond. The inclusion of partial triple excitations into the EOM-CC wave function affects the geometry and relative energy of the BOH  $\tilde{A}^{1}$ A' state more so than other excited electronic states of HBO and BOH. As will be discussed below, the ground state BOH total energy rises sharply upon  $r_{e}$ (OH) elongation, and it is expected that at the  $\tilde{A}^{1}$ A' optimized geometry the ground state wave function contains multireference character as well, justifying the benefits of the EOM-CC3 method. An analysis of the MOs and the similarities between the BOH  $\tilde{A}^{1}$ D<sup>+</sup> and  $\tilde{A}^{1}$ A' bond distances provide a convincing argument that the  $\tilde{A}^{1}$ A' state is derived from the <sup>1</sup>A' resolution of the  $\tilde{A}^{1}$ D<sup>+</sup> state rather than the <sup>1</sup>A' component of the  $\tilde{B}^{1}$ IT state.

As noted, upon bending either of the BOH $\tilde{B}$  <sup>1</sup> $\Pi$  state or the  $\tilde{b}$  <sup>3</sup> $\Pi$  state, Renner-Teller splitting necessarily forms non-degenerate electronic states. Since the  $\omega_2(\pi)$  a' component of the BOH $\tilde{B}$  <sup>1</sup> $\Pi$  state has a larger imaginary frequency than the a'' component, the  $\tilde{B}$  <sup>1</sup>A' state connected to the  $\tilde{B}$  <sup>1</sup> $\Pi$  state lies energetically between the bent  $\tilde{A}$  <sup>1</sup>A' state and the  $\tilde{C}$  <sup>1</sup>A'' state. The bond lengths and harmonic vibrational frequencies of all investigated BOH bent excited electronic states generally resemble their linear counterparts. The  $\tilde{b}$  <sup>3</sup>A',  $\tilde{c}$  <sup>3</sup>A'',  $\tilde{A}$  <sup>1</sup>A',  $\tilde{B}$  <sup>1</sup>A', and  $\tilde{C}$  <sup>1</sup>A'' excited electronic states of BOH each have three real harmonic vibrational frequencies, and thus each is a genuine minimum. Figure 3.1 schematically depicts adiabatic transition energies relative to the linear HBO  $\tilde{X}$   ${}^{1}\Sigma^{+}$  ground state, and all investigated excited electronic states show bent minima and a likely isomerization TS (to BOH) at a  $\angle$ BOH of 40 – 80°. The same qualitative "double-well" phenomenon as Gole and Michels<sup>31</sup> and Peng<sup>38</sup> is observed for the PES of the two lowest-lying triplet states. The electronic structure of the system changes dramatically in the region of the isomerization transition states, from preferential HBO  $\pi \rightarrow \pi^*$  character to BOH  $\sigma \rightarrow \pi^*$  or  $\sigma \rightarrow \sigma^*$  character. As a consequence, the excited state isomerization PESs could connect different linear electronic states.

## ADIABATIC AND VERTICAL TRANSITION ENERGIES OF EXCITED STATES

Adiabatic transition energies of the stationary points are displayed in the last column of Tables 3.3 - 3.7 and pictorially in Figure 3.1. For HBO, the energetic EOM-CC3  $T_e$  ordering for minima found in this research is in kcal mol<sup>-1</sup>, 0 ( $\tilde{X} \, {}^{1}\Sigma^{+}$ ) < 115 ( $\tilde{a} \, {}^{3}A'$ ) < 132 ( $\tilde{b} \, {}^{3}A''$ ) < 139 ( $\tilde{A} \, {}^{1}A''$ ) < 151 ( $\tilde{B} \, {}^{1}A'$ ) and the BOH energetic ranking is 0 ( $\tilde{X} \, {}^{1}A'$ ) < 70 ( $\tilde{b} \, {}^{3}A'$ ) < 86 ( $\tilde{c} \, {}^{3}A''$ ) < 102 ( $\tilde{A} \, {}^{1}A'$ ) < 128 ( $\tilde{B} \, {}^{1}A'$ ) < 141 ( $\tilde{C} \, {}^{1}A''$ ). As expected, the smaller and highly geometry-dependent HOMO-LUMO gap of  $\tilde{X} \, {}^{1}A'$  BOH brings about a denser cluster of BOH excited electronic states. Our adiabatic energies are in excellent agreement for those of the  $\tilde{b} \, {}^{3}A'$  electronic state investigated by Gole and Michels<sup>31</sup>. However, while our HBO  $T_e$ 's agree with those of the Peng study<sup>38</sup>, our BOH adiabatic transition energies are often 13 – 15 kcal mol<sup>-1</sup> larger. We suspect that their use of different active spaces for the  ${}^{3}A'$  and  ${}^{3}A''$  states may create an artificial lowering of the  ${}^{3}A''$  PES total energy. It is also likely that the MR-BWPT2 method

does not recover enough dynamical correlation in the near-equilibrium region of the BOH  $\tilde{X}^{1}A'$  ground state.

The CC3  $\tilde{b}^{3}A' \leftarrow \tilde{X}^{1}A'$  adiabatic  $T_{e}$  for BOH is 3.04 eV; in agreement with the theoretical prediction of 2.99 eV by Gole and Michels<sup>31</sup>, while the CC3 BOH  $\tilde{c}^{3}A'' \leftarrow \tilde{X}^{1}A'$  adiabatic excitation energy is 3.71 eV. The vertical  $\tilde{b}^{3}A' \leftarrow \tilde{X}^{1}A'$  transition energy is 3.10 eV with the CC3 method, and the  $\tilde{c}^{3}A'' \leftarrow \tilde{X}^{1}A'$  vertical excitation energy is 3.81 eV, which is much larger than the prediction of ~3.05 eV by Peng.<sup>38</sup>

Because of the large geometric perturbation of the OH bond length at the BOH  $\tilde{A}$  <sup>1</sup>A' excited state minimum (compared to that of the  $\tilde{X}$  <sup>1</sup>A' BOH ground state), the singlet vertical excitation energies require careful analysis and are represented pictorially in Figure 3.2. In the PES region of  $\tilde{A}$  <sup>1</sup>A' geometric equilibrium (with the OH bond significantly elongated), the ground state is much higher in energy, with an EOM-CCSD  $\tilde{X}$  <sup>1</sup>A' –  $\tilde{A}$  <sup>1</sup>A' excitation energy of only 1.90 eV. Note that the ground state energy required for such an *r*(OH) elongation is approximately 3.06 eV. Figure 3.2 indicates that the BOH ground state, the  $\tilde{B}$  <sup>1</sup>A' state, and the  $\tilde{C}$  <sup>1</sup>A'' state all travel significantly "uphill" along the stretched OH bond coordinate.

The  $\tilde{X}^{1}A'$  BOH equilibrium geometry resembles the geometries of the  $\tilde{B}^{1}A'$  and  $\tilde{C}^{1}A''$  excited electronic states more than that of the  $\tilde{A}^{1}A'$  state. Hence the  $\tilde{B}^{1}A'$  state has a lower EOM-CCSD vertical excitation energy (5.64 eV) than the  $\tilde{A}^{1}A'$  state (7.12 eV). Due to the large shift in relative state energies along the potential energy curve for  $r_{e}$ (OH) stretching, both conical intersections<sup>63-65</sup> and avoided crossings occur. Along this stretching coordinate, there will be  $\tilde{A}^{1}A' / \tilde{C}^{1}A''$  and  $\tilde{B}^{1}A' / \tilde{C}^{1}A''$  conical intersections, as well as an  $\tilde{A}^{1}A' / \tilde{B}^{1}A'$  avoided

crossing. The mapping of PESs and such conical intersections may lend well to theoretical elaboration, but is outside the scope of this investigation.

Gole and Michels infer that for excitation intensity borrowing to be possible, the energy difference between the first excited singlet and lowest triplet BOH states at the  $\tilde{X}^{1}A'$  BOH equilibrium geometry should be similar to the isoelectronic  $A^{-1}\Pi / a^{-3}\Pi$  boron monofluoride vertical excitation energy difference of 2.73 eV.<sup>31</sup> The computed CC3 / EOM-CC3 vertical energy difference between the  $\tilde{b}^{-3}A' \leftarrow \tilde{X}^{-1}A' / \tilde{B}^{-1}A' \leftarrow \tilde{X}^{-1}A'$  electronic transitions is 2.78 eV. Our agreement with previous theoretical work and empirical observation sustains the possibility of singlet-triplet excited state intensity borrowing.

To function as a HEDM material, electronic excitation to a vibrationally excited triplet BOH state will be necessary to allow possible isomerization via the TS barriers in Figure 1. However, dissociative HBO electronic states from the  $\pi \rightarrow \sigma^*$  excitation and unbound BOH electronic states from the  $\pi \rightarrow \pi^*$  or  $\pi \rightarrow \sigma^*$  excitations may lie near the surface of highly vibrationally excited low-lying triplet states. Quanta absorbed into BOH stretching modes may break apart the molecule if the bent  $\tilde{b}^{3}A'$  and  $\tilde{c}^{3}A''$  PESs approach dissociative pathways.

## CONCLUSIONS

The  $\tilde{X} \, {}^{1}\Sigma^{+}$  HBO ground state global minimum, the  $\tilde{X} \, {}^{1}A'$  BOH ground state, and the linear  $\tilde{X} \, {}^{1}\Sigma^{+}$  BOH transition state have been studied using *ab initio* methods with the cc-pVQZ basis sets. Stationary points for the HBO  $\tilde{A} \, {}^{1}\Sigma^{-}$ ,  $\tilde{B} \, {}^{1}\Delta$ ,  $\tilde{a} \, {}^{3}\Sigma^{+}$ , and  $\tilde{b} \, {}^{3}\Delta$  excited states as well as the BOH  $\tilde{A} \, {}^{1}\Sigma^{+}$ ,  $\tilde{B} \, {}^{1}\Pi$ , and  $\tilde{b} \, {}^{3}\Pi$  excited states and their bent counterparts have been characterized with new implementations of excited state coupled cluster theory (CC3). Harmonic vibrational

frequency analyses of the linear and bent excited states indicate that all excited electronic states characterized here have bent minima.

This study provides the first consistent set of predictions for the singlet excited electronic states of HBO and BOH. The energy ordering of the located, bound minima are  $\tilde{X}^{1}\Sigma^{+} < \tilde{a}^{3}A' < \tilde{b}^{3}A'' < \tilde{A}^{1}A'' < \tilde{B}^{1}A'' < \tilde{B}^{1}A'$  for HBO and  $\tilde{X}^{1}A' < \tilde{b}^{3}A' < \tilde{c}^{3}A'' < \tilde{A}^{1}A' < \tilde{B}^{1}A' < \tilde{C}^{1}A''$  for BOH. The  $\tilde{a}^{3}A'$  HBO and  $\tilde{b}^{3}A'$  BOH states are both ~115 kcal mol<sup>-1</sup> (5.0 eV) higher in energy than  $\tilde{X}^{1}\Sigma^{+}$  HBO. The lowest excited singlet states are  $\tilde{A}^{1}A''$  for HBO, with a predicted  $T_{e}$  of 139 kcal mol<sup>-1</sup> (6.01 eV) and  $\tilde{A}^{1}A'$  for BOH, with a  $T_{e}$  value of 148 kcal mol<sup>-1</sup> (6.40 eV). The HBO  $\pi \rightarrow \pi^{*}$  excitation from the ground electronic state causes lengthening of the BO bond and lessening of the dipole moment magnitude, while the BOH  $\sigma \rightarrow \sigma^{*}$  excitation severely lengthens the OH bond and causes a change in the direction of the dipole moment. On the other hand, the BOH  $\sigma \rightarrow \pi^{*}$  excitation slightly elongates the BO bond and decreases the dipole moment.

The EOM-CC3 method is found to be more accurate than the EOM-CCSD method, especially for the two BOH excited states ( $\tilde{a}^{3}$ A' and  $\tilde{A}^{1}$ A') arising from the  $\sigma \rightarrow \sigma^{*}$  excitation. The EOM-CC methods provide both closed- and open-shell excited electronic state total energies, geometric properties, and harmonic vibrational frequencies in a nearly "black box" manner. Singlet-triplet vertical and adiabatic transition energies are predicted at an accuracy that exceeds previous theoretical studies. Assuming the challenge of synthesizing and storing BOH in sufficient amounts is met, traversing the excited state isomerization PES of BOH to HBO may be treacherous due to dissociative excited electronic states along the proposed reaction pathway. Obviously much more theoretical and experimental work must be carried out to test the viability of BOH as a high energy-density material.

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Table 3.1: Valence molecular orbital (MO) ordering of HBO and BOH in  $C_{2v}$  and  $C_s$  point group symmetries. Note that in-plane bending is considered to occur in the *yz*-plane. MO energy increases downwards.

HBO C <sub>2v</sub>	HBO C <sub>s</sub>	BOH $C_{2v}$	BOH C <sub>s</sub>
3σ	3a'	3σ	3a'
4σ	4a′	4σ	4a′
5σ	5a'	$1\pi_{x}$	1a''
$1\pi_x$ (HOMO)	1a'' (HOMO)	$1\pi_y$	5a'
$1\pi_y$ (HOMO)	6a' (HOMO)	5σ (HOMO)	6a' (HOMO)
$2\pi_x$ (LUMO)	2a'' (LUMO)	6σ (LUMO)	7a' (LUMO)
$2\pi_y$ (LUMO)	7a' (LUMO)	$2\pi_{\rm x}$	2a''
6σ	8a'	$2\pi_y$	8a'

Level of Theory	Energy	$r_e(\text{H-B})$	$r_e(B-O)$	$\mu_e^b$	$\omega_1(\sigma)$	$\omega_2(\pi)$	$\omega_3(\sigma)$
$\tilde{X}^{-1}\Sigma^+$ HBO							
cc-pVQZ RHF	-100.212875	1.1643	1.1788	3.210	2994	863	2009
cc-pVQZ CCSD	-100.567370	1.1680	1.1983	2.799	2905	778	1882
cc-pVQZ CC3	-100.585344	1.1692	1.2075		2885	753	1810
cc-pVQZ CCSDT	-100.583483	1.1690	1.2048	2.703	2890	759	1838
cc-pVQZ CCSD(T) <sup>c</sup>	-100.641033	1.1663	1.2019	2.690 {	$\omega = 2899$ $\nu = 2810$	$\omega = 749$ v = 759	$\omega = 1847$ $\nu = 1831$
6-311++G(2df,2pd) QCISD(T) <sup>d</sup>		1.169	1.208		2894	780	1825
cc-pVTZ MR-BWPT2 <sup>e</sup>		1.1590	1.2093				
$TZ2P(f,d) CCSD(T)^{f}$		1.1694	1.2064	2.692	2888	766	1831
Experiment <sup>g</sup>		1.1667	1.2007		2821 <sup>h</sup>	v=754	v=1826
Experiment <sup>i</sup>					v = 2849		
	Energy	<i>r</i> <sub>e</sub> (B-O)	<i>r</i> е(О-Н)	$\mu_e{}^b$	$\omega_1(\sigma)$	$\omega_2(\pi)$	$\omega_3(\sigma)$
$\tilde{X}^{-1}\Sigma^{+}$ BOH							
cc-pVQZ RHF	-100.143860	1.2598	0.9319	3.872	4301	529i	1572
cc-pVQZ CCSD	-100.492240	1.2751	0.9462	3.687	4070	497i	1493
cc-pVQZ CC3	-100.507434	1.2804	0.9498		4009	485i	1464
cc-pVQZ CCSDT	-100.506530	1.2791	0.9493	3.687	4018	487i	1473
cc-pVQZ CCSD(T)	-100.562678	1.2748	0.9480	3.723			
6-311++G(2df,2pd) QCISD(T) <sup>d</sup>		1.309	0.9630				
cc-pVTZ MR-BWPT2 <sup>e</sup>		1.2680	0.9493				
$TZ2P(f.d) CCSD(T)^{t}$		1.2814	0.9508	3.660			

Table 3.2: Total energies and physical properties for the linear HBO and BOH ground electronic states.<sup>a</sup>

<sup>a</sup>Energies are in hartrees, bond distances in Å, dipole moments in D, and harmonic vibrational frequencies in cm<sup>-1</sup>.

<sup>b</sup>The directions of the dipole moments are <sup>+</sup>HBO<sup>-</sup> and <sup>-</sup>BOH<sup>+</sup>, respectively.

<sup>c</sup>The second set of CCSD(T) vibrational frequencies are fundamental frequencies computed via finite-differences of analytic second derivatives. Due to program requirements in the analytic gradient code, all electrons were correlated when obtaining CCSD(T) data.

<sup>d</sup>Reference 32.

<sup>e</sup>Reference 38.

<sup>f</sup>Reference 30.

<sup>g</sup>References 24 and 26.

<sup>h</sup>From reference 26,  $v_2(\pi)$  and  $v_3(\sigma)$  are observed fundamental frequencies, while the  $\omega_1(\sigma)$  is an estimated harmonic frequency.

<sup>i</sup>Reference 12 is an Ar-matrix isolation experiment, and the fundamental frequency is estimated to have error bars of 10 cm<sup>-1</sup>.

BOH $\tilde{X}^{1}$ A'	Energy	$r_e(B-O)$	$r_e(\text{O-H})$	∠BOH		$\omega_1(a')$	$\omega_2(a')$	ω <sub>3</sub> (a')	$\Delta E^{b}$
cc-pVQZ RHF	-100.150111	1.2854	0.9436	123.51		4127	1501	683	-3.92
cc-pVQZ CCSD	-100.498312	1.3018	0.9587	121.42		3901	1417	636	-3.81
cc-pVQZ CC3	-100.513218	1.3061	0.9621	121.45		3849	1396	615	-3.63
cc-pVQZ CCSDT	-100.512394	1.3051	0.9617	121.36		3855	1402	619	-3.68
cc-pVQZ CCSD(T) <sup>c</sup>	-100.568182	1.3003	0.9601	121.84	{	$\omega = 3864$ $\nu = 3679$	$\omega = 1418$ $\nu = 1399$	$\omega = 613$ $\nu = 563$	-3.45
$TZ2P[f,d] CCSD(T)^d$		1.3068	0.9635	121.45		3852	1397	607	-3.51
6-311++G(2df,2pd) QCISD(T) <sup>e</sup>		1.309	0.963	121.1		3870	1393	616	
cc-pVTZ MR-BWPT2 <sup>f</sup>		1.2946	0.9597	123.96					-0.99
aug-cc-pVTZ MP2 <sup>g</sup>		1.298	0.962	124.2		v = 3680	1436	v = 506	-3.0

Table 3.3: Total energies and geometric parameters of bent  $\tilde{X}^{-1}A'$  BOH.<sup>a</sup>

<sup>a</sup>Energies are in hartrees, bond distances in Å, harmonic vibrational frequencies in cm<sup>-1</sup>, and energy differences in kcal mol<sup>-1</sup>.

<sup>b</sup>Energy differences are relative to the optimized linear structure of  $\tilde{X}^{1}\Sigma^{+}$  BOH.

<sup>e</sup>The second set of CCSD(T) vibrational frequencies are fundamental frequencies computed via finite-differences of analytic second derivatives. Due to program requirements in the analytic gradient code, all electrons were correlated when obtaining CCSD(T) data.

<sup>d</sup>Reference 30.

<sup>e</sup>Reference 32.

<sup>f</sup>Reference 38.

<sup>g</sup>Reference 29.
Level of Theory	Energy	$r_e(H-B)$	$r_e(B-O)$	$\mu_{e}$	$\omega_1(\sigma)$	$\omega_2(\pi)$	$\omega_3(\sigma)$	$\Delta E^{c}$
HBO $\tilde{A}^{-1}\Sigma^{-}$ cc-pVQZ EOM-CCSD	-100.302082	1.1623	1.3945	0.842	2916	938i	1222	166.5 (7.22)
cc-pvQZ EOM-CC3	-100.326390	1.1655	1.4219		2882	9741	1095	162.5 (7.05)
HBO $\tilde{B}^{-1}\Delta$ cc-pVOZ EOM-CCSD	-100 298394	1 1625	1 3976	0 941	2915	909i	1210	168 8 (7 32)
cc-pVQZ EOM-CC3	-100.323321	1.1657	1.4276	0.9.11	2880	954i	1072	164.4 (7.13)
HBO $\tilde{a}^{3}\Sigma^{+}$ cc-pVOZ EOM-CCSD	-100.342747	1.1642	1.3767	0.468	2888	900i	1300	141.0 (6.11)
cc-pVQZ EOM-CC3 6-311+G(d,p) QCISD <sup>b</sup>	-100.360915	1.1674 1.1682	1.3937 1.3945		2857	907i	1208	140.8 (6.11) 145.0 (6.29) <sup>c</sup>
cc-pVTZ MRBWPT2 <sup>d</sup>		1.1495	1.3885					144.0 (6.25)
HBO $\tilde{b}^{3}\Delta$								
cc-pVQZ EOM-CCSD	-100.319317	1.1624	1.3841	0.671	2913	974i	1267	155.7 (6.75)
cc-pVQZ EOM-CC3	-100.340569	1.1658	1.4055		2877	993i	1160	153.6 (6.66)
cc-pVTZ MRBWPT2 <sup>d</sup>		1.1564	1.4046					155.2 (6.73)

Table 3.4: Total energies and physical properties for linear HBO excited electronic states.<sup>a</sup>

<sup>a</sup>Energies are in hartrees, bond distances in Å, dipole moments in D, harmonic vibrational

frequencies in cm<sup>-1</sup>, and transition energies in kcal mol<sup>-1</sup> (eV, in parentheses) relative to the  $\tilde{X}$   $^{1}\Sigma^{+}$ 

HBO minimum.

<sup>b</sup>Reference 31.

<sup>c</sup>Relative energies from Reference 31 are obtained with 6-311+G(d,p) QCISD(T) single points at the 6-311+G(d,p) QCISD optimized geometry.

<sup>d</sup>Reference 38.

Table 3.5: Total energies and physical properties for linear BOH excited electronic states.<sup>a</sup> Note that the  $\tilde{a}$   ${}^{3}\Sigma^{+}$  BOH excited electronic state dissociates to BO X  ${}^{2}\Sigma^{+}$  radical and a  ${}^{2}S$  H atom, and is not presented in the Table.

Level of Theory	Energy	$r_e(B-O)$	$r_e(\text{O-H})$	$\mu_e^{b}$	$\omega_1(\sigma)$	$\omega_2(\pi)$	$\omega_3(\sigma)$	$\Delta E^{c}$
$\operatorname{BOH}  ilde{A}  {}^1\Sigma^+$								
cc-pVQZ EOM-CCSD	-100.301881	1.1896	1.4151	1.465	2360	523i	1820	123.3 (5.35)
cc-pVQZ EOM-CC3	-100.337488	1.2002	1.4451		2684	480i	1802	110.3 (4.78)
BOH $\tilde{B}$ <sup>1</sup> $\Pi$								
cc-pVQZ EOM-CCSD	-100.257256	1.2893	0.9419	2.787	4143	1324i (647i) <sup>d</sup>	1484	151.3 (6.56)
cc-pVQZ EOM-CC3	-100.274430	1.2948	0.9453		4089	1443i (640i)	1459	149.8 (6.50)
$\operatorname{BOH}\tilde{b}$ <sup>3</sup> $\Pi$								
cc-pVQZ CCSD	-100.356655	1.3098	0.9388	2.077	4195	1121i (528i)	1451	88.9 (3.85)
cc-pVQZ CC3	-100.369583	1.3142	0.9417		4149	1122i (523i)	1430	90.1 (3.91)
6-311+G(d,p) QCISD <sup>e</sup>		1.3214	0.9454					90.1 (3.91) <sup>f</sup>
		1.3009 /	0.9428 /					76.7 (3.33) /
cc-pv1Z MKBWP12°		1.3079	0.9369					73.3 (3.18)

<sup>a</sup>Energies are in hartrees, bond distances in Å, dipole moments in D, harmonic vibrational frequencies in cm<sup>-1</sup>, and energy differences in kcal mol<sup>-1</sup> (eV).

<sup>b</sup>The dipole direction of the  $\tilde{A}^{1}\Sigma^{+}$  state is <sup>+</sup>BOH<sup>-</sup>, whereas the dipole direction of the  $\tilde{B}^{1}\Pi$  and  $\tilde{b}^{3}\Pi$  states is <sup>-</sup>BOH<sup>+</sup>.

<sup>c</sup>Energy differences are relative to the optimized  $\tilde{X}^{-1}A'$  BOH structure.

<sup>d</sup>Due to the Renner-Teller splitting, the a' and a'' components of the  $\omega_2(\pi)$  harmonic vibrational

frequency are non-degenerate. The a'' component is listed in parentheses.

<sup>e</sup>Reference 31.

<sup>f</sup>Relative energies from Reference 31 are obtained with 6-311+G(d,p) QCISD(T) single points at the 6-311+G(d,p) QCISD optimized geometry.

<sup>g</sup>Reference 38.

Table 3.6: Total energies and physical properties of bent HBO excited electronic states.<sup>a</sup>

	Energy	$r_e(\text{H-B})$	$r_e(B-O)$	∠HBO	$\omega_1(a')$	$\omega_2(a')$	$\omega_3(a')$	ΔΕ
HBO $\tilde{A}^{1}A''$								
cc-pVQZ EOM-CCSD	-100.336308	1.1999	1.3864	125.33	2555	991	1274	145.0 (6.29)
cc-pVQZ EOM-CC3	-100.364432	1.2043	1.4160	123.15				138.6 (6.01)
HBO $\tilde{B}$ <sup>1</sup> A'								
cc-pVQZ EOM-CCSD	-100.314316	1.1993	1.3818	130.92	2541	840	1290	158.8 (6.89)
cc-pVQZ EOM-CC3	-100.344300	1.2063	1.4111	126.75				151.3 (6.56)
HBO $\tilde{a}^{3}A'$								
cc-pVQZ EOM-CCSD	-100.383485	1.2110	1.3439	109.82	2439	754	1352	115.4 (5.00)
cc-pVQZ EOM-CC3	-100.402666	1.2171	1.3556	108.79				114.6 (4.97)
6-311+G(d,p) QCISD <sup>b</sup>		1.2129	1.3609	110.94	2457	769	1306	$113.9 (4.94)^{c}$
cc-pVTZ MRBWPT2 <sup>d</sup>		1.2124	1.3475	109.1				110.7 (4.80)
HBO $\tilde{b}$ <sup>3</sup> A''								
cc-pVQZ EOM-CCSD	-100.350892	1.1977	1.3838	124.83	2580	982	1273	135.8 (5.89)
cc-pVQZ EOM-CC3	-100.375607	1.2019	1.4100	122.94				131.6 (5.71)
cc-pVTZ MRBWPT2 <sup>d</sup>		1.1797	1.3914	120.1				125.9 (5.46)

<sup>a</sup>Energies are in hartrees, bond distances in Å, bond angles in degrees, harmonic vibrational frequencies in cm<sup>-1</sup>, and relative energies

in kcal mol<sup>-1</sup> (eV, in parentheses) relative to the linear  $\tilde{X}^{1}\Sigma^{+}$  HBO ground state.

<sup>b</sup>Reference 31.

<sup>°</sup>Relative energies from Reference 31 were obtained with the 6-311+G(d,p) QCISD(T) // QCISD 6-311+G(d,p) level of theory.

<sup>d</sup>Reference 38.

Table 3.7: Total energies and physical properties of bent BOH excited electronic states.<sup>a</sup> Note that the  $\tilde{a}^{3}A'$  excited state dissociates to BO  $X^{2}\Sigma^{+}$  radical and a <sup>2</sup>S H atom and is not presented in the Table.

	Energy	$r(B_{-}O)$	$r(\Omega_{-}H)$	/POH	(a')	(a')	(a')	٨E
~ .	Lifetgy	/ <sub>e</sub> (D-O)	<i>r<sub>e</sub></i> (0-11)	∠в0п	$w_1(a)$	$\omega_2(a)$	w3(a)	ΔE
BOH $A'A'$								
cc-pVQZ EOM-CCSD	-100.316612	1.2278	1.5311	115.18	2156	558	1498	114.0 (4.94)
cc-pVQZ EOM-CC3	-100.350887	1.2423	1.5711	114.82				101.9 (4.42)
1 -								× /
BOH $\tilde{B}^{-1}A'$								
cc-pVOZ EOM-CCSD	-100 293121	1 3455	0 9690	113 71	3475	989	1308	128 8 (5 58)
cc-pVOZ FOM-CC3	-100.310081	1 3490	0.9766	114.16	5.70	, 0,	1000	1275(553)
ee-pvQZ LOM-CC5	100.510001	1.5470	0.9700	114.10				127.5 (5.55)
BOH $\tilde{C}^{1}\Lambda''$								
a TVOZ FOM CCSD	100 271645	1 2720	0.0616	112.01	2000	0.05	1155	142 2 (6 17)
cc-pvQZ EOM-CCSD	-100.2/1645	1.3/39	0.9616	112.01	3866	825	1155	142.2 (6.17)
cc-pVQZ EOM-CC3	-100.288666	1.3811	0.9657	111.45				140.9 (6.11)
BOH b 'A'								
cc-pVQZ CCSD	-100.388092	1.3402	0.9603	113.98	3792	1081	1363	69.2 (3.00)
cc-pVQZ CC3	-100.401354	1.3457	0.9641	113.55	3730	1064	1338	70.2 (3.04)
6-311+G(d,p) OCISD <sup>b</sup>		1.3506	0.9640	112.49	3794	1094	1328	$68.8(2.99)^{\circ}$
cc-pVTZ MRBWPT2 <sup>d</sup>		1.3409	0.9641	113.05				58.2 (2.52)
••• k								
BOH $\tilde{c}^{3}A''$								
cc-pVOZ CCSD	-100 364030	1 3585	0 9530	120 10	3982	699	1298	84 3 (3 65)
cc-nVOZ CC3	-100.376887	1 3633	0.9563	119 76	3935	686	1278	85 5 (3 71)
$a_{\rm p}$ with $VTT MPPW PT2^{\rm d}$	100.570007	1 2 4 0 6	0.9503	125.20	5,55	000	1270	70.4(2.05)
UU-PVIZ WINDWFIZ		1.3400	0.9314	123.30				70.4 (3.03)

<sup>a</sup>Energies are in hartrees, bond distances in Å, bond angles in degrees, harmonic vibrational frequencies in cm<sup>-1</sup>, and adiabatic

transition energies in kcal mol<sup>-1</sup> (eV, in parentheses) relative to the bent  $\tilde{X}$  <sup>1</sup>A' BOH ground state.

<sup>b</sup>Reference 31.

<sup>e</sup>Relative energies from Reference 31 were obtained with the 6-311+G(d,p) QCISD(T) // QCISD 6-311+G(d,p) level of theory. <sup>d</sup>Reference 38.



Figure 3.1: Schematic of the HBO and BOH ground and excited electronic state transition energies (in eV). Adiabatic transition energies at the cc-pVQZ CC3 / EOM-CC3 level of theory are reported relative to the CC3  $\tilde{X}$  <sup>1</sup> $\Sigma$ <sup>+</sup> HBO minimum. Isomeric CCSDT ground state energies are reported in italics relative to the CCSDT  $\tilde{X}$  <sup>1</sup> $\Sigma$ <sup>+</sup> HBO global minimum. In parentheses, CCSD / EOM-CCSD adiabatic energies are reported relative to the CCSD  $\tilde{X}$  <sup>1</sup> $\Sigma$ <sup>+</sup> HBO global minimum. As indicated by the question marks, the positions of the transition states are less well-known, but sketched here from the work of references 31 and 38.



Figure 3.2: Vertical excitation energies at the cc-pVQZ CCSD / EOM-CCSD level of theory of singlet BOH excited states (in eV) at a) the equilibrium geometry of the  $\tilde{X}^{-1}A'$  BOH ground electronic state; and b) the equilibrium geometry of the  $\tilde{A}^{-1}A'$  BOH excited electronic state. The arrow connecting the two columns shows the difference of the  $\tilde{X}^{-1}A'$  ground state energy at its equilibrium geometry (a) and at the  $\tilde{A}^{-1}A'$  equilibrium geometry (b) with an elongated OH bond.

# CHAPTER 4

# THE CURIOUS ACTIVE SPACE OF BORON HYDROXIDE $\left(\text{BOH}\right)^1$

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### ABSTRACT

Equilibrium structures and physical properties of the  $\tilde{X}^{1}\Sigma^{+}$  linear HBO ground state, linear BOH  $\tilde{X}^{1}\Sigma^{+}$  transition state and bent  $\tilde{X}^{1}A'$  BOH ground state are investigated using complete active space self-consistent field (CASSCF), and internally-contracted multireference or secondorder configuration interaction with single and double substitutions (MRCISD / SOCISD). Using the full-valence active space with SOCISD gives  $\tilde{X}^{1}\Sigma^{+}$  HBO bond lengths of  $r_{e}(HB) = 1.166$  Å and  $r_{\rm e}({\rm BO}) = 1.207$  Å, which compare favorably with experimental values of  $r_{\rm e}({\rm HB}) = 1.167$  Å and  $r_{\rm e}({\rm BO}) = 1.201$  Å. However, the full-valence SOCISD BOH  $\tilde{X}^{1}{\rm A}'$  OH bond length deviates from the previous best coupled cluster geometries by 0.08 Å and the  $\angle$ BOH is  $\sim$ 36° smaller. The electron-deficient nature of the BO bond causes an unphysical distortion of the full-valence complete active space, creating a false destabilization of the oxygen 2s-like molecular orbital (MO). Adding or deleting MOs from the reference active space lowers the total energy of both the HBO and BOH ground states and improves their geometries. However, active space manipulation creates a non-systematic approach to multireference investigations. A more straightforward method of obtaining a physically reasonable description of the active space is to use single reference CISD natural orbitals (CINOs) in the CASSCF reference set instead of optimizing the full-valence MOs. At the SOCISD + CINO level of theory, the BOH  $\tilde{X}^{1}A'$  OH bond distance is 0.9621 Å and the  $\angle$ BOH is 120.3°. With the improved MOs, the relative energy of the HBO / BOH ground states is 46 - 47 kcal mol<sup>-1</sup>.

### INTRODUCTION

HBO and its isomer boron hydroxide (BOH) have been frequent targets of experimental and theoretical characterization.<sup>1-18</sup> In 1979 Zyubina, Charkin, and Gurvich analyzed the potential energy surface (PES) of the isomerization from HBO to BOH and found a local minimum for bent BOH at  $\angle$ BOH = 125°, lying approximately 4 kcal mol<sup>-1</sup> lower in energy than linear BOH.<sup>19</sup> This revealed BOH to be an unusual violator of the Walsh-Mulliken qualitative MO rules for 14-electron systems.<sup>20-25</sup> The first gas phase detections of monomeric HBO by Hirota's group<sup>10,26,27</sup> using the discharge modulation technique have provided gas-phase vibrational frequencies and rotational spectra, but BOH has not yet been experimentally isolated. Bent BOH has also been found to have unusual quasilinear behavior and can easily tunnel through its linear energy barrier.<sup>9</sup> Large anharmonicity of the BOH fundamental vibrational frequencies has perhaps hindered spectroscopic characterization.

In 1995, Gole and Michels<sup>16</sup> provided isomerization PESs for the ground and first excited triplet states of HBO and BOH at the QCISD(T) level of theory and speculated that crystalline BOH could function as a possible high energy-density material (HEDM).<sup>28</sup> A recent theoretical study conducted by Peng et al.<sup>29</sup> was the first application of a multireference method on excited electronic states of HBO and BOH, mapping isomerization PESs for two triplet states using second-order multireference Brillouin-Wigner perturbation theory (MRBWPT2). Most recently, a study in our laboratory characterized the HBO / BOH ground states, as well as four linear excited transition states and the respective bent excited state minima of each isomer with coupled cluster and equation-of-motion coupled cluster theory (EOM-CC).<sup>30</sup> It has been found that the

characterization of HBO and BOH with multireference methods requires special attention, even for the ground state.

#### ELECTRONIC STRUCTURE CONSIDERATIONS

The electronic configuration of  $\tilde{X} \, {}^{1}\Sigma^{+}$  HBO is described in zeroth-order as

[core]
$$3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 \qquad \tilde{X} \ ^1\Sigma^+$$
, HBO.

The symbol [core] pertains to the occupied 1s-like oxygen and boron orbitals. The ground electronic configuration of the linear BOH molecule is similar to HBO, with the exception of the  $1\pi$  orbital having a lower energy than the  $5\sigma$  orbital;

$$[\operatorname{core}] 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 \qquad \tilde{X} \, {}^{1}\!\Sigma^+, \, \operatorname{BOH}.$$

For bent  $\tilde{X}^{1}A'$  BOH, the Hartree-Fock electronic configuration is expressed as

$$[\operatorname{core}](3a')^2(4a')^2(5a')^2(1a'')^2(6a')^2 \quad \tilde{X}^{-1}A'.$$

The occupied  $1\pi$  orbital of linear BOH splits into the 5a' and 1a'' MOs when the molecule is bent. The 5a' orbital is more stabilized than the 1a'' orbital, which is contrary to the qualitative description of the Walsh diagrams.<sup>20</sup>

### THEORETICAL METHODS AND STRUCTURE OF CASSCF WAVE FUNCTIONS

The zeroth-order description of  $\tilde{X}$   ${}^{1}\Sigma^{+}$  HBO and  $\tilde{X}$   ${}^{1}\Sigma^{+}$  BOH was obtained using the restricted Hartree-Fock (RHF) wave function. To obtain a multireference description of the reference wave function, the complete active space self-consistent field (CASSCF)<sup>31-33</sup> technique was employed. The correlation consistent polarized valence quadruple-zeta (cc-pVQZ) basis sets developed by Dunning and coworkers were used in this study.<sup>34,35</sup> All computations were carried out with MOLPRO 2002.6.<sup>36</sup> All internally-contracted multireference configuration interaction with single and double substitutions (MRCISD)<sup>37</sup> computations included all CASSCF reference configurations with a CI coefficient greater than 0.001, while all second-order configuration interaction (SOCISD)<sup>37-40</sup> computations used all CASSCF reference configurations. The number of configuration state functions (CSFs) used as references are listed in Tables 4.1, 4.2, and 4.4. In the smallest MRCISD computation, there are approximately a million variation CI parameters, internally contracted to nearly 400 000. The largest SOCISD computation involves approximately 14 million variational parameters, internally contracted to 2.2 million.

The "full-valence" active space can be considered the most "black box" type of active space. It is defined as the combination of valence occupied and unoccupied MOs from the component atoms of the system. In the case of HBO and BOH, these would be the 1s AO of hydrogen and the 2s / 2p AOs of boron and oxygen. In the molecules, this combination would result in an  $10e^{-}$  / 9 MO active space. In Abelian  $C_{2v}$  point group symmetry, these MOs are described as the  $3a_1 - 7a_1$  orbitals, and the  $1-2 b_1 / b_2$  orbitals. In  $C_s$  point group symmetry, the full-valence active space includes the 3a' - 9a' and the 1 - 2a'' MOs.

The 1995 study by Peterson<sup>41</sup> of BO<sup>+</sup> has cast suspicion on the straightforwardness of constructing a CASSCF reference wave function for boron-containing molecules. In that study, the ground state BO<sup>+</sup> MO with the highest energy in the active space (6a<sub>1</sub>) had almost solely oxygen 2s character instead of valence  $2p_z$  anti-bonding character. State-averaging of excited electronic states fixed the unbalanced active space, but greatly affected the quality of properties and transition energies. The problem was finally alleviated by adding small weighting of the *a*  ${}^{3}\Pi$  state to computations involving the X  ${}^{1}\Sigma^{+}$  ground state, and vice versa. For BOH, a similar

problem occurs where the  $3a_1$  MO is destabilized, creating a falsely correlating unoccupied 2slike oxygen lone pair instead of a  $2p_z$  anti-bonding MO.

Common disadvantages of the CASSCF method, such as an overemphasis of antibonding or false localization of orbitals, are usually eliminated when including dynamical correlation effects via MRCI or complete active space plus second-order perturbation theory (CASPT2) methods. An unusually contrasting effect is evident with BOH. Geometries and HBO / BOH isomeric energy differences are in fortuitous agreement with previous results at the CASSCF level of theory. However, as the BOH active space is actually quite distorted, utilizing these "optimized" CASSCF natural orbitals (NOs) in an MRCISD or SOCISD computation fails completely. The electronic structure of the HBO / BOH isomeric pair is expected to be welldescribed by single reference theory, and indeed all leading ground state CI coefficients are greater than 0.95. Therefore it is expected that single reference methods such as coupled cluster should match the accuracy of MRCI / SOCI wave functions that recover both nondynamical correlation and a fair amount of dynamical correlation. It is indeed surprising that SOCISD performs so poorly for BOH, and two possible remedies have been devised in this investigation in order to fix the "broken" full-valence active space.

The first approach is the most simple; adjusting the active space size. However, this technique highlights the most frequent complaints about multireference methodology. Variation of the active space size is regarded as an unsystematic way to improve the wave function, and increasing the active space size does not necessarily increase the amount of correlation energy recovered. Modification of the active space can often involve parameterization, and often requires multi-step computations in order to validate the appropriate nature of the optimized CASSCF NOs. Indeed many of the CASSCF-"dressing" procedures are difficult to reproduce.<sup>42</sup>

In this study, four different active spaces were tested. The full-valence  $10e^{-1}/9$  MO active space is designated as "5220a" in molecular C<sub>2v</sub> symmetry or "72a" in C<sub>s</sub> symmetry. An  $8e^{-1}/8$  MO "4220" or "62" active space is obtained by freezing the 2s-like oxygen lone-pair (the  $3a_1$  or 3a' MO). Holding the 2s-like O lone pair frozen, but including the  $8a_1$  or 10a' MO is designated "5220b" or "72b". Lastly, the active space including both the 2s-like oxygen MO and the  $8a_1/10a'$  MO gives a  $10e^{-1}/9$  MO active space designated "6220" or "82".

The second tactic is based on the unrestricted natural orbital CAS (UNO-CAS) method of Bofill and Pulay,<sup>43</sup> and some recent papers have focused attention towards the use of natural orbitals (NOs)<sup>44,45</sup> from a dynamically correlated single reference computation as a way to smooth out problems in a full-valence CAS.<sup>42,46,47</sup> Instead of optimizing the MOs within the CASSCF procedure, the MOs are taken from a single-reference configuration interaction with singles and doubles (CISD) computation, and the active space CI coefficients are optimized. This procedure has been historically called the CASCI method.<sup>43</sup>

### **RESULTS AND DISCUSSION**

#### VARIATION OF ACTIVE SPACE IN CASSCF

The equilibrium bond lengths of  $\tilde{X}^{1}\Sigma^{+}$  HBO have been determined by gas phase microwave spectroscopy to be  $r_{e}(\text{HB}) = 1.1667$  Å and  $r_{e}(\text{BO}) = 1.2007$  Å.<sup>10,27</sup> Total electronic energies and equilibrium geometries of the singlet ground electronic states of HBO and BOH at the CASSCF and CASCI level of theories are reported in Table 4.1. Except for the "5220b"  $\tilde{X}^{1}\Sigma^{+}$  HBO geometries, with a shorter  $r_{e}(\text{HB})$  of 1.1790 Å, the CASSCF  $r_{e}(\text{HB})$  values are between 1.185 and 1.186 Å. All four  $r_{e}(\text{BO})$  values are between 1.205 and 1.210 Å, approximately the same deviation from experiment as previous studies employing frozen-core dynamically correlated wave functions. Compared to  $\tilde{X}^{1}\Sigma^{+}$  HBO, the CASSCF bond distances of linear and bent BOH minima compare quite well to those obtained at the coupled cluster level of theory (CCSDT), usually within the maximum deviation of 0.011 Å. The ∠BOH of the  $\tilde{X}^{1}A'$  BOH ground state shows the largest difference compared to CCSDT. Except for the full-valence active space, within 0.7° of the CCSDT bond angle, the error in bond angle among the nonstandard active spaces is between 1.9 and 6.5°. The CASCI wave functions provide HBO / BOH bond lengths within a moderately acceptable accuracy for the linear isomers. However, the CASCI ∠BOH of the bent ground state is ~23° smaller than the CCSDT bond angle. Table 4.2 shows the ground state NO occupation numbers for the various active spaces have extremely similar NO occupation numbers. For the  $\tilde{X}^{1}A'$  BOH ground state, the "72a" full-valence active space shows a curious lack of 7a' occupation compared to the other active spaces, foreshadowing problems when correlated wave functions are computed with this set of MOs.

### VARIATION OF ACTIVE SPACE IN CORRELATED METHODS

Total energies and bond distances are presented in Table 4.3 for the linear ground state isomers at the CISD, MRCISD, and SOCISD levels of theory. Intuitively, the total energy would decrease and the accuracy of geometric parameters would systematically increase as the active space size and the number of CSFs selected to be dynamically correlated increases. For  $\tilde{X} \, {}^{1}\Sigma^{+}$ HBO and  $\tilde{X} \, {}^{1}\Sigma^{+}$  BOH, this pattern holds, except that the total energy of the full-valence "5220a" active space is inexplicably the highest. The effect of the lowest occupied MO having 2s oxygen character clearly manifests itself with the  $\tilde{X}^{1}\Sigma^{+}$  BOH electronic state, as the MRCISD / SOCISD total energies are *higher* than that obtained using single reference CISD. Such a phenomenon is theoretically impossible unless the reference MOs are very flawed in their description of the bonding / antibonding characteristics of the system under investigation. The geometries with this active space are quite different, most noticeably the  $r_{\rm e}$ (OH) of the  $\tilde{X}^{1}\Sigma^{+}$ BOH state being more than 0.05 Å longer than the  $r_{\rm e}$ (OH) predicted by all other levels of theory.

The flawed active space shows an even more pronounced effect in its description of the  $\tilde{X}^{1}A'$  BOH ground state geometries. The  $r_{e}(OH)$  predicted using the "5220a" full-valence active space is more than 0.08 Å longer that obtained with the other active spaces and at the CCSDT level of theory. The  $\angle$ BOH is grossly underestimated by more than 35°, an unacceptable difference than that obtained using any other *ab initio* method. With the full-valence active space, the SOCISD ground state HBO / BOH energy difference is 62.0 kcal mol<sup>-1</sup>, almost 13 kcal mol<sup>-1</sup> higher than the isomeric energy difference found in most other theoretical studies.<sup>15-17,30</sup> On the contrary, comparing the  $\tilde{X}^{1}\Sigma^{+}$  HBO "6220" active space with the  $\tilde{X}^{1}A'$  BOH "82" active space gives a 46.2 kcal mol<sup>-1</sup> isomeric energy difference, in excellent agreement with the CCSDT energy difference of 45.8 kcal mol<sup>-1</sup>.

#### USE OF NATURAL ORBITALS

The use of natural orbitals from a dynamically correlated wave function in subsequent MRCI computations could serve as a possible starting point towards a more "black box" approach to multireference methods. If the molecular system is of single-reference character, but presents an obtusely constructed active space, the use of configuration interaction or coupled cluster NOs

may avoid the unphysical distortion of the MO description. Indeed in the case of HBO and BOH, the use of CISD NOs (or CINOs) serves to vastly improve the accuracy of the MRCISD / SOCISD wave functions. The only bond length that differs more than 0.002 Å from the CCSDT geometry is the HBO  $r_e(HB)$ , which is 0.01 Å shorter. The SOCISD total energies are now lower than the CISD energies, and the  $\tilde{X}^{1}A'$  BOH bond angle is only 1.02° shorter than that obtained with CCSDT. The SOCISD + CINO  $\tilde{X}^{1}\Sigma^{+}$  HBO –  $\tilde{X}^{1}A'$  BOH isomeric energy difference is 47.1 kcal mol<sup>-1</sup>, larger than the CCSDT and the "6220" / "82" SOCISD active space energy differences. In good agreement with the CCSDT level of theory, the BOH barrier to linearity is 3.8 kcal mol<sup>-1</sup>.

### CONCLUSIONS

Minima of the  $\tilde{X}$   ${}^{1}\Sigma^{+}$  HBO and  $\tilde{X}$   ${}^{1}A'$  BOH ground states *ab initio* methods were determined with multireference methods and correlation-consistent quadruple-zeta basis sets. Using the fullvalence MOs of the HBO / BOH system in the multireference active space, considered the simplest description of the active space, gives extraordinarily poor results. By adjusting the size of the active space or using NOs from an initial CISD computation, serious deficiencies in the CASSCF reference wave function are eradicated. It is recommended that a dynamically correlated set of NOs should be used as a starting point for studies involving a CASSCF wave function, even in a molecular system where application of high-level *ab initio* techniques would assumedly be straightforward. In the case of BOH, a correctly described active space is integral for the success of multireference methods. Used as a reference wave function for excited state investigations, an unbalanced active space that gives unusual ground state properties might then have deleterious effects on the accuracy of excited electronic state properties. As a result, in order for an extension of the multireference methods to consider an accurate treatment of HBO / BOH excited states, it is imperative that the ground state is properly described.

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$ ilde{X}^{-1}\Sigma^+$ HBO	active space	CSFs	Energy	<i>r</i> <sub>e</sub> (H-B)	<i>r</i> <sub>e</sub> (B-O)	
RHF			-100.212875	1.1643	1.1788	
CASSCF	4220	492	-100.342941	1.1854	1.2083	
	5220a	1436	-100.346108	1.1851	1.2095	
	5220b	1436	-100.350028	1.1790	1.2082	
	6220	5180	-100.377318	1.1855	1.2057	
CASCI	5220a	1436	-100.347356	1.1584	1.2044	
cc-pVQZ CCSDT <sup>a</sup>			-100.583483	1.1690	1.2048	
Experiment <sup>b</sup>				1.1667	1.2007	
$ ilde{X}^{-1}\Sigma^{+}$ BOH	active space	CSFs	Energy	<i>r</i> <sub>e</sub> (B-O)	<i>r</i> <sub>e</sub> (O-H)	
RHF			-100.143860	1.2592	0.9319	
CASSCF	4220	492	-100.274312	1.2792	0.9509	
	5220a	1436	-100.275643	1.2791	0.9513	
	5220b	1436	-100.283070	1.2788	0.9508	
	6220	5180	-100.285198	1.2772	0.9520	
CASCI	5220a	1436	-100.247004	1.2769	0.9542	
CCSDT <sup>a</sup>			-100.506530	1.2791	0.9493	
BOH $\tilde{X}^{1}A'$	active space	CSFs	Energy	<i>r</i> <sub>e</sub> (B-O)	<i>r</i> <sub>e</sub> (O-H)	∠ BOH
RHF			-100.150111	1.2854	0.9436	123.51
CASSCF	62	924	-100.260479	1.3169	0.9676	114.94
	72a	2744	-100.281661	1.3070	0.9631	122.03
	72b	2744	-100.269481	1.3144	0.9683	114.91
	82	9996	-100.301635	1.3148	0.9646	119.44
CASCI	72a	2744	-100.246889	1.3100	0.9971	97.98
cc-pVQZ CCSDT <sup>a</sup>			-100.512394	1.3051	0.9617	121.36

Table 4.1: Total CASSCF energies (in Hartrees) and equilibrium geometries (in Å) for the  $\tilde{X}^{1}\Sigma^{+}$ HBO ground state, the linear  $\tilde{X}^{1}\Sigma^{+}$  BOH transition state, and the  $\tilde{X}^{-1}A'$  BOH ground state.

<sup>a</sup>Reference 30.

<sup>b</sup>References 26 and 10.

Table 4.2: CASSCF natural orbital occupation numbers of highest occupied and lowest occupied MOs for the  $\tilde{X}^{1}\Sigma^{+}$  HBO ground state, the linear  $\tilde{X}^{1}\Sigma^{+}$  BOH transition state and the  $\tilde{X}^{-1}$ A' BOH ground state.

$\tilde{X}^{1}\Sigma^{+}$ HBO	(4220)	(5220a)	(5220b)	(6220)	CASCI
3a <sub>1</sub>	2.000	1.998	2.000	1.988	1.996
4a <sub>1</sub>	1.982	1.983	1.980	1.982	1.992
5a <sub>1</sub>	1.978	1.978	1.975	1.977	1.978
6a <sub>1</sub>	0.027	0.027	0.027	0.026	0.023
7a <sub>1</sub>	0.014	0.013	0.013	0.014	0.009
8a <sub>1</sub>	0.000	0.000	0.006	0.012	0.000
$1b_1 / 1b_2$	1.958	1.958	1.958	1.961	1.958
$2b_1/2 b_2$	0.042	0.043	0.042	0.039	0.043
$\tilde{X}^{1}\Sigma^{+}$ BOH	(4220)	(5220a)	(5220b)	(6220)	CASCI
3a <sub>1</sub>	2.000	2.000	2.000	1.990	1.991
4a <sub>1</sub>	1.987	1.987	1.986	1.982	1.980
5a <sub>1</sub>	1.981	1.980	1.978	1.978	1.972
6a <sub>1</sub>	0.019	0.019	0.020	0.021	0.018
7a <sub>1</sub>	0.014	0.014	0.014	0.019	0.016
8a <sub>1</sub>	0.000	0.000	0.004	0.011	0.000
$1b_1 / 1b_2$	1.976	1.976	1.975	1.975	1.976
$2b_1/2b_2$	0.023	0.024	0.024	0.024	0.035
$\tilde{X}^{1}A'$ BOH	(62)	(72a)	(72b)	(82)	CASCI
3a'	2.000	2.000	2.000	1.988	1.995
4a′	1.982	1.988	1.982	1.979	1.981
5a'	1.978	1.980	1.977	1.976	1.973
6a'	1.923	1.977	1.916	1.925	1.956
7a′	0.078	0.022	0.071	0.078	0.045
8a'	0.021	0.020	0.022	0.021	0.024
9a'	0.018	0.014	0.020	0.018	0.019
10a′	0.000	0.000	0.011	0.013	0.000
1a''	1.976	1.975	1.976	1.975	1.974
2a''	0.024	0.024	0.024	0.025	0.034

Table 4.3: Total energies (in Hartrees) and equilibrium geometries (in Å) for the  $\tilde{X} \,^{1}\Sigma^{+}$  HBO ground state and the linear  $\tilde{X} \,^{1}\Sigma^{+}$  BOH transition state using dynamically correlated multireference methods.

$\begin{array}{cccc} {\rm CISD} & 1 & -100.544752 & 1.1640 & 1.1929 \\ {\rm MRCISD} & 4220 & 216 & -100.571129 & 1.1697 & 1.2047 \\ & 5220a & 307 & -100.570832 & 1.1656 & 1.2065 \\ & 5220b & 353 & -100.572022 & 1.1690 & 1.2047 \\ & 6220 & 663 & -100.574151 & 1.1691 & 1.2042 \\ & 302 & 331 & -100.571163 & 1.1695 & 1.2047 \\ & 5220a & 1436 & -100.570880 & 1.1657 & 1.2065 \\ & 5220b & 1436 & -100.572064 & 1.1690 & 1.2047 \\ & 6220 & 5180 & -100.574251 & 1.1695 & 1.2044 \\ & {\rm SOCISD} + {\rm CINO} & 1436 & -100.571933 & 1.1599 & 1.2050 \\ & {\rm cc-pVQZ\ CCSDT^a} & -100.583483 & 1.1690 & 1.2047 \\ & & & & & & & & & & & \\ \hline $X\ ^1\Sigma^+ {\rm BOH} $ & {\rm active \ space \ } {\rm reference \ cSFs \ } {\rm Energy \ } r_e({\rm B-O}) \ r_e({\rm O-H}) \\ \hline $X\ ^1\Sigma^+ {\rm BOH} $ & {\rm active \ space \ } {\rm reference \ cSFs \ } {\rm Energy \ } r_e({\rm B-O}) \ r_e({\rm O-H}) \\ \hline $X\ ^1\Sigma^+ {\rm BOH} $ & {\rm active \ space \ } {\rm CSFs \ } {\rm Energy \ } r_e({\rm B-O}) \ r_e({\rm O-H}) \\ \hline $X\ ^1\Sigma^+ {\rm BOH} $ & {\rm active \ space \ } {\rm cSFs \ } {\rm Energy \ } r_e({\rm B-O}) \ r_e({\rm O-H}) \\ \hline $X\ ^1\Sigma^+ {\rm BOH} $ & {\rm active \ space \ } {\rm cSFs \ } {\rm Energy \ } r_e({\rm B-O}) \ r_e({\rm O-H}) \\ \hline $SOCISD + {\rm CINO \ } $ & {\rm active \ space \ } {\rm cSFs \ } {\rm active \ } {\rm cond \ } {\rm active \ } {\rm$	$ ilde{X}^{-1}\Sigma^+$ HBO	active space	reference CSFs	Energy	<i>r<sub>e</sub></i> (H-B)	$r_e(\text{B-O})$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	CISD		1	-100.544752	1.1640	1.1929
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	MRCISD	4220	216	-100.571129	1.1697	1.2047
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		5220a	307	-100.570832	1.1656	1.2065
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		5220b	353	-100.572022	1.1690	1.2047
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		6220	663	-100.574151	1.1691	1.2042
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	SOCISD	4220	331	-100.571163	1.1695	1.2047
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		5220a	1436	-100.570880	1.1657	1.2065
$ \begin{array}{c} 6220 & 5180 & -100.574251 & 1.1695 & 1.2044 \\ \text{SOCISD + CINO} & 1436 & -100.571993 & 1.1599 & 1.2050 \\ \text{cc-pVQZ CCSDT}^{\text{a}} & -100.583483 & 1.1690 & 1.2048 \\ \text{Experiment}^{\text{b}} & 1.1667 & 1.2007 \\ \hline \tilde{X} \ ^{1}\Sigma^{+}\text{BOH} & \text{active space CSFs} & \text{Energy } r_{e}(\text{B-O}) \ r_{e}(\text{O-H}) \\ \hline \text{CISD} & 1 & -100.468243 & 1.2687 & 0.9423 \\ \text{MRCISD} & 4220 & 157 & -100.490394 & 1.2769 & 0.9487 \\ 5220a & 200 & -100.465775 & 1.2876 & 1.0025 \\ 5220b & 269 & -100.491737 & 1.2772 & 0.9490 \\ 6220 & 694 & -100.492202 & 1.2767 & 0.9490 \\ 6220 & 694 & -100.490429 & 1.2768 & 0.9486 \\ 5220a & 1436 & -100.490429 & 1.2768 & 0.9486 \\ 5220b & 1436 & -100.491817 & 1.2769 & 0.9489 \\ 6220 & 5180 & -100.491226 & 1.2767 & 0.9491 \\ \text{SOCISD + CINO} & 1436 & -100.490222 & 1.2773 & 0.9489 \\ \text{cc-pVQZ CCSDT}^{\text{a}} & -100.506530 & 1.2791 & 0.9493 \\ \end{array} $		5220b	1436	-100.572064	1.1690	1.2047
$\begin{array}{cccc} {\rm SOCISD} + {\rm CINO} & 1436 & -100.571993 & 1.1599 & 1.2050 \\ {\rm cc-pVQZ\ CCSDT^a} & -100.583483 & 1.1690 & 1.2048 \\ {\rm Experiment^b} & 1.1667 & 1.2007 \\ \hline \tilde{X}\ {}^1\Sigma^+ {\rm BOH} & {\rm active\ space\ CSFs} & {\rm Energy\ } r_e ({\rm B-O})\ r_e ({\rm O-H}) \\ {\rm CISD\ } & 1 & -100.468243 & 1.2687 & 0.9423 \\ {\rm MRCISD\ } & 4220 & 157 & -100.490394 & 1.2769 & 0.9487 \\ {\rm 5220a\ } 200 & -100.465775 & 1.2876 & 1.0025 \\ {\rm 5220b\ } 269 & -100.491737 & 1.2772 & 0.9490 \\ {\rm 6220\ } 694 & -100.492202 & 1.2767 & 0.9490 \\ {\rm 6220\ } 694 & -100.492202 & 1.2768 & 0.9486 \\ {\rm 5220a\ } 1436 & -100.490429 & 1.2768 & 0.9489 \\ {\rm 5220b\ } 1436 & -100.491817 & 1.2769 & 0.9489 \\ {\rm 6220\ } 5180 & -100.492296 & 1.2767 & 0.9491 \\ {\rm SOCISD\ } & 4260 & 5180 & -100.490222 & 1.2773 & 0.9489 \\ {\rm 6220\ } 5180 & -100.490922 & 1.2773 & 0.9489 \\ {\rm 6220\ } 5180 & -100.490922 & 1.2773 & 0.9489 \\ {\rm 6220\ } 5180 & -100.490922 & 1.2773 & 0.9489 \\ {\rm cc-pVQZ\ CCSDT^a\ } & -100.506530 & 1.2791 & 0.9493 \\ \end{array}$		6220	5180	-100.574251	1.1695	1.2044
$\begin{array}{c} {\rm cc-pVQZ\ CCSDT^a} & -100.583483 & 1.1690 & 1.2048 \\ {\rm Experiment^b} & 1.1667 & 1.2007 \\ \hline \\ \tilde{X} \ ^1\Sigma^+ {\rm BOH} & {\rm active\ space\ CSFs\ } & {\rm Energy\ } r_e ({\rm B-O}) \ r_e ({\rm O-H}) \\ {\rm CISD\ } & 1 & -100.468243 & 1.2687 & 0.9423 \\ {\rm MRCISD\ } & 4220 & 157 & -100.490394 & 1.2769 & 0.9487 \\ 5220a \ 200 & -100.465775 & 1.2876 & 1.0025 \\ 5220b \ 269 & -100.491737 & 1.2772 & 0.9490 \\ 6220 \ 694 & -100.492202 & 1.2767 & 0.9490 \\ 6220 \ 694 & -100.492202 & 1.2768 & 0.9486 \\ 5220a \ 1436 & -100.465805 & 1.2875 & 1.0025 \\ 5220b \ 1436 & -100.491817 & 1.2769 & 0.9489 \\ 6220 \ 5180 & -100.492296 & 1.2767 & 0.9491 \\ {\rm SOCISD\ } & 4230 & 5180 & -100.490229 & 1.2773 & 0.9489 \\ {\rm soclisp\ } & -100.506530 & 1.2791 & 0.9493 \\ \end{array}$	SOCISD + CINO		1436	-100.571993	1.1599	1.2050
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	cc-pVQZ CCSDT <sup>a</sup>			-100.583483	1.1690	1.2048
$ \begin{array}{cccc} \tilde{X} \ ^1\Sigma^+ {\rm BOH} & \begin{array}{c} {\rm active} & {\rm reference} \\ {\rm space} & {\rm CSFs} \end{array} & {\rm Energy} & r_e({\rm B-O}) \ r_e({\rm O-H}) \\ \end{array} \\ \begin{array}{c} {\rm CISD} & 1 & -100.468243 \ 1.2687 & 0.9423 \\ {\rm MRCISD} & 4220 & 157 & -100.490394 \ 1.2769 & 0.9487 \\ 5220a & 200 & -100.465775 \ 1.2876 & 1.0025 \\ 5220b & 269 & -100.491737 \ 1.2772 & 0.9490 \\ 6220 & 694 & -100.492202 \ 1.2767 & 0.9490 \\ 6220 & 694 & -100.490429 \ 1.2768 & 0.9486 \\ 5220a & 1436 & -100.465805 \ 1.2875 & 1.0025 \\ 5220b & 1436 & -100.491817 \ 1.2769 & 0.9489 \\ 6220 & 5180 & -100.492296 \ 1.2767 & 0.9491 \\ {\rm SOCISD} + {\rm CINO} & 1436 & -100.490222 \ 1.2773 & 0.9489 \\ {\rm cc-pVQZ \ CCSDT^a} & -100.506530 \ 1.2791 & 0.9493 \\ \end{array} $	Experiment <sup>b</sup>				1.1667	1.2007
XZBOHspaceCSFsEnergy $r_e(B-0)$ $r_e(0-n)$ CISD1 $-100.468243$ $1.2687$ $0.9423$ MRCISD4220 $157$ $-100.490394$ $1.2769$ $0.9487$ $5220a$ 200 $-100.465775$ $1.2876$ $1.0025$ $5220b$ 269 $-100.491737$ $1.2772$ $0.9490$ $6220$ 694 $-100.492202$ $1.2767$ $0.9490$ SOCISD4220331 $-100.490429$ $1.2768$ $0.9486$ $5220a$ 1436 $-100.465805$ $1.2875$ $1.0025$ $5220b$ 1436 $-100.491817$ $1.2769$ $0.9489$ $6220$ $5180$ $-100.492296$ $1.2767$ $0.9491$ SOCISD + CINO1436 $-100.490922$ $1.2773$ $0.9489$ $cc-pVQZ CCSDT^a$ $-100.506530$ $1.2791$ $0.9493$	$\tilde{v}$ 15+ DOU	active	reference	Enorm	$r(\mathbf{D},\mathbf{O})$	"(O II)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	X Z BOH	space	CSFs	Energy	$r_e(D-U)$	$r_e(0-\pi)$
$\begin{array}{llllllllllllllllllllllllllllllllllll$		-p				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CISD	-p	1	-100.468243	1.2687	0.9423
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	CISD MRCISD	4220	1 157	-100.468243 -100.490394	1.2687 1.2769	0.9423 0.9487
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CISD MRCISD	4220 5220a	1 157 200	-100.468243 -100.490394 -100.465775	1.2687 1.2769 1.2876	0.9423 0.9487 1.0025
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	CISD MRCISD	4220 5220a 5220b	1 157 200 269	-100.468243 -100.490394 -100.465775 -100.491737	1.2687 1.2769 1.2876 1.2772	0.9423 0.9487 1.0025 0.9490
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CISD MRCISD	4220 5220a 5220b 6220	1 157 200 269 694	-100.468243 -100.490394 -100.465775 -100.491737 -100.492202	1.2687 1.2769 1.2876 1.2772 1.2767	0.9423 0.9487 1.0025 0.9490 0.9490
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CISD MRCISD SOCISD	4220 5220a 5220b 6220 4220	1 157 200 269 694 331	-100.468243 -100.490394 -100.465775 -100.491737 -100.492202 -100.490429	1.2687 1.2769 1.2876 1.2772 1.2767 1.2768	0.9423 0.9487 1.0025 0.9490 0.9490 0.9486
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CISD MRCISD SOCISD	4220 5220a 5220b 6220 4220 5220a	1 157 200 269 694 331 1436	-100.468243 -100.490394 -100.465775 -100.491737 -100.492202 -100.490429 -100.465805	1.2687 1.2769 1.2876 1.2772 1.2767 1.2768 1.2875	0.9423 0.9487 1.0025 0.9490 0.9490 0.9486 1.0025
SOCISD + CINO         1436         -100.490922         1.2773         0.9489           cc-pVQZ CCSDT <sup>a</sup> -100.506530         1.2791         0.9493	CISD MRCISD SOCISD	4220 5220a 5220b 6220 4220 5220a 5220a	1 157 200 269 694 331 1436 1436	$\begin{array}{r} -100.468243\\ -100.490394\\ -100.465775\\ -100.491737\\ -100.492202\\ -100.490429\\ -100.465805\\ -100.491817\end{array}$	1.2687 1.2769 1.2876 1.2772 1.2767 1.2768 1.2875 1.2769	0.9423 0.9487 1.0025 0.9490 0.9490 0.9486 1.0025 0.9489
cc-pVQZ CCSDT <sup>a</sup> -100.506530 1.2791 0.9493	CISD MRCISD SOCISD	4220 5220a 5220b 6220 4220 5220a 5220b 6220	1 157 200 269 694 331 1436 1436 1436 5180	-100.468243 -100.490394 -100.465775 -100.491737 -100.492202 -100.490429 -100.465805 -100.491817 -100.492296	1.2687 1.2769 1.2876 1.2772 1.2767 1.2768 1.2875 1.2769 1.2769	0.9423 0.9487 1.0025 0.9490 0.9490 0.9486 1.0025 0.9489 0.9491
	CISD MRCISD SOCISD SOCISD + CINO	4220 5220a 5220b 6220 4220 5220a 5220b 6220	1 157 200 269 694 331 1436 1436 5180 1436	$\begin{array}{r} -100.468243\\ -100.490394\\ -100.465775\\ -100.491737\\ -100.492202\\ -100.490429\\ -100.465805\\ -100.491817\\ -100.492296\\ -100.490922\end{array}$	1.2687 1.2769 1.2876 1.2772 1.2767 1.2768 1.2875 1.2769 1.2769 1.2767 1.2773	0.9423 0.9487 1.0025 0.9490 0.9490 0.9486 1.0025 0.9489 0.9491 0.9489

<sup>a</sup>Reference 30.

<sup>b</sup>References 26 and 10.

BOH $\tilde{X}^{1}A'$	active space	Reference CSFs	Energy	$r_e(\text{B-O})$	$r_e(\text{O-H})$	ang(BOH)
CISD		1	-100.473920	1.2945	0.9543	122.32
MRCISD	62	253	-100.496406	1.3041	0.9619	120.03
	72a	250	-100.472071	1.3028	1.0440	84.95
	72b	351	-100.498143	1.3046	0.9617	120.23
	82	891	-100.500599	1.3048	0.9619	120.90
SOCISD	62	924	-100.496446	1.3041	0.9619	120.01
	72a	2744	-100.472123	1.3027	1.0440	84.96
	72b	2744	-100.498362	1.3033	0.9620	120.31
	82	9996	-100.500689	1.3049	0.9671	120.78
SOCISD + CINO		2744	-100.496998	1.3046	0.9621	120.34
cc-pVQZ CCSDT <sup>a</sup>			-100.512394	1.3051	0.9617	121.36

Table 4.4: Total energies (in Hartrees) and equilibrium geometries (in Å) of the  $\tilde{X}^{-1}A'$  BOH electronic state.

<sup>a</sup>Reference 30.

# CHAPTER 5

## CONCLUDING REMARKS

Clearly the characterization of small transition-metal complexes and excited electronic states represent areas of small-molecule *ab initio* chemistry that have been largely unexplored with highly-accurate levels of theory. The reasons for this are evident as well; treatment of such systems with sufficient accuracy requires developmental algorithms and techniques, while interpretation and compilation of results necessitates considerable rigor and patience. Conclusions about the electronic structure of both molecular systems discussed in this dissertation are based on little or no experimental evidence for comparison. These studies represent the surprising fragility of *ab initio* methods in dealing with the electron correlation problem.

However, future research prospects are quite exciting. As the treatment of electron correlation will undoubtedly continue to improve, both FeNC / FeCN and HBO / BOH could become systems subject to continual revisitation for both experimental and theoretical chemists. For FeNC and FeCN, accounting for higher excitation levels than are currently possible for coupled cluster and multireference configuration interaction methods is necessary. Improved basis sets, treatment of spin-orbit coupling, and a refined treatment of relativistic effects could also have a significant effect on the relative energies of the  ${}^{4}\Delta$  and  ${}^{6}\Delta$  electronic states. Other low-lying electronic states should be present as well, and numerous electronic transitions in the IR and near-UV spectral regions might be eventually characterized. Or it is possible that FeNC and FeCN will further elude an improved theoretical treatment or experimental isolation, generating the same magnitude of controversy as iron hydride (FeH).

The wealth of experimental knowledge on HBO and BOH has been unelaborated upon for more than a decade. The electronic structure of this isomeric pair is remarkably

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challenging for its rather miniscule size. Adiabatic transition energies of both ground states to singlet and triplet excited states determined in this research could assist in the identification of BOH. A forthcoming study of the potential energy surfaces of HBO / BOH excited states will aid in the viability of BOH as a high energy-density material.

In the 1980's, the research groups of Prof. Nicholas Handy and Prof. Henry Schaefer took technology into their own hands, running larger and larger computations on smaller and smaller machines. As a testament to the explosive growth of computational chemistry on microcomputers, rudimentary CCSD(T) code on a 1.3 GHz Pentium M laptop processor, written with my meager three years of experience in the field of theoretical chemistry, runs *fourteen* times faster than the CADPAC SCF code on an IBM PC XT for DZ water. My SCF code is more than 8500 times faster than the CADPAC microcomputer software benchmarks from 1985. However, writing code is only a small step in understanding electronic structure theory. These difficult applications of the software and methods have personally become a rewarding "no-nonsense path to progress". The development of coupled cluster, multireference, and excited state methods continue unabated, but remarks and investigations on the limitations and propriety of widely-used *ab initio* techniques should never be ignored for the sake of constant theoretical development.

# APPENDIX A

## SUPPLEMENTAL MATERIAL FOR CHAPTER 2

Table A.1. CASSCF reference coefficients in the natural orbital representation for lowlying electronic states of FeNC and FeCN using the cc-pVQZ/aug-cc-pVQZ basis set. Doubly-occupied core orbitals excluded from the active space are signified as  $[core] = 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4 8\sigma^2 9\sigma^2$ 

FeCN:

$$\begin{split} \Psi (^{4}\Delta) &= 0.642 \ \Phi_{1} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{2}4\pi_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy} \right] \\ &= 0.452 \ \Phi_{2} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{2}2\sigma^{4}\pi_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy} \right] \\ &= 0.419 \ \Phi_{3} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{1}2\sigma 4\pi_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy} \right] \\ &= 0.296 \ \Phi_{4} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{1}2\sigma 4\pi_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy} \right] \\ &= 0.233 \ \Phi_{5} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{1}2\sigma 4\pi_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy} \right] \\ &= 0.233 \ \Phi_{5} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{2}\sigma^{4}\pi_{x}^{2}4\pi_{y}1\delta_{x^{2}-y^{2}} \right]^{2}1\delta_{xy} \right] \\ &= 0.443 \ \Phi_{2} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}12\sigma^{2}4\pi_{x}^{2}4\pi_{y}1\delta_{x^{2}-y^{2}} \right]^{2}1\delta_{xy} \right] \\ &= 0.443 \ \Phi_{2} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{2}\sigma^{4}\pi_{x}^{2}4\pi_{y}1\delta_{x^{2}-y^{2}} \right]^{2}\delta_{xy} \right] \\ &= 0.362 \ \Phi_{3} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{1}2\sigma^{4}\pi_{x}^{2}4\pi_{y}1\delta_{x^{2}-y^{2}} \right]^{2}\delta_{xy} \right] \\ &= 0.280 \ \Phi_{4} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{1}2\sigma^{4}\pi_{x}^{2}4\pi_{y}1\delta_{x^{2}-y^{2}} \right]^{2}\delta_{xy} \right] \\ &= 0.233 \ \Phi_{5} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{1}2\sigma^{4}\pi_{x}^{2}4\pi_{y}1\delta_{x^{2}-y^{2}} \right]^{2}\delta_{xy} \right] \\ &= 0.209 \ \Phi_{6} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{1}2\sigma^{4}\pi_{x}^{2}4\pi_{y}1\delta_{x^{2}-y^{2}} \right]^{2}\delta_{xy} \right] \\ &= 0.209 \ \Phi_{6} \left[ \operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{2}\pi^{2}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy} \right]^{2}\sigma^{2}\pi_{x}^{2} \right] \\ &= 0.122 \ \Phi_{2} \left[ \operatorname{core} 3\pi_{x}^{2}1\sigma^{2}11\sigma^{4}\pi_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy} \right]^{2}\sigma^{2}\pi_{x}^{2} \right] \\ &= 0.122 \ \Phi_{3} \left[ \operatorname{core} 3\pi_{x}^{2}10\sigma^{2}11\sigma^{4}\pi_{x}^{2}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy} \right]^{2}\sigma^{2}\pi_{y}^{2} \right] \\ &= 0.122 \ \Phi_{2} \left[ \operatorname{core} 3\pi_{x}^{2}1\sigma^{2}11\sigma^{4}\pi_{x}^{2}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}12\sigma^{2}\pi_{y}^{2} \right] \\ &= 0.122 \ \Phi_{3} \left[ \operatorname{core} 3\pi_{x}^{2}10\sigma^{2}11\sigma^{4}\pi_{x}^{2}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}12\sigma^{2}\pi_{y}^{2} \right] \\ &= 0.122 \ \Phi_{3} \left[ \operatorname{core} 3\pi_{x}^{2}10\sigma^{2}11\sigma^{4}\pi_{x}^{2}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}12\sigma^{2}\pi_{y}^{2} \right] \\ &= 0.122 \ \Phi_{3} \left[ \operatorname{core} 3\pi_{x}^{2}10\sigma^{2}11\sigma^{4}\pi_{x}^{2}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}12\sigma^{2}\pi_{y}^{2} \right] \\ &= 0.121 \ \Phi_{3} \left[$$

## FeNC:

$$\Psi ({}^{4}\Delta) = 0.645 \Phi_{1} [\operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma^{2}4\pi_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy}] - 0.457 \Phi_{2} [\operatorname{core} 3\pi^{4}10\sigma^{2}12\sigma^{2}4\pi_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy}] + 0.423 \Phi_{3} [\operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma12\sigma4\overline{\pi}_{x}4\pi_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy}] + 0.299 \Phi_{4} [\operatorname{core} 3\pi^{4}10\sigma^{2}11\sigma12\sigma4\pi_{x}4\overline{\pi}_{y}(1\delta_{x^{2}-y^{2}})^{2}1\delta_{xy}]$$

+ 0.233 
$$\Phi_5$$
 [core  $3\pi^4 10\sigma^2 11\sigma 12\sigma 4\pi_x 4\pi_y (1\delta_{x^2-y^2})^2 1\overline{\delta}_{xy}$ ]  
 $\Psi$  (<sup>4</sup> $\Pi$ ) = 0.656  $\Phi_1$  [core  $3\pi^4 10\sigma^2 11\sigma^2 4\pi_x^2 4\pi_y 1\delta_{x^2-y^2} 1\delta_{xy}$ ]  
- 0.450  $\Phi_2$  core  $3\pi^4 10\sigma^2 12\sigma^2 4\pi_x^2 4\pi_y 1\delta_{x^2-y^2} 1\delta_{xy}$ ]  
+ 0.307  $\Phi_3$  [core  $3\pi^4 10\sigma^2 11\sigma 12\sigma 4\pi_x^2 4\pi_y 1\delta_{x^2-y^2} 1\overline{\delta}_{xy}$ ]  
+ 0.306  $\Phi_4$  [core  $3\pi^4 10\sigma^2 11\sigma 12\sigma 4\pi_x^2 4\overline{\pi}_y 1\delta_{x^2-y^2} 1\delta_{xy}$ ]  
- 0.210  $\Phi_5$  [core  $3\pi^4 10\sigma^2 11\sigma 12\sigma 4\pi_x^2 4\pi_y 1\overline{\delta}_{x^2-y^2} 1\delta_{xy}$ ]  
- 0.210  $\Phi_6$  [core  $3\pi^4 10\sigma^2 11\sigma 12\overline{\sigma} 4\pi_x^2 4\pi_y 1\delta_{x^2-y^2} 1\delta_{xy}$ ]  
- 0.210  $\Phi_6$  [core  $3\pi^4 10\sigma^2 11\sigma 12\overline{\sigma} 4\pi_x^2 4\pi_y 1\delta_{x^2-y^2} 1\delta_{xy}$ ]  
 $\Psi$  (<sup>6</sup> $\Delta$ ) = 0.973  $\Phi_1$  [core  $3\pi^4 10\sigma^2 11\sigma 4\pi_x 4\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy} 12\sigma 5\pi_x^2$ ]  
- 0.104  $\Phi_2$  [core  $3\pi_x^2 10\sigma^2 11\sigma 4\pi_x 4\pi_y (1\delta_{x^2-y^2})^2 1\delta_{xy} 12\sigma 5\pi_y^2$ ]  
 $\Psi$  (<sup>6</sup> $\Pi$ ) = 0.973  $\Phi_1$  [core  $3\pi^4 10\sigma^2 11\sigma 4\pi_x^2 4\pi_y (1\delta_{x^2-y^2})^2 12\sigma 5\pi_y^2$ ]  
 $\Psi$  (<sup>6</sup> $\Pi$ ) = 0.973  $\Phi_1$  [core  $3\pi_x^2 10\sigma^2 11\sigma 4\pi_x^2 4\pi_y (1\delta_{x^2-y^2})^2 12\sigma 5\pi_y^2$ ]  
- 0.105  $\Phi_2$  [core  $3\pi_y^2 10\sigma^2 11\sigma 4\pi_x^2 4\pi_y (1\delta_{x^2-y^2})^2 12\sigma 5\pi_y^2$ ]

		FeNC FeCN				
	Energy	r(Fe-N)	<i>r</i> (N-C)	Energy	r(Fe-C)	<i>r</i> (C-N)
Wachters/DZP CISD						
$^{4}\Sigma^{-}$	-1355.020647	1.9115	1.1810	-1355.030164	1.9600	1.1720
$^{4}\Delta$	-1355.036728	1.8938	1.1815	-1355.040433	1.9857	1.1699
<sup>4</sup> П	-1355.032847	1.9230	1.1813	-1355.038880	1.9925	1.1712
$\Pi^{d}$	-1355.073122	1.9698	1.1844	-1355.072366	2.0773	1.1715
$^{6}\Delta$	-1355.085306	1.9561	1.1849	-1355.081616	2.0819	1.1709
Roos ANO CISD						
$4\Sigma^{-}$	-1355.184052	1.9155	1.1709	-1355.194592	1.9557	1.1588
$^{4}\Delta$	-1355.198230	1.9045	1.1716	-1355.203351	1.9867	1.1569
<sup>4</sup> П	-1355.196393	1.9286	1.1711	-1355.203257	1.9899	1.1580
$\Pi^{d}$	-1355.227585	1.9695	1.1738	-1355.226968	2.0702	1.1584
$^{6}\Delta$	-1355.239358	1.9539	1.1744	-1355.235681	2.0742	1.1579
Nasa ANO CISD						
$4\Sigma^{-}$	-1355.261919	1.9165	1.1616	-1355.263823	1.9528	1.1499
$^{4}\Delta$	-1355.266196	1.8977	1.1626	-1355.271851	1.9835	1.1480
<sup>4</sup> П	-1355.264706	1.9204	1.1619	-1355.272129	1.9857	1.1491
$\Pi^{d}$	-1355.294071	1.9613	1.1646	-1355.294066	2.0658	1.1492
$^{6}\Delta$	-1355.305640	1.9460	1.1653	-1355.302520	2.0699	1.1488
cc-pVTZ / aug-cc-PVTZ CISD						
$^{4}\Sigma^{-}$	-1355.232349	1.9130	1.1649	-1355.241506	1.9603	1.1531
$^{4}\Delta$	-1355.236366	1.8955	1.1658	-1355.241437	1.9788	1.1513
<sup>4</sup> П	-1355.234809	1.9175	1.1652	-1355.241682	1.9805	1.1524
$\Pi^{B}$	-1355.265201	1.9543	1.1679	-1355.264385	2.0541	1.1524
<sup>6</sup> Δ	-1355.276798	1.9407	1.1686	-1355.272899	2.0597	1.1520
Wachters/DZP CASSCF						
$^{4}\Delta$	-1354.835682	1.9603	1.1945	-1354.843824	2.0795	1.1849
$^{4}\Pi$	-			-1354.835755	2.0704	1.1851
$\Pi^{6}$	-1354.852850	2.0031	1.1946	-1354.861646	2.1129	1.1858
$^{6}\Delta$	-1354.865599	1.9867	1.1965	-1354.872599	2.1104	1.1853
Roos ANO CASSCF						
$^{4}\Delta$	-1354.891652	1.9634	1.1864	-1354.898878	2.0780	1.1749
$^{4}\Pi$	-1354.881149	1.9720	1.1861	-1354.890573	2.0700	1.1747
$\Pi^{6}$	-1354.908466	2.0081	1.1863	-1354.916337	2.1121	1.1758
$^{6}\Delta$	-1354.921090	1.9905	1.1866	-1354.927124	2.1094	1.1754
Nasa ANO CASSCF						
$^{4}\Delta$	-1354.897246	1.9607	1.1824	-1354.904163	2.0772	1.1706
<sup>4</sup> П	-1354.886554	1.9700	1.1820	-1354.895896	2.0699	1.1707
<sup>6</sup> П	-1354.913825	2.0061	1.1821	-1354.921481	2.1123	1.1713
$^{6}\Delta$	-1354.926581	1.9882	1.1825	-1354.932361	2.1091	1.1710
cc-pVTZ / aug-cc-PVTZ CASSCF						
$^{4}\Delta$	-1354.891524	1.9599	1.1837	-1354.898333	2.0753	1.1717

Table A.1: Total energies and physical properties for FeNC/FeCN at correlated levels of theory not listed in Tables 2.4 and 2.5.<sup>a</sup>

$^{4}\Pi$	-1354.880796	1.9692	1.1833	-1354.890036	2.0681	1.1719
<sup>6</sup> П	-1354.908135	2.0056	1.1835	-1354.915714	2.1110	1.1725
<sup>6</sup> Δ	-1354.920952	1.9877	1.1838	-1354.926686	2.1080	1.1722
Wachters/DZP MRCISD+Q						
$^{4}\Delta$	-1355.110672	1.8977	1.1993	-1355.112724	1.9980	1.1897
<sup>4</sup> Π	_			-1355.108297	1.9747	1.1889
$\Pi^{6}$	-1355.120295	1.9652	1.1998	-1355.123429	2.0638	1.1900
$^{6}\Delta$	-1355.132168	1.9528	1.2001	-1355.132581	2.0713	1.1896
Wachters/DZP CCSD						
<sup>4</sup> ∑ <sup>-</sup>	-1355.070745	1.9004	1.1908	-1355.082602	1.9433	1.1836
$^{4}\Delta$	-1355.102251	1.9137	1.1927	-1355.102838	2.0100	1.1810
<sup>4</sup> П	-1355.077193	1.9222	1.1913	-1355.095703	1.9848	1.1817
$\Pi^{9}$	-1355.107673	1.9647	1.1929	-1355.109328	2.0674	1.1819
$^{6}\Delta$	-1355.119610	1.9517	1.1933	-1355.118201	2.0736	1.1814
Roos ANO CCSD						
<sup>4</sup> ∑ <sup>-</sup>	-1355.248645	1.9003	1.1819	-1355.261881	1.9333	1.1709
$^{4}\Delta$	-1355.272404	1.8947	1.1835	-1355.275604	1.9781	1.1688
<sup>4</sup> П	-1355.262098	1.9031	1.1826	-1355.270545	1.9601	1.1698
β	-1355.276865	1.9656	1.1837	-1355.278486	2.0600	1.1697
$^{6}\Delta$	-1355.288377	1.9496	1.1843	-1355.286807	2.0652	1.1693
Nasa ANO CCSD						
<sup>4</sup> Σ <sup>-</sup>	-1355.323358	1.8907	1.1172	-1355.337436	1.9272	1.1616
$^{4}\Delta$	-1355.345465	1.8832	1.1739	-1355.349719	1.9701	1.1594
<sup>4</sup> П	-1355.335933	1.8934	1.1729	-1355.345433	1.9542	1.1605
$^{6}\Pi$	-1355.349092	1.9548	1.1742	-1355.351492	2.0536	1.1601
$^{6}\Delta$	-1355.360445	1.9398	1.1749	-1355.359560	2.0593	1.1597
cc-pVTZ / aug-cc-pVTZ CCSD						
<sup>4</sup> Σ <sup>-</sup>	-1355.291310	1.1887	1.1758	-1355.304657	1.9211	1.1653
$^{4}\Delta$	-1355.313477	1.8827	1.1773	-1355.316723	1.9656	1.1629
<sup>4</sup> П	-1355.303876	1.8902	1.1764	-1355.312437	1.9477	1.1640
<sup>6</sup> П	-1355.317625	1.9455	1.1776	-1355.319000	2.0382	1.1635
<sup>6</sup> Δ	-1355.328901	1.9327	1.1783	-1355.327020	2.0459	1.1631
Wachters/DZP CCSD(T)						
$^{4}\Delta$	-			-1355.116961	1.9620	1.1882
$^{4}\Pi$	-1355.095681	1.9200	1.1980	-1355.108441	1.8987	1.1905
$\Pi^{6}$	-1355.122719	1.9623	1.1995	-1355.125075	2.0632	1.1886
$^{6}\Delta$	-1355.134674	1.9497	1.1998	-1355.133765	2.0702	1.1880
Roos ANO CCSD(T)						
$^{4}\Delta$	-1355.297506	1.8707	1.1906	-1355.303923	1.9551	1.1770
<sup>4</sup> Π	-1355.288311	1.8842	1.1900	-1355.299345	1.9380	1.1782
<sup>6</sup> П	-1355.298547	1.9620	1.1915	-1355.300845	2.0539	1.1776
$^{6}\Delta$	-1355.309968	1.9466	1.1921	-1355.308984	2.0599	1.1772
Nasa ANO CCSD(T)						
<sup>4</sup> A	-1355 377431	1 8620	1 1813	-1355 384489	1 9494	1 1677
	1555.577451	1.0020	1.1015	1555.504407	1.7 171	1.10//

<sup>4</sup> Π	-1355.368760	1.8751	1.1807	-1355.380408	1.9314	1.1682
$\Pi^{d}$	-1355.375675	1.9508	1.1819	-1355.379042	2.0462	1.1682
<sup>6</sup> Δ	-1355.386949	1.9359	1.1827	-1355.386923	2.0528	1.1678
cc-pVTZ / aug-cc-PVTZ CCSD(T)						
$^{4}\Delta$	-1355.342368	1.8597	1.1846	-1355.348646	1.9435	1.1713
<sup>4</sup> Π	-1355.333820	1.8713	1.1840	-1355.344824	1.9247	1.1726
$\Pi^{6}$	-1355.342544	1.9413	1.1854	-1355.344759	2.0305	1.1716
<sup>6</sup> Δ	-1355.353645	1.9290	1.1861	-1355.352502	2.0393	1.1712
Wachters/DZP CCSDT-1b						
$^{4}\Delta$	-1355.120680	1.8785	1.2001	-1355.123223	1.9640	1.1883
$^{6}\Delta$	-1355.136337	1.9485	1.2017	-1355.134610	2.0700	1.1887
Roos ANO CCSDT-1b						
$\Delta_{e}$	-1355.302946	1.8709	1.1931	-1355.307791	1.9550	1.1776
<u>о</u>	-1355.311883	1.9454	1.1940	-1355.310420	2.0594	1.1781
Wachters/DZP CCSDT-3						
$^{4}\Delta$	-1355.11996	1.8941	1.1990	-1355.121639	1.9885	1.1872
$^{4}\Pi$	-1355.109760	1.9017	1.1992	-1355.115754	1.9586	1.1882
$^{6}\Pi$	-1355.122644	1.9618	1.1999	-1355.124160	2.0635	1.1881
$^{6}\Delta$	-1355.134458	1.9490	1.2003	-1355.132807	2.0705	1.1875
Roos ANO CCSDT-3						
$^{4}\Delta$	-1355.300539	1.8818	1.1916	-1355.304761	1.9630	1.1762
<sup>4</sup> П	-1355.290982	1.8836	1.1911	-1355.300104	1.9388	1.1773
$\Pi^{6}$	-1355.297878	1.9613	1.1917	-1355.299772	2.0540	1.1771
<sup>6</sup> Δ	-1355.309330	1.9458	1.1924	-1355.307904	2.0601	1.1767
Nasa ANO CCSDT-3						
$^{4}\Delta$	-1355.379731	1.8695	1.1822	-1355.385201	1.9545	1.1672
<sup>4</sup> Π	-1355.370733	1.8724	1.1816	-1355.381151	1.9310	1.1684
$\Pi^{6}$	-1355.375129	1.9501	1.1823	-1355.378142	2.0462	1.1678
$^{6}\Delta$	-1355.386433	1.9352	1.1832	-1355.386014	2.0523	1.1675

<sup>a</sup>Energies are in hartrees, bond distances in Å.

# APPENDIX B

## SUPPLEMENTAL MATERIAL FOR CHAPTER 3

Table B.1. Electron configurations of HBO / BOH singlet and triplet excited states in linear and bent geometries. Note that in-plane bending is considered to occur in the *yz*-plane. The  $C_s$  wave functions are written using the  $C_{2v} - C_s$  MO correspondence from Table I. Only the open-shell portions of the wave functions are written.

$C_{\infty v}(C_{2v})$ electronic state	$HBO / BOH C_{\infty_V} wave function$	HBO C <sub>s</sub> wave function	BOH C <sub>s</sub> wave function
$1\pi^3 2\pi$			
$^{1}\Delta \rightarrow ^{1}A_{1} \rightarrow ^{1}A'$	$(1\pi_x \alpha(1))(2\pi_x \beta(2))1{\pi_y}^2$	$(1a''\alpha(1))(2a''\beta(2))(6a')^2$	$(1a''\alpha(1))(2a''\beta(2))(5a')^2$
	$-(1\pi_x\beta(1))(2\pi_x\alpha(2))1\pi_y^2$	$-(1a''\beta(1))(2a''\alpha(2))(6a')^2$	$-(1a''\beta(1))(2a''\alpha(2))(5a')^2$
	$-(1\pi_y\alpha(1))(2\pi_y\beta(2))1\pi_x^2$	$-(6a'\alpha(1))(7a'\beta(2))(1a'')^2$	$-(5a'\alpha(1))(8a'\beta(2))(1a'')^2$
	+ $(1\pi_{y}\beta(1))(2\pi_{y}\alpha(2))1\pi_{x}^{2}$	$+(6a'\beta(1))(7a'\alpha(2))(1a'')^2$	+ $(5a'\beta(1))(8a'\alpha(2))(1a'')^2$
$^{1}\Delta \rightarrow ^{1}A_{2} \rightarrow ^{1}A^{\prime\prime}$	$(1\pi_x \alpha(1))(2\pi_y \beta(2))1{\pi_y}^2$	$(1a''\alpha(1))(7a'\beta(2))(6a')^2$	$(1a''\alpha(1))(8a''\beta(2))(5a')^2$
	$-(1\pi_x\beta(1))(2\pi_y\alpha(2))1\pi_y^2$	$-(1a''\beta(1))(7a'\alpha(2))(6a')^2$	$-(1a''\beta(1))(8a'\alpha(2))(5a')^2$
	$+(1\pi_y\alpha(1))(2\pi_x\beta(2))1{\pi_x}^2$	$+(6a'\alpha(1))(2a''\beta(2))(1a'')^2$	$+(5a'\alpha(1))(2a''\beta(2))(1a'')^2$
	$-(1\pi_{y}\beta(1))(2\pi_{x}\alpha(2))1\pi_{x}^{2}$	$-(6a'\beta(1))(2a''\alpha(2))(1a'')^2$	$-(5a'\beta(1))(2a''\alpha(2))(1a'')^2$
$^{1}\Sigma^{-} \rightarrow ^{1}A_{2} \rightarrow ^{1}A^{\prime\prime}$	$(1\pi_x \alpha(1))(2\pi_y \beta(2))1{\pi_y}^2$	$(1a''\alpha(1))(7a''\beta(2))(6a')^2$	$(1a''\alpha(1))(8a'\beta(2))(5a')^2$
	$-(1\pi_{v}\beta(1))(2\pi_{v}\alpha(2))1\pi_{v}^{2}$	$-(1a''\beta(1))(7a'\alpha(2))(6a')^2$	$-(1a''\beta(1))(8a'\alpha(2))(5a')^2$
	$-(1\pi_{x}\alpha(1))(2\pi_{x}\beta(2))1\pi_{x}^{2}$	$-(6a'\alpha(1))(2a''\beta(2))(1a'')^2$	$-(5a'\alpha(1))(2a''\beta(2))(1a'')^2$
	+ $(1\pi_y\beta(1))(2\pi_x\alpha(2))1{\pi_x^2}$	+ $(6a'\beta(1))(2a''\alpha(2))(1a'')^2$	$+(5a'\beta(1))(2a''\alpha(2))(1a'')^2$
$^{1}\Sigma^{+} \rightarrow ^{1}A_{1} \rightarrow ^{1}A'$	$(1\pi_x \alpha(1))(2\pi_x \beta(2))1{\pi_y}^2$	$(1a''\alpha(1))(2a''\beta(2))(6a')^2$	$(1a''\alpha(1))(2a''\beta(2))(5a')^2$
	$-(1\pi_x\beta(1))(2\pi_x\alpha(2))1\pi_y^2$	$-(1a''\beta(1))(2a''\alpha(2))(6a')^2$	$-(1a''\beta(1))(2a''\alpha(2))(5a')^2$
	$+(1\pi_y\alpha(1))(2\pi_y\beta(2))1\pi_x^2$	$+(6a'\alpha(1))(7a'\beta(2))(1a'')^2$	$+(5a'\alpha(1))(8a'\beta(2))(1a'')^2$
	$-(1\pi_{y}\beta(1))(2\pi_{y}\alpha(2))1\pi_{x}^{2}$	$-(6a'\beta(1))(7a'\alpha(2))(1a'')^2$	$-(5a'\beta(1))(8a'\alpha(2))(1a'')^2$
$^{3}\Delta \rightarrow ^{3}A_{1} \rightarrow ^{3}A'$	$(1\pi_x\alpha(1))(2\pi_x\alpha(2))1\pi_y^2$	$(1a''\alpha(1))(2a''\alpha(2))(6a')^2$	$(1a''\alpha(1))(2a''\alpha(2))(5a')^2$
	$-(1\pi_y \alpha(1))(2\pi_y \alpha(2))1{\pi_x}^2$	$-(6a'\alpha(1))(7a'\alpha(2))(1a'')^2$	$-(5a'\alpha(1))(8a'\alpha(2))(1a'')^2$
$^{3}\Delta \rightarrow ^{3}A_{2} \rightarrow ^{3}A^{\prime\prime}$	$(1\pi_x \alpha(1))(2\pi_y \alpha(2))1{\pi_y}^2$	$(1a''\alpha(1))(7a'\alpha(2))(6a')^2$	$(1a''\alpha(1))(8a'\alpha(2))(5a')^2$
	$+(1\pi_y\alpha(1))(2\pi_x\alpha(2))1{\pi_x}^2$	$+(6a'\alpha(1))(2a''\alpha(2))(1a'')^2$	$+(5a'\alpha(1))(2a''\alpha(2))(1a'')^2$

$^{3}\Sigma^{-} \rightarrow ^{3}A_{2} \rightarrow ^{3}A^{\prime\prime}$	$(1\pi_x \alpha(1))(2\pi_y \alpha(2))1{\pi_y}^2$	$(1a''\alpha(1))(7a'\alpha(2))(6a')^2$	$(1a''\alpha(1))(8a'\alpha(2))(5a')^2$
	$-(1\pi_y\alpha(1))(2\pi_x\alpha(2))1{\pi_x}^2$	$-(6a'\alpha(1))(2a''\alpha(2))(1a'')^2$	$-(5a'\alpha(1))(2a''\alpha(2))(1a'')^2$
$^{3}\Sigma^{+} \rightarrow ^{3}A_{1} \rightarrow ^{3}A'$	$(1\pi_x \alpha(1))(2\pi_x \alpha(2))1{\pi_y}^2$	$(1a''\alpha(1))(2a''\alpha(2))(6a')^2$	$(1a''\alpha(1))(2a''\alpha(2))(5a')^2$
	$+(1\pi_y\alpha(1))(2\pi_y\alpha(2))1{\pi_x}^2$	$+(6a'\alpha(1))(7a'\alpha(2))(1a'')^2$	$+(5a'\alpha(1))(8a'\alpha(2))(1a'')^2$
5σ2π			
$^{1}\Pi \rightarrow ^{1}B_{l} \rightarrow ^{1}A^{\prime \prime}$	$(5\sigma\alpha(1))(2\pi_x\beta(2))$	$(5a'\alpha(1))(2a"\beta(2))$	$(6a'\alpha(1))(2a"\beta(2))$
	$-(5\sigma\beta(1))(2\pi_x\alpha(2))$	$-(5a'\beta(1))(2a''\alpha(2))$	$-(6a'\beta(1))(2a''\alpha(2))$
$^{1}\Pi \rightarrow ^{1}B_{2} \rightarrow ^{1}A'$	$(5\sigma\alpha(1))(2\pi_{y}\beta(2))$	$(5a'\alpha(1))(7a'\beta(2))$	$(6a'\alpha(1))(8a'\beta(2))$
	$-(5\sigma\beta(1))(2\pi_y\alpha(2))$	$-(5a'\beta(1))(7a'\alpha(2))$	$-(6a'\beta(1))(8a'\alpha(2))$
$^{3}\Pi \rightarrow ^{3}B_{1} \rightarrow ^{3}A^{\prime\prime}$	$(5\sigma\alpha(1))(2\pi_x\alpha(2))$	$(5a'\alpha(1))(2a''\alpha(2))$	$(6a'\alpha(1))(2a''\alpha(2))$
$^{3}\Pi \rightarrow ^{3}B_{2} \rightarrow ^{3}A'$	$(5\sigma\alpha(1))(2\pi_y\alpha(2))$	$(5a'\alpha(1))(7a'\alpha(2))$	$(6a'\alpha(1))(8a'\alpha(2))$
1π <sup>3</sup> 6σ			
$^{1}\Pi \rightarrow ^{1}B_{l} \rightarrow ^{l}A^{\prime \prime}$	$(1\pi_x \alpha(1))(6\sigma\beta(2))1\pi_y^2$	$(1a''\alpha(1))(8a'\beta(2))(6a')^2$	$(1a''\alpha(1))(7a'\beta(2))(5a')^2$
	$-(1\pi_x\beta(1))(6\sigma\alpha(2))1\pi_y^2$	$-(1a''\beta(1))(8a'\alpha(2))(6a')^2$	$-(1a''\beta(1))(7a'\alpha(2))(5a')^2$
$^{1}\Pi \rightarrow ^{1}B_{2} \rightarrow ^{1}A'$	$(1\pi_{v}\alpha(1))(6\sigma\beta(2))1\pi_{x}^{2}$	$(6a'\alpha(1))(8a'\beta(2))(1a'')^2$	$(5a'\alpha(1))(7a'\beta(2))(1a'')^2$
	$-(1\pi_{y}\beta(1))(6\sigma\alpha(2))1\pi_{x}^{2}$	$-(6a'\beta(1))(8a'\alpha(2))(1a'')^2$	$-(5a'\beta(1))(7a'\alpha(2))(1a'')^2$
$^{3}\Pi \rightarrow ^{3}B_{1} \rightarrow ^{3}A^{\prime\prime}$	$(1\pi_x\alpha(1))(6\sigma\alpha(2))1\pi_y^2$	$(1a''\alpha(1))(8a'\alpha(2))(6a')^2$	$(1a''\alpha(1))(7a'\alpha(2))(5a')^2$
$^{3}\Pi \rightarrow ^{3}B_{2} \rightarrow ^{3}A'$	$(1\pi_y \alpha(1))(6\sigma \alpha(2))1{\pi_x}^2$	$(6a'\alpha(1))(8a'\alpha(2))(1a'')^2$	$(5a'\alpha(1))(7a'\alpha(2))(1a'')^2$
5თ6თ			
$^{1}\Sigma^{+} \rightarrow ^{1}A_{1} \rightarrow ^{1}A'$	$(5\sigma\alpha(1))(\overline{6\sigma\beta(2))}$	$(5a'\alpha(1))(\overline{8a'\beta(2)})$	$(6a'\alpha(1))(\overline{7a'\beta(2)})$
	$-(5\sigma\beta(1))(6\sigma\alpha(2))$	$-(5a'\beta(1))(8a'\alpha(2))$	$-(6a'\beta(1))(7a'\alpha(2))$
$^{3}\Sigma^{+} \rightarrow ^{3}A_{1} \rightarrow ^{3}A'$	$(5\sigma\alpha(1))(6\sigma\alpha(2))$	$(5a'\alpha(1))(8a'\alpha(2))$	$(6a'\alpha(1))(7a'\alpha(2))$