DEVELOPMENT AND APPLICATION OF COUPLED-CLUSTER METHODS CAPABLE OF CORRECTLY DESCRIBING DYNAMICAL AND NON-DYNAMICAL CORRELATION IN RADICALS AND BIRADICALS

by

KURT W. SATTELMEYER

(Under the direction of H. F. Schaefer III)

ABSTRACT

A general scheme for the treatment of multi-reference radical and biradical systems within the coupled-cluster method has been derived, implemented, and applied to a number of problematic systems related to combustion and atmospheric chemistry. These include the vinyl radical, doublet isomers of the HCCO system, and ozone. With respect to traditional coupled cluster techniques, results indicate that the proposed method offers worthwhile accuracy enhancements while concurrently retaining many of the useful convergence properties which allow for the qualitative assessment of the quality of the results obtained.

INDEX WORDS: Coupled-Cluster, Equation-of-Motion, Ionization Potentials, Multi-Reference, Radicals, Biradicals, Vinyl Radical, Ketenyl Radical, Hydroxyethynl Radical, Oxiryl Radical, Ozone

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Chapter 1

Introduction, Motivation, and Theory

1.1 Introduction

While undoubtedly surpassed over the past decade by density functional theory (DFT) in terms of popularity in the literature, coupled cluster techniques remain the methods of choice for chemical systems of small or moderate size. The principle advantage offered by the coupled cluster approach is that it systematically converges towards the Full CI limit (that is, the exact, non-relativistic solution to the Schrödinger equation for a given basis set). Thus, upon application of the least expensive commonly used coupled cluster method, CCSD [1, 2, 3] (coupled cluster, including single and double excitations), one knows not only approximately how close the generated wavefunction is to the exact one, but also the nature of the corrections necessary to arrive at the exact wavefunction. Such a qualitative, *a priori* knowledge of the quality of the results obtained is not possible with DFT.

The aforementioned "cheap" CCSD method scales as n^6, where n corresponds to the number of basis functions and thereby the size of the system, and systematic inclusion of higher order correlation effects increases this scaling by a factor of n^2 (i.e. CCSDT scales as n^8, CCSDTQ scales as n^{10}, etc.). Despite the fact that for most systems of chemical interest, some inclusion of the effects of triple excitations is necessary to describe the electron correlation accurately, the widely used CCSD(T) [4, 5] method offers a nice compromise, closely reproducing full CCSDT results. Here, the CCSD equations are solved, and then the CCSD(T) energy is found via a single n^7 step. Therefore, the necessary correlation needed to achieve chemical accuracy of roughly 1.0 kcal/mol for energetic properties does not preculde the standard application of such techniques to a wide variety of systems.

However, convergence with respect to basis set size is not as well-behaved. The work of Feller and coworkers [6, 7] has shown that the coupled cluster energy converges very slowly with respect to the basis set size. Even with extrapolation via Dunning's cc-pVXZ series of basis sets [8], the energy converges only as

$$E_{corr} = E_\infty + \frac{B}{X^3},$$

where B is the fitting parameter and X relates to the quality of the basis set. The source for this slow convergence is well understood to be resultant from the use of contracted gaussian functions, which are still used due to being much easier to deal with computationally.

In this context, the work of primarily Allen and coworkers [9] has helped to systematize the above convergence relationships via the so-called "focal point" procedure. The crux of this approach is that corrections due to increasing the basis set size at a given level of theory (and, similarly, increasing the amount of correlation with the same basis set) can be taken as additive corrections to results at a higher level of theory. Thus, one can approximately determine the Full CI, complete basis set energy without actually having to perform the calculation explicitly, which would be (and likely will be for the foreseeable future) an intractable problem. Additionally, the focal point scheme (and its variants) readily lends itself to other corrections which may be necessary for a given system, and those due relativity, core correlation, and r$_{12}$ methods are commonly reported in the literature.

1.2 The Necessity of New Methods

It should be noted that, while easily and routinely used to describe a wide range of systems, standard coupled cluster techniques are only applicable when the electronic structure is well-described by a single Slater determinant. This excludes a large number of systems which have multi-reference character. That is, the traditional coupled cluster approach will fail for systems in which there is more than one energetically relevant occupation for which the wavefunction transforms as the same overall symmetry.

The detrimental effects of this can be marked. Consider the triatomic molecule ozone (Chapter 4). The ground state ($^1A_1$) is dominated by two occupations, with the HOMO corresponding to double occupation of either of two frontier molecular orbitals, which have a_2 and b_2 symmetries, respectively. For this system, CC2[10], an iterative method which approximates the CCSD procedure, does not even converge, and the minimum energy structure corresponds to three oxygen atoms at infinity[1]!

While ozone is definitely an extreme example, radicals and open-shell singlet biradicals[2] are the most widespread class of problematic molecules, and a method generally applicable to the determination of their molecular properties within the coupled cluster approximation serves as the subject of this dissertation.

1.3 Theory

As reviews on the coupled cluster [11] method and its linear response extensions [12, 13] are both readily available and transparent, the author will not rederive them in this dissertation. Instead, we focus on the current implementation, which

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[1] The reader is directed to Chapter 4 for a more thorough description of the failure of traditional CC approaches for this system.

[2] Ozone can be technically considered a closed-shell system although it has many properties of open-shell singlet biradicals, including multi-reference character due to a strong $\alpha\beta$ double excitation.

allows for the accurate and systematic treatment of radical and biradical systems with multi-reference character.

The principle realization of the current work is that the vast majority of radicals and biradicals are related to well-behaved (in the sense that their wavefunctions can be reasonably represented by a single Slater determinant) systems by addition or subtraction of one or two electrons. While there are certainly numerous systems for which this is not true (with many examples coming from transition metal compounds, for example), the author's interests rest in combustion and atmospheric chemistry, where the paradigm largely holds.

The method, then, follows in a straightforward manner. First, one finds a well-behaved system close [3] to the target state, and equation-of-motion coupled cluster theory for ionization potentials or electron affinities is invoked in the appropriate sense in order to arrive at the desired state.

Consider the simplest case, the hydrogen atom. We could procede in one of two ways

1) Solve the Hartree Fock and coupled cluster equations for the hydride anion and perform equation-of-motion for ionization potentials (EOMIP) theory on this reference wavefunction to obtain the radical, or

2) Solve the trivial Hartree Fock and coupled cluster equations for a proton and perform equation-of-motion for electron affinities (EOMEA) theory on this reference wavefunction to obtain the radical.

While at first glance it may appear that the latter choice is preferable, as the resultant calculations are less expensive [4], experience indicates that the former produces better results. This can be rationalized when one considers how the solution of the

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[3] In this context, "close" is used to describe a state differing by one or two electrons from the desired state and is not a reflection of the energetics of the new systems.

[4] This characteristic holds for larger systems, as well.

Hartree Fock equations is used to generate the molecular orbitals. Namely, the occupied orbital space is roughly accurate while the unoccupied orbital space is not. This necessitates including the singly occupied molecular orbital (SOMO) of the target radical in the occupied space, which means that we must doubly occupy it in the reference state.

Such a scheme has a number of advantages over other methods one sees in the literature. First, this method is easily incorporated into existing equation-of-motion coupled cluster programs, and I have implemented the scheme (energy and analytical gradients) into a local version of the ACESII program system [14]. Second, in all cases, calculations are performed on closed-shell reference states. This feature, which is inherent in the manner in which one chooses the coupled cluster reference state from which to apply equation-of-motion coupled cluster theory to arrive at the target state, significantly reduces the computational costs. Finally, as the following applications indicate, many of the convergence relationships that have led to the desirability of coupled cluster methods are retained.

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Chapter 2

The ν_5 Vibrational Frequency of the Vinyl Radical: Conflict between Theory and Experiment[1]

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[1] Kurt W. Sattelmeyer and Henry F. Schaefer. 2002. Journal of Chemical Physics. 117:7914-7916. Reprinted per conditions stated in the Transfer of Copyright Agreement with the American Institue of Physics.

2.1 Abstract

A balanced theoretical treatment of the $\tilde{X}\ ^2\mathrm{A}'$ state of the vinyl radical is performed via application of equation-of-motion coupled cluster theory for ionized states (EOMIP-CC) from the anion. Good agreement with experiment is generally found. The only exception is the ν_5 vibrational mode, which seems to have been misassigned experimentally.

2.2 Introduction

Interest in the vinyl radical stems from its role in combustion chemistry as an intermediate [1, 2, 3, 4], where pathways via reaction with hydrogen [5] and oxygen [6] appear to be the most crucial. Furthermore, as C_2H_3 is the smallest open-shell olefinic molecule, it serves as an important test case for olefinic systems.

Although C_2H_3 is the easiest species of its kind to handle computationally, its radical character still makes it a non-trivial case. The first comprehensive attempt to characterize C_2H_3 is the work of Paddon-Row and Pople [7], who determined the ground state structure at the UMP2/6-31G* level and the harmonic vibrational frequencies at the UHF level with the same basis set. More than a decade later, Wang, Chang, and Chen [8] reported similar results at the CCSD(T)/TZ2P level. Here, the vibrational frequencies are all within 10 percent of (and below) the UHF ones while differences in geometries are no larger than would be expected. A number of other theoretical studies [9, 10, 11] have largely confirmed these results for the ground state.

Experimental literature on the vinyl system has been less profuse. Its transient nature makes vibrational spectroscopy difficult, as C_2H_3 is both unstable and not easily produced in large quantities. Indeed, until recently, the only direct assignment of a ground state frequency was achieved by Kanamori, Endo, and Hirota [12], who

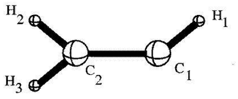

Figure 2.1: Atom labelling and structure for C_2H_3

were able to detect the theoretically predicted most intense mode (ν_7) via IR diode laser absorption. This finding was later supported by low-temperature FTIR Ar matrix work [13], which found a lone peak at a similar frequency.

Subsequently, a very important paper by Letendre, Liu, Pibel, Halpern, and Dai [14] reported *all* nine vibrational modes via time-resolved Fourier transform emission spectroscopy. The agreement with theory here is encouraging, with only the CH_2 scissors (ν_5) mode showing a marked contrast. This mode is reported experimentally to have a frequency of 1277 cm^{-1} and to be the most intense frequency. This finding confirmed earlier, tentative assignments seen in F + C_2H_4 by Moehlmann, Gleaves, Hudgens, and McDonald [15] and the photolysis of vinyl chloride by Moss, Ensminger, and McDonald [16] while all previous theoretical results find it to lie more than 100 wavenumbers higher and be some 5 to 10 percent as intense as ν_7. Letendre and coworkers point to a number of reasons, such as the rigidity of the structure influencing the intensities, for this discrepancy. More recent experimental studies [17, 18] have focused on the excited state dynamics, and no resolution of this issue is available in the literature.

The goal of this work is then twofold. First, a recently introduced approach [19] to the treatment of radicals via equation-of-motion coupled cluster theory for ionized states (EOMIP-CC) [20] from their respective closed shell anions is used to determine ground state properties of the vinyl radical. This scheme has been shown to offer substantial improvements [21, 22] versus traditional ones, which often suffer from non-satisfactory descriptions of the open-shell reference functions used for the correlation treatment. Second, we show that with the demonstrated accuracy in molecular properties [23, 24] of such techniques (using a large basis set and the inclusion of triples in the correlation treatment) for systems with well-described reference functions, the experimentally reported mode at 1277 cm^{-1} is quite unlikely to be a ground state fundamental of the vinyl radical.

2.3 Computational Details

The Hartree-Fock and coupled cluster reference functions are selected to be the 16-electron anions differing from the neutral by double occupation of the highest-lying, occupied a$^{'}$ orbital. From there, the ground state wave function is constructed as the lowest energy single ionization of A$'$ symmetry with EOMIP-CC.

Values reported are resultant from the inclusion of single and double ionizations (EOMIP-CCSD) with the series of three Dunning correlation-consistent basis sets: cc-pVXZ (X = D, T, and Q)[25]. No electrons were frozen, so the effects of core correlation are determined by comparison to cc-pCVDZ geometries at the CCSD level. Similary, differences between EOMIP-CCSD and EOMIP-CC3 [26] values offer an indication of the effects of correlation beyond doubles. All computations were performed with a local version of the ACESII program system[27].

2.4 Results

Optimized geometries for the $\tilde{X}$ ^{2}A$'$ state of C_2H_3 are reported in Tables 2.1 and 2.2, along with the best previous theoretical and experimental structures. The

Table 2.1: Bond distances for the $\tilde{X}$ ^{2}A$'$ state of C_2H_3 in Ångstroms.

	$r_{C_1H_1}$	$r_{C_1C_2}$	$r_{C_2H_2}$	$r_{C_2H_3}$
EOMIP-CCSD/cc-pVDZ	1.0927	1.3236	1.1013	1.0966
EOMIP-CCSD/cc-pVTZ	1.0712	1.3024	1.0833	1.0784
EOMIP-CCSD/cc-pVQZ	1.0737	1.2999	1.0848	1.0801
EOMIP-CCSD/cc-pCVDZ	1.0921	1.3217	1.1007	1.0960
EOMIP-CC3/cc-pVDZ	1.0956	1.3341	1.1052	1.0994
Recommended	1.0760	1.3085	1.0881	1.0823
	±0.002	±0.004	±0.002	±0.002
CCSD(T)/TZ2P[a]	1.078	1.314	1.088	1.083
Experiment[b]	1.080	1.3160	1.085	1.085
	±0.010	±0.0063	±0.010	±0.010

[a] Reference 8.

[b] Reference 12.

Table 2.2: Bond angles for the $\tilde{X}$ ^{2}A$'$ state of C_2H_3 in degrees.

	$r_{C_1H_1}$	$r_{C_1C_2}$	$r_{C_2H_3}$
EOMIP-CCSD/cc-pVDZ	136.17	121.31	116.71
EOMIP-CCSD/cc-pVTZ	137.60	121.47	116.68
EOMIP-CCSD/cc-pVQZ	137.42	121.46	116.44
EOMIP-CCSD/cc-pCVDZ	136.17	121.31	116.68
EOMIP-CC3/cc-pVDZ	135.84	121.35	116.72
Recommended	137.09	121.50	116.42
	±0.1	±0.1	±0.1
CCSD(T)/TZ2P[a]	136.6	121.2	116.7
Experiment[b]	137.3	121.5	117.0
	±4.0	±1.0	±1.4

[a] Reference 8.

[b] Reference 12.

Table 2.3: Absolute energies in hartrees of the $\tilde{X}$ ^{2}A$'$ state of C_2H_3.

Theory	Basis Set	E
EOMIP-CCSD	cc-pVDZ	-77.66721
EOMIP-CCSD	cc-pVTZ	-77.76342
EOMIP-CCSD	cc-pVQZ	-77.80975
CCSD(T)	TZ2P[a]	-77.76493
MRCI+D(7,7)	ANO(2+)**[b]	-77.75250

[a] Reference 8.
[b] Reference 10.

quality of the EOMIP-CCSD/cc-pVQZ results is evident upon comparison with CCSD(T)/TZ2P and experimental values. All bond lengths here (except the C-C bond, with the difference being nicely accounted for by the inclusion of partial triples in the correlation treatment) agree to within seven thousandths of an Ångstrom. The agreement in bond angles is similarly encouraging.

Furthermore, there is no doubt that the reference wavefunction (in this case the anion at the CCSD level) is an appropriate one for application of a single reference method, with the manifold of converged single and double excitation amplitudes all less than 0.03 and 0.08, respectively. Additional evidence for the quality of the wavefunction is demonstrated in Table 2.3, which gives the absolute energies from this work and previous theoretical works. Even without the inclusion of triples, the balanced treatment used here is able to rival the traditional open-shell approach, CCSD(T), used by Wang, Chang, and Chen. The latter approach, of course, may be subject to symmetry breaking.

Also included in Tables 2.1 and 2.2 is a recommended structure, which has been constructed by taking geometry differences (EOMIP-CCSD/cc-pCVDZ and EOMIP-CC3/cc-pVDZ versus EOMIP-CCSD/cc-pVDZ) as additive corrections to the converged EOMIP-CCSD/cc-pVQZ structure. Given the readily apparent convergence with respect to basis size at the quadruple zeta level and the small magnitudes of the aforementioned corrections, we predict these parameters to have error bars of ±0.002 Å for bond lengths (with the C-C bond, as mentioned above, being somewhat less well-converged) and ±0.1 Å for bond angles.

Having determined a well-behaved reference function and corresponding structure, we report harmonic vibrational frequencies and intensities in Table 2.4. While it is plausible that the combination of a reference function with strong multi-reference character used for the computation of molecular properties in Reference 8 and a large anharmonic correction could account for the discrepancy seen for ν_5 experimentally by Letendre *et al.*, the work done in this paper makes this possibility a quite unlikely one.

First, it has been shown that EOMIP-CCSD/cc-pVQZ produces harmonic frequencies accurate versus experiment to at least 100 cm^{-1} for processes of dominant single-replacement character [23, 24], such as the present case. Indeed, *all* eight other frequencies reported match the experimental values to well within this expectation [28], and only the ν_5 CH_2 symmetric bending mode agrees poorly. Additionally, a comparison of the intensities from Reference 14 with those determined here points to another source for the strong band at 1277 cm^{-1}. The authors of Reference 14 suggest a number of sources for this observed intensity coupled with the aforementioned large difference between theory for the vibrational energy, such as a C_{2v} geometry with a linear CCH framework increasing this intensity but not influencing the vibrational energies; however, we find the most probable scenario to be that this band is due to one or more different sources entirely. While it is perhaps an unlikely one due

Table 2.4: Vibrational frequencies in cm^{-1}, with relative intensities in parentheses, for the $\tilde{X}\ ^2$A$'$ state of C_2H_3.

Fundamental	Exp.[a]	CCSD(T) TZ2P[b]	EOMIP-CCSD cc-pVQZ
ν_1(a$'$)	3235±12 (7)	3215 (1.4)	3298 (1.4)
ν_2(a$'$)	3164±20 (11)	3156 (1.4)	3222 (6.1)
ν_3(a$'$)	3103±11 (0.5)	3049 (1.3)	3118 (6.0)
ν_4(a$'$)	1700±35 (0.1)	1609 (4.3)	1689 (1.4)
ν_5(a$'$)	1277±20 (100)	1411 (8.5)	1419 (10.6)
ν_6(a$'$)	1099±16 (43)	1098 (8.9)	1077 (12.5)
ν_7(a$''$)	955±7 (32)	944 (100)	965 (100)
ν_8(a$'$)	758±5 (11)	764 (23.0)	730 (29.8)
ν_9(a$''$)	895±9 (93)	830 (12.9)	850 (13.7)

[a] Reference 14.
[b] Reference 8.

to the evidence that the first excited state is predissociative, one interesting possibility is the recently detected ν_5 mode in the $\tilde{A}\ ^2$A$''$ excited state [17, 18], which rests at 1306 cm^{-1} at the EOMIP-CCSD/cc-pVQZ level. In all probability, however, the source of this emitter will remain in question until a high resolution measurement at 1277 cm^{-1} in a supersonically cooled jet is performed.

Thus, we have reported the most thorough treatment of the vinyl radical ground state to date. Structures and properties match well versus previous theoretical and experimental values, and a host of evidence suggests that the ν_5 mode has yet to be identified experimentally.

2.5 ACKNOWLEDGMENTS

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[28] There may be some confusion in Reference 14 about the labelling of the least energetic frequency of each symmetry, as they have been switched. We have therefore changed these values in Table 2.4 to match the correct ordering.

CHAPTER 3

ENERGETICS OF THE LOW-LYING ISOMERS OF HCCO[1]

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[1] Kurt W. Sattelmeyer, Yukio Yamaguchi, and Henry F. Schaefer. 2003. Chemical Physics Letters. 383:266-269. Reprinted per conditions stated in the Transfer of Copyright Agreement with Elsevier Science B.V.

3.1 Abstract

High level ab initio coupled cluster (CC) and equation-of-motion (EOM) CC methods have been used to characterize the lowest doublet state of the ketenyl radical (HCCO) and its four low-lying isomers: the quartet *trans*- and *cis*- states of ketenyl, the hydroxyethynyl radical, and the oxiryl radical. These four isomers are found to be minima and to lie between 50 and 70 kcal/mol higher in energy than the ketenyl radical.

3.2 Introduction

While the HCCO radical (**1d**, Fig. 1) was first suggested 40 years ago as an intermediate in combustion processes by Fenimore and Jones[1] via the reaction

$$O(^3P) + C_2H_2 \longrightarrow HCCO + H,$$

only recently has the predominance of this pathway, as opposed to that corresponding to the formation of methylene and carbon monoxide, been definitively demonstrated[2-5]. Given these findings, one would therefore predict a number of plausible combustion reactions involving the ketenyl radical[5, 6]. With the recent experimental work of Krisch, Miller, Butler, Su, Bersohn, and Shu[7] offering a clean source of the HCCO radical, further experimental exploration of these reactions, among others, is anticipated.

The ground state of this system is unquestionably the Renner-Teller[8-10] split ^{2}A$''$ state of the ketenyl radical[11-15]; however, a number of isomers have been explored theoretically. These include both the cis- (**1qc**) and trans- (**1qt**) ^{4}A$''$ states of the ketenyl radical[16], the ^{2}A$''$ state of the hydroxyethynyl radical (**2d**)[17], and the ^{2}A$''$ state of the bridged oxiryl radical (**3d**)[18]. Despite the amount of information available in the literature for these isomers, the use of a wide range of levels of

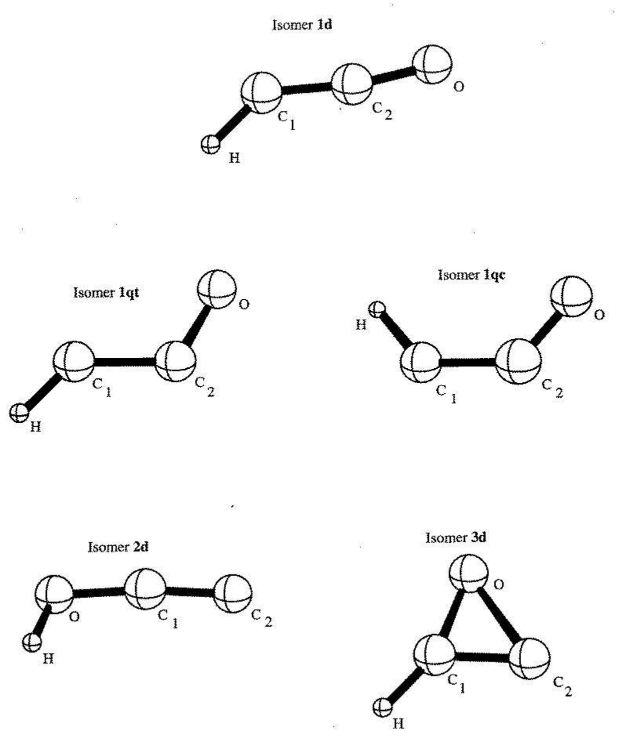

Figure 3.1: Atom labelling for the five structures considered in this paper.

theory and basis sets has unfortunately precluded a global interpretation of their relative stabilities. Therefore, this letter seeks to provide both a consistent and the most complete computational description of the energetics and geometrical parameters of these radicals.

3.3 Computational Methods

Two computational approaches have been used in this paper. First, the geometries (Tables 3.1-3.3) and harmonic vibrational frequencies (Table 3.4) of all five species have been determined with the coupled-cluster singles and doubles (CCSD) model[19] augmented by the popular non-iterative, perturbative treatment of triple excitations, CCSD(T)[20], using the frozen core approximation and a series of three of Dunning's correlation-consistent basis sets: cc-pVXZ (X = D,T,Q)[21]. In order to gauge the effects of the inclusion of full triple excitations to the correlation treatment (and thereby measure the quality of the CCSD(T) description), optimizations at the coupled-cluster singles, doubles, and full triples level (CCSDT) with a cc-pVDZ basis set have also been performed for all structures except **2d**, which was an unmanageble calculation due to the lack of symmetry. The effects of core correlation have been determined by comparison of the aforementioned data to similar computations using the cc-pCVDZ[22] basis set, correlating all electrons.

Additionally, the doublet states have been examined with equation-of-motion coupled-cluster theory for ionization potentials (EOMIP-CC)[23-29] with the same range of basis sets. Here, the reference wavefunction is taken to be that resultant from double (instead of single) occupation of the SOMO $2a''$ orbital, and the ground state is constructed via excitations into a continuum orbital[30]. Such an approach, which generally helps circumvent problems that have limited the applicability of coupled-cluster methods to open-shell systems[31] (and particularly those possessing significant multi-reference character), has been used before for the ketenyl radical by Szalay, Fogarasi, and Nemes[15]. Thus, we add to this data by considering the effects of full (EOMIP-CCSDT) triple excitations and providing comparable data for both the hydroxyethynyl (**2d**) and oxiryl (**3d**) radicals.

3.4 RESULTS

Optimized structures at the EOMIP-CCSD/cc-pVQZ and CCSD(T)/cc-pVQZ levels for Isomers **1d**, **1qt**, and **1qc**; **2d**; and **3d** are given in Tables 3.1, 3.2, and 3.3, respectively. In order to estimate the effects of all triple excitations and core correlation on the coupled cluster wavefunctions, these tables also include extrapolated geometries derived via the approximation that the effects to internal coordinates with smaller basis sets (cc-pVDZ and cc-pCVDZ) may be taken as additive corrections to the cc-pVQZ values. Harmonic vibrational frequencies at the CCSD(T)/cc-pVTZ level are included in Table 3.4 while relative energies are presented in Table 3.5.

The data in Table 3.1 shows good agreement both between the methods used in this study and previous theoretical results for the doublet ketenyl radical (**1d**). The $\theta_{HC_1C_2}$ coordinate is seen to vary by nearly 6°. However, as noted by Szalay et al.[15], this coordinate is very soft, and little physical significance can be given to it, as there is easy interconversion between the two identical Renner-Teller split components.

The quartet states of the *trans*- and *cis*- ketenyl radicals (**1qt** and **1qc**) have both been determined to be minima, resting 64.4 and 57.1 kcal/mol higher than the doublet ketenyl radical (**1d**), respectively, at the CCSD(T)/cc-pVQZ level. Krisch and coworkers[7] have proposed these *trans*- and *cis*- isomers as the products formed in the lower recoil kinetic energy channel of their photofragment translational spectroscopy experiments. They have observed internal energies between 55 and 96.6 kcal/mol for the product of this channel, which appears entirely consistent with the relative energetics of these two isomers versus **1d**. That is, if the relative energy of one of these species with respect to the doublet ketenyl radical (**1d**) were substantially less than 55 kcal/mol, it could likely be ruled out as the product formed via this channel.

Despite the good agreement with past results for the ketenyl radical and its quartet homologs, we differ somewhat from the results of Yamaguchi et al.[17] for the hydroxyethynyl radical (**2d**). Namely, at all levels in the current work, we find this isomer's minima to be substantially non-planar while their previous work indicates C_s symmetry for the $\tilde{X}$ state. The lack of a CC extrapolation here is due to the fact

Table 3.1: Optimized and extrapolated structures for Isomers **1d**, **1qt**, and **1qc**, along with best previous theoretical structures. Bond distances are in Å, and bond angles are in degrees.

1d	r_{HC_1}	$r_{C_1C_2}$	r_{OC_2}	$\theta_{HC_1C_2}$	$\theta_{C_1C_2O}$
EOMIP-CCSD/cc-pVQZ	1.0677	1.2834	1.1677	138.27	170.48
CCSD(T)/cc-pVQZ	1.0731	1.3039	1.1712	132.20	168.95
EOMIP extrapolated[a]	1.0712	1.2983	1.1716	134.49	171.25
CC extrapolated[b]	1.0702	1.3082	1.1579	128.70	170.40
CCSD(T)/cc-pVTZ[c]	1.0660	1.2972	1.1728	134.6	169.4
1qt					
CCSD(T)/cc-pVQZ	1.0769	1.4371	1.2007	134.97	119.02
CC extrapolated[b]	1.0707	1.4400	1.1882	134.43	120.40
CISD/TZ2P[d]	1.073	1.453	1.180	133.6	120.6
1qc					
CCSD(T)/cc-pVQZ	1.0868	1.4410	1.1949	131.30	125.28
CC extrapolated[b]	1.0799	1.4463	1.1831	131.13	126.01
CISD/TZ2P[d]	1.078	1.456	1.176	130.7	126.5

[a] Determined via the relation (EOMIP-CCSD/cc-pVQZ) + (EOMIP-CCSDT/cc-pVDZ) - (EOMIP-CCSD/cc-pVDZ) + (EOMIP-CCSD/cc-pCVDZ) - (EOMIP-CCSD/cc-pVDZ)

[b] Determined via the relation (CCSD(T)/cc-pVQZ) + (CCSDT/cc-pVDZ) - (CCSD(T)/cc-pVDZ) + (CCSD(T)/cc-pCVDZ) - (CCSD(T)/cc-pVDZ)

[c] Reference 15, all electrons correlated.

[d] Reference 16, with frozen core and virtual approximation.

Table 3.2: Optimized and extrapolated structures for Isomer **2d**, along with best previous theoretical structure. Bond distances are in Å, and bond angles are in degrees.

	r_{HO}	r_{C_1O}	$r_{C_2C_1}$	θ_{C_1OH}	$\theta_{C_2C_1O}$	$\tau_{C_2C_1OH}$
EOMIP-CCSD/cc-pVQZ	0.9646	1.2855	1.2705	110.40	167.71	106.10
CCSD(T)/cc-pVQZ	0.9677	1.2885	1.2903	110.12	171.97	121.70
EOMIP extrapolated[a]	0.9662	1.2880	1.2853	110.23	168.36	108.68
CISD/TZ3P(2f,2d)[b]	0.9567	1.2762	1.2720	111.04	176.84	180.00

[a] Determined via the relation (EOMIP-CCSD/cc-pVQZ) + (EOMIP-CCSDT/cc-pVDZ) - (EOMIP-CCSD/cc-pVDZ) + (EOMIP-CCSD/cc-pCVDZ) - (EOMIP-CCSD/cc-pVDZ)

[b] Reference 17, determined to have C_s symmetry.

Table 3.3: Optimized and extrapolated structures for Isomer **3d**. Bond distances are in Å, and bond angles are in degrees.

	r_{HC_1}	$r_{C_1C_2}$	r_{OC_1}	θ_{HC_1O}	$\theta_{C_2C_1O}$
EOMIP-CCSD/cc-pVQZ	1.0725	1.3361	1.3326	130.08	72.59
CCSD(T)/cc-pVQZ	1.0771	1.3525	1.3216	129.67	75.09
EOMIP extrapolated[a]	1.0793	1.3581	1.3032	128.71	80.43
CC extrapolated[b]	1.0771	1.3557	1.3134	129.16	77.56

[a] Determined via the relation (EOMIP-CCSD/cc-pVQZ) + (EOMIP-CCSDT/cc-pVDZ) - (EOMIP-CCSD/cc-pVDZ) + (EOMIP-CCSD/cc-pCVDZ) - (EOMIP-CCSD/cc-pVDZ)

[b] Determined via the relation (CCSD(T)/cc-pVQZ) + (CCSDT/cc-pVDZ) - (CCSD(T)/cc-pVDZ) + (CCSD(T)/cc-pCVDZ) - (CCSD(T)/cc-pVDZ)

Table 3.4: Harmonic vibrational frequencies in cm^{-1} for the five isomers.

	1d	**1qt**	**1qc**	**2d**[a]	**3d**
ν_1 $(a^{'})$	3323	3264	3145	3724	3273
ν_2 $(a^{'})$	2079	1713	1772	1953	1542
ν_3 $(a^{'})$	1224	1096	1095	1274	1275
ν_4 $(a^{'})$	579	831	942	1049	1026
ν_5 $(a^{'})$	525	470	476	301	338
ν_6 $(a^{''})$	493	481	674	148	774

[a] All vibrational frequencies for **2d** are *a* modes by symmetry.

that an open-shell CCSDT optimization with even the modest cc-pVDZ basis set is unwieldy in C_1 symmetry and points to the preferability of the EOMIP technique, which is performed within a less computationally demanding closed-shell context.

As we were able to reproduce the results of Reference 17, in which structures were optimized with several basis sets at the SCF and CISD levels of theory, we conclude that the discrepancy is resultant from the less thorough inclusion of electron correlation in the CISD wavefunction as compared to the coupled cluster methods used here. It is important to note, however, that the torsional angle is quite floppy, and the overall energetics of the system are not skewed significantly by the relaxation from the C_s transition state structure to the C_1 minimum. Thus, the readily apparent difference in τ of over 15° upon inspection of Table 3.2 is not crucial.

The doublet oxiryl radical **3d** is unique amongst the isomers in this paper in having a bridged structure. Previous theoretical work in the literature appears to be nonexistent although unpublished energetics using DFT have been recently made

Table 3.5: Total energies in hartrees and relative energies in kcal/mol (zero-point vibrational energy corrected values obtained using the CCSD(T)/cc-pVTZ harmonic frequencies of Table 3.4 in parentheses) for the five isomers.

Isomer	EOMIP-CCSD cc-pVQZ	ΔE	CCSD(T) cc-pVQZ	ΔE
1d	-151.688473	0.0 (0.0)	-151.724635	0.0 (0.0)
1qt			-151.622080	64.4 (63.8)
1qc			-151.633676	57.1 (56.9)
2d	-151.601629	54.5 (54.8)	-151.638277	54.2 (54.5)
3d	-151.607361	50.9 (50.9)	-151.640923	52.5 (52.5)

available to the current authors[18]. Our work is consistent with that of Durant, placing the ring structure (**3d**) just over 50 kcal/mol above the ketenyl radical. Similarly, the EOMIP and traditional coupled cluster methods are in mutual agreement. While there is a noticable discrepancy for the C_2C_1O bond angle (the ordering of which switches upon inclusion of triples, indicating sensitivity with respect to added correlation), this is not predicted to markedly effect the energetics.

In conclusion, we have performed the most exhaustive study of the low-lying isomers of HC_2O, using up to the EOMIP-CCSD and CCSD(T) levels with the cc-pVQZ basis set, followed by a qualitative extrapolation in order to determine the effects of both triple excitations and core correlation on the wavefunction. Structures **1qt**, **1qc**, **2d**, and **3d** are all found to lie between 50 and 70 kcal/mol above the energetically most favored doublet ketenyl radical **1d**.

3.5 Acknowledgements

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Chapter 4

Use of $2h$ and $3h-p$-like Coupled-Cluster Tamm-Dancoff Approaches for the Equilibrium Properties of Ozone[1]

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4.1 Abstract

Equation-of-motion coupled cluster theory in a $2h$ and $3h - p$-like TDA approach has been utilized to determine properties of the ground state of ozone (O_3). Many of the values produced with this scheme are better than those obtained with other approaches with similar computational scaling properties.

4.2 Introduction

The amount of effort afforded to the determination of the ground state properties of O_3 via *ab initio* methods [1-14] is not surprising. Its multiconfigurational ground state makes ozone an ideal and challenging candidate for testing methods, especially those which treat correlation based on a zeroth-order single reference Slater determinant. However, the size of the system necessitates comparison directly to experiment [15] rather than to values obtained in full configuration interaction calculations.

Much of the earlier work on this system employed multi-reference methods, the results of which are far from encouraging. MR-CI predicts both an incorrect ordering and an overestimation by more than 100 cm^{-1} of the two stretching modes in comparison to experiment [1] while CASPT2 offers only modest improvements [8]. Recent applications of multi-reference coupled cluster schemes are similarly disappointing. One such work [13], using a Brillouin-Wigner scheme corrected for size-consistency errors yields ground state properties with no better accuracy than the aforementioned ones and an unphysical asymmetric stretching frequency of 1505 cm^{-1} (Expt. 1089 cm^{-1}).

In this context, considerable computational effort (up to partial inclusion of fourfold excitations through a non-iterative treatment of the T_4 operator in the coupled cluster expansion and the use of arguments for the applicability of taking basis set effects as additive corrections) has allowed the Gainesville group to come close to experimental values using single-reference coupled cluster methods [2, 4, 7, 10, 12]. However, at least partial inclusion of quadruple excitations is needed [12], and the least computationally intensive method that is seen to be capable of quantitatively describing the ground state correctly has steps that scale as n^8 and are iterative [16].

Linear response coupled cluster theory [17] has been shown to be quite useful in the study of radicals via application of EOMIP (equation-of-motion theory for ionization potentials) to the corresponding closed shell anion [18, 19, 20, 21]. However, a related scheme (in which two, rather than one, electrons are removed from the reference) can potentially be used for multireference cases in which a singlet state is qualitatively described by two Slater determinants differing by a double excitation. Such an approach is conceptually simliar to the DIP-STEOM approach of Nooijen and Bartlett [14], except that it is based on just one rather than three similarity transformations of the electronic Hamiltonian. Thus, this simpler method, which has also been explored by Nooijen to some extent [22], is expected to be somewhat less accurate than DIP-STEOM although it is much more straightforward to apply in a black-box fashion.

It is the aim of this paper to explore how well the above mentioned approach – which is essentially a $2h$ and $3h-p$-type coupled-cluster based Tamm-Dancoff approximation (here called EOMDIP) performs for the ground state of ozone and, by extrapolation, its suitability for treating other multireference systems that have the same qualitative features as ozone.

4.3 COMPUTATIONAL METHODS

The reference state for determination of the molecular orbitals and amplitudes for the similarity transformation is the ozone double anion [23]. This state differs from the neutral by double occupation of the low-lying b_2 orbital. From this reference, the ground state neutral properties are then obtained with the EOMDIP procedures mentioned in the preceding section. In this work, we have carried out the calculations with an EOM-CC excitation energy [24-27] code together with a continuum orbital (defined as a single *s*-type function of very low orbital exponent [28]), selecting only those final states which involve excitation of two electrons to the continuum orbital [29].

Calculations were performed using the series of three Dunning correlation-consistent basis sets (cc-pVXZ; X = D, T, and Q) [30] augmented by a single continuum orbital. For O_3, this corresponds to 43, 91, and 166 basis functions, respectively. Additionally, effects of core correlation were assessed via comparison of properties at the CCSD level with the cc-pCVXZ (X = D, T) basis sets [31].

Optimizations and frequencies at the EOMDIP-CCSD level utilized analytic first derivative techniques while those at the EOMDIP-CCSDT level (which corresponds to a CC-based $3h$-p TDA) were obtained from numerical differentiation procedures. All electrons were included in the correlation treatment, except where noted by the frozen core approximation for the most demanding compuations at the EOMDIP-CCSDT level. All calculations were performed with a local version of the ACESII program system [32].

4.4 Results and Discussion

Table 4.1 details the results of this study while Table 4.2 highlights some previous theoretically and experimentally determined properties for the ground state of ozone. From inspection of Table 4.1, it is apparent that core correlation has only a small effect on the geometry of this system; equilibrium bond distances and angles calculated at the EOMDIP-CCSD/cc-pVDZ and EOMDIP-CCSD/cc-pVTZ levels do not show significant differences with respect to optimized geometries obtained with

Table 4.1: Structure and vibrational frequencies of O_3 via the EOMDIP approach

Level	Basis Set	r_e	θ	ω_1	ω_2	ω_3
EOMDIP-CCSD	cc-pVDZ	1.298	114.4	1057	709	1061
EOMDIP-CCSD	cc-pVTZ	1.282	115.2	1078	730	1132
EOMDIP-CCSD	cc-pVQZ	1.273	115.8	1080	745	1166
EOMDIP-CCSD[a]	cc-pVDZ	1.298	114.4	1057	708	1061
EOMDIP-CCSD	cc-pCVDZ	1.297	114.4	1058	710	1062
EOMDIP-CCSD[a]	cc-pVTZ	1.287	115.2	1069	722	1115
EOMDIP-CCSD	cc-pCVTZ	1.284	115.2	1074	726	1124
EOMDIP-CCSDT	cc-pVDZ	1.279	115.9	1125	720	1149
EOMDIP-CCSDT[a]	cc-pVDZ	1.280	115.9	1123	719	1148
EOMDIP-CCSDT[a]	cc-pVTZ	1.275	116.1	1139	724	1181

[a] Denotes use of the frozen core approximation for the three oxygen 1s type orbitals. Bond lengths are in Ångstroms, bond angles are in degrees, and harmonic vibrational frequencies are in wavenumbers (cm^{-1}).

either the frozen core approximation or the corresponding cc-pCVXZ basis. Therefore, we use the frozen core approximation for the three oxygen 1s-like orbitals when considering the effects of triple excitations.

Optimized structures obtained here at the EOMDIP-CCSD/cc-pVQZ level compare favorably against any previous theoretical result. However, as has been noted by the extensive work of the Gainesville group, the effects of correlation beyond the singles and doubles level are essential in the treatment of this system with the standard coupled cluster heirarchy. As may be seen in Table 4.2, inclusion of triple excitations acts to elongate r_e by more than two hundredths of an Ångstrom while the increase due to a non-iterative inclusion of quadruples increases r_e by another 0.005 Å.

Table 4.2: Previously determined properties of O_3

Level	Basis Set	r_e	θ	ω_1	ω_2	ω_3
CCSD[a]	cc-pVTZ	1.250	117.6	1278	763	1266
CCSD(T)[a]	cc-pVTZ	1.275	116.9	1153	716	1054
CCSDT[a]	cc-pVTZ	1.274	116.8	1163	717	1117
CCSDT(Q_f)[b]	cc-pVTZ	1.279	116.6	1133	709	1112
2R CISD[c]	TZ2P	1.252	116.7	1242	770	1353
CASPT2-N[d]	ANO	1.285	116.8	1088	691	997
2R BWCCSD[e]	cc-pVTZ	1.280	116.8	1095	703	1505
Expt.[f]		1.272	116.8	1135	716	1089

[a] Ref. 10
[b] Ref. 12
[c] Ref. 1
[d] Ref. 8
[e] Ref. 13
[f] Ref. 15

Bond lengths are in Ångstroms, bond angles are in degrees, and harmonic vibrational frequencies are in wavenumbers (cm^{-1}).

The incremental triples change (CCSDT - CCSD difference) with the same basis set determined in this work is not only much smaller (-0.007 Å), but also has the opposite sign from that associated with traditional coupled-cluster calculations. This is associated with the multireference nature of the present approach, in which the effects of antibonding orbitals (arising here from the doubly-occupied b_2 π orbital) are exaggerated and dynamical correlation is needed to provide balance. Similar phenomena are well-known and seen in comparing MR-CI data with CASSCF results. In addition, the magnitude of the triples correction decreases significantly with increasing size of the basis. A similar trend is evident in θ_e.

Correlation and basis set effects on the harmonic vibrational frequencies appear to be more pronounced. Although the best results obtained here (EOMDIP-CCSDT) are within 10 cm^{-1} for both of the totally symmetric modes, the asymmetric stretch (which presents the greatest challenge to theory) is nearly 100 cm^{-1} above the result obtained from a Dunham expansion based on the experimentally observed levels. It is interesting to note in the present context that traditional CCSDT both with (CCSDT(Q_f)) and without a correction for “factorized” quadruple excitations gives a value in much better agreement with experiment. Presumably, this is associated with the more complete treatment of dynamic correlation in traditional CC methods relative to the EOMDIP method explored here, rather than to the non-dynamical effects that can make it difficult to get a physically reasonable and qualitatively correct prediction for ω_3.

Given that the EOMDIP-CCSD method gives quite good results for ozone, in the sense that the effects of residual final state dynamic electron correlation obtained with EOMDIP-CCSDT are not dramatic, this appears to be a good method for getting reasonable estimates for the properties of multireference cases known as biradicals, in which there are substantial contributions to the wavefunction due to determinants that differ by a double excitation. Thus, the main advantages of the present scheme are two-fold:

1) Results from n^6 scaling methods (EOMDIP-CCSD, here) with an appropriately sized basis set perform nearly as well as previously reported n^8 methods using a traditional approach, and

2) Triples corrections are smaller than via the standard coupled cluster heirarchy for biradical systems, offering faster convergence of molecular properties.

4.5 ACKNOWLEDGMENTS

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CHAPTER 5

A COMPARISON OF EXCITED STATE PROPERTIES FOR ITERATIVE APPROXIMATE TRIPLES LINEAR RESPONSE COUPLED CLUSTER METHODS[1]

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[1] Kurt W. Sattelmeyer, John F. Stanton, Jeppe Olsen, Jürgen Gauss. 2001. Chemical Physics Letters. 347:499-504. Reprinted per conditions stated in the Transfer of Copyright Agreement with Elsevier Science B.V.

5.1 ABSTRACT

A computational study of the potential energy curves of the $^1\Pi$ state of BH, $^1\Pi$ state of CH^+, $^1\Sigma_u$ and $^1\Pi_u$ states of C_2, $^1\Pi$ state of CO, and $^1\Pi_g$ and $^1\Sigma_u^-$ states of N_2 is carried out with the CC3 and CCSDT-3 corrections to EOMEE-CCSD. Good agreement in structure, vibrational frequencies, and excitation energies of these iterative triples-corrected methods with respect to experiment is found for most of these examples. However, deficiencies in the approximate treatment of triples is evident for BH and CH^+.

5.2 INTRODUCTION

Coupled cluster linear response theory (CCLRT) [1, 2], which in certain cases is equivalent to the equation-of-motion coupled cluster (EOM-CC) [3, 4] approach, has emerged in the last decade as a powerful tool for treating electronically excited states. In the singles and doubles approximation (CCSDLRT, or EOM-CCSD), excitation energies are usually within 0.5 eV and nearly always above (exact) results obtained with full configuration interaction (FCI) for states of predominantly single replacement character [5, 6]. Further improvement in accuracy for these states requires some treatment of triple excitation effects; to this end, several non-iterative and iterative approaches have been suggested [7, 8, 9, 10, 11]. All of these have been touted to give more reliable transition energies than CCSD-based calculations although it is our experience that the iterative methods (which are proper linear response methods, unlike their noniterative counterparts) based on the CC3 [12] and CCSDT-3 [13] models are more robust and consistently accurate. Regrettably, however, very little (an exception being recent work on N_2 [15]) has been done to calibrate the accuracy of these approaches for calculating excited state properties, largely because analytic derivatives have not been developed for these methods.

In this letter, CCLRT calculations based on the CCSD, CC3, and CCSDT-3 treatments of electron correlation are presented for selected diatomic molecules. Geometry optimizations have been carried out for the ground and certain excited states for all species using the hierarchy of correlation-consistent basis sets [14]. Bond lengths, harmonic vibrational frequencies, and adiabatic excitation energies (T_e) obtained with the largest basis sets are compared to experimental values, a means of comparison that is necessitated by the dearth of FCI results for these excited state properties. Although restricted to diatomic examples, this work should provide some idea of how accurately excited state properties can be calculated with the most sophisticated CCLRT techniques that have been implemented.

5.3 Methods

An approach that can be used to calculate excitation energies for any coupled-cluster (CC) method that can be precisely associated with a particular wavefunction parametrization [thereby excluding the popular CCSD(T) method] is to diagonalize the matrix that appears in the equation for the derivative of the cluster amplitudes (T) with respect to the generic perturbation χ, viz.

$$\frac{\partial T}{\partial \chi} = A^{-1} b^{\chi}, \tag{5.1}$$

where the perturbation-dependent inhomogeneous term b^{χ} is of no consequence for the present discussion. For methods such as CCSD, CCSDT, etc., unperturbed amplitudes T are obtained by solving the coupled system of nonlinear equations

$$< \Phi | \bar{H} | 0 >= 0, \tag{5.2}$$

where Φ are singly and doubly excited determinants in the CC singles and doubles method (CCSD), singly, doubly, and triply excited determinants in the CC singles, doubles, and triples approach (CCSDT), etc. and $\bar{H}$ is the similarity transformed

Hamiltonian, e^{-T}He^{T}. For methods such as CCSD, CCSDT, CCSDTQ, etc., **A** is simply equal to $\bar{H}$, but it has a more complicated definition for methods such as CC3 and CCSDT-3 in which the triples amplitude equation excludes some of the terms arising from $< T|\bar{H}|0 >$ that are included in the full CCSDT approach. For CCSDT-3 and CC3, subblocks of the non-Hermitian matrix **A** are given by

$$\mathbf{A} = \begin{array}{c} \\ < S| \\ < D| \\ < T| \end{array} \begin{array}{c} \begin{array}{ccc} |S> & |D> & |T> \end{array} \\ \left(\begin{array}{ccc} (e^{-T}He^{T})_{SS} & (e^{-T}He^{T})_{SD} & (W)_{ST} \\ (e^{-T}He^{T}+WT_3)_{DS} & (e^{-T}He^{T})_{DD} & (W+[WT_1])_{DT} \\ (e^{-T}He^{T}-\xi)_{TS} & (e^{-T}He^{T}-\Omega)_{TD} & f_{TT} \end{array} \right) \end{array}$$

where T is the set of single and double excitation operators, and the designation $()_{ij}$ denotes that the parenthetical quantity projects onto bra and ket determinants of excitation level i and j, respectively. The normal ordered Hamiltonian H$_N$ is decomposed as usual

$$H_N = f + W, \tag{5.3}$$

where f is the Fock operator; $\xi = \Omega = 0$ for CCSDT-3 while $\xi = (\frac{1}{2}WT_2^2)_c$ and $\Omega = (WT_2^2 + WT_2^2T_1)_c$ for CC3. In the preceding, the subscript c means that only those terms having a connected diagrammatic representation are included.

Eigenvalues of **A** are obtained by the eigenvalue-dependent partitioning scheme discussed in Ref. 8. Our implementation uses a modified Davidson algorithm designed so that the most recent approximation to the eigenvector of interest is added to the iterative subspace after each iteration. This guarantees that the correspondingeigenvalue of the subspace representation of **A** converges precisely to an element of the spectrum of the operator projected onto the space of singly, doubly, and triply excited determinants.

It should be noted that the CC3 and CCSDT-3 methods are rather similar. Mathematically, the only difference is that the triples equation contains the contributions $< T|\frac{1}{2}WT_2^2 + \frac{1}{2}WT_2^2T_1|0 >$ in the latter, but not in the former. Formal justification for CCSDT-3 is that it is the most theoretically complete method that avoids the expensive (N^8 scaling) terms in the triples equation that involve T_3 itself. CC3 can be rationalized from the viewpoint of response theory; it treats T_1, T_2, and T_3 as zeroth, first, and second-order quantities, respectively, and retains all terms in the triples equation that are overall second order in the perturbation W. Although T_1 is a second-order quantity in the ground state description, this reasoning is justified since the differentiated T_1 amplitudes correspond to elements of the single excitation vector in response theory, and these are of greatest importance in describing most excited states of chemical interest.

5.4 Results and Discussion

Properties of diatomic molecules obtained in CCLRT calculations at the CCSD, CC3, and CCSDT-3 levels with the hierarchy of correlation consistent basis sets (cc-pVXZ; X = D, T, Q, and 5) [14] are presented in Tables 5.1-5.7 for the $^1\Pi$ state of BH, $^1\Pi$ state of CH^+, $^1\Sigma_u$ and $^1\Pi_u$ states of C_2, $^1\Pi$ state of CO, and $^1\Pi_g$ and $^1\Sigma_u^-$ states of N_2, respectively, where the lowest state of the designated symmetry is chosen in each case. Inclusion of Rydberg functions were seen to have very little effect and are therefore excluded. Additionally, EOM-CCSDT, EOM-CCSDTQ, and full CI r_e and ω_e values are included for the BH and CH^+ systems; these numbers were calculated using the LUCIA program of Olsen and coworkers [16]. The coupled cluster calculations with LUCIA used the algorithms described in [17]. Also listed are the corresponding experimentally inferred values of r_e, ω_e, and T_e, which are taken from the compilation of Huber and Herzberg [18].

All of the electronically excited states considered in this work are of dominant single-excitation character. To the extent that the largest (cc-pV5Z) basis set is appropriate for comparison with experiment, the CCSD adiabatic excitation energies

Table 5.1: Equilibrium geometries (in Å), harmonic vibrational frequencies (in cm^{-1}), and adiabatic exictation energies (in cm^{-1}) for the $^1\Pi$ State of BH

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
CCSD				
r_e	1.2500	1.2144	1.2172	1.2104
ω_e	2207	2347	2347	2399
T_e	24555	23727	23459	23358
CC3				
r_e	1.2525	1.2170	1.2198	1.2128
ω_e	2179	2317	2319	2371
T_e	24775	23595	22751	23216
CCSDT-3				
r_e	1.2512	1.2167	1.2195	1.2125
ω_e	2191	2320	2322	2374
T_e	24720	23619	23344	23242
CCSDT				
r_e	1.2558			
ω_e	2143			
CCSDTQ				
r_e	1.2559			
ω_e	2141			
Full CI				
r_e	1.2559			
ω_e	2141			
Experiment				
r_e	1.219			
ω_e	2251			
T_e	23136			

seem to exhibit a characteristic overestimation of 0.1-0.5 eV (800-4000 cm^{-1}) in all cases. All errors are reduced significantly when triple excitations are included at either the CC3 or CCSDT-3 levels. With the largest basis set, *all* T_e values fall within 0.07 eV of the experimental values. This finding is largely consistent with, and supportive of, the occasionally-mentioned claim that these methods are typically accurate to 0.1 eV for excitation processes of dominant single-replacement character [19].

The principal purpose of the present study, however, is to assess the potential accuracy of CC3 and CCSDT-3 excitation energy methods for properties other than the energy, specifically molecular geometries and force constants. That the improvement in these properties (as characterized by values of r_e and ω_e for the set of diatomics studied here) achieved when triple excitation effects are treated at these levels of theory is comparable to that in the adiabatic excitation energies is evident upon inspection of the tables.

For the diatomics studied, CC3 and CCSDT-3 methods usually give equilibrium distances and frequencies within .005 Å and 50 cm^{-1} of experiment, respectively. Indeed, in many cases, such as the EOM-CCSDT-3/cc-pV5Z r_e and the EOM-CC3/cc-pV5Z ω_e for the $^1\Pi_u$ state of C_2, the theoretically determined values are in essentially perfect agreement with those inferred from experiment.

The only significant deviation from the behavior described above occurs for the harmonic vibrational frequency of the $^1\Pi$ state of BH, which is perhaps not so well established experimentally because this state is believed to exhibit a double minimum potential curve and the existing Dunham expansion was fit to only the minimum number of levels [20, 21]. Taking the FCI correction based on the cc-pVDZ data and applying it to the large basis set results does not adequately resolve this discrepancy; such an approach would still lead to a difference of approximately 70 wavenumbers. Surprisingly, the bond distance of the isoelectronic $^1\Pi$ state of

Table 5.2: Equilibrium geometries (in Å), harmonic vibrational frequencies (in cm^{-1}), and adiabatic exictation energies (in cm^{-1}) for the $^1\Pi$ State of CH^+

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
CCSD				
r_e	1.2633	1.2203	1.2235	1.2221
ω_e	1827	1938	1955	1938
T_e	24934	24789	24520	24471
CC3				
r_e	1.2703	1.2262	1.2293	1.2281
ω_e	1765	1883	1901	1882
T_e	24719	24598	24341	24299
CCSDT-3				
r_e	1.2698	1.2257	1.2288	1.2275
ω_e	1769	1888	1905	1887
T_e	24729	24620	24368	24327
CCSDT				
r_e	1.2743			
ω_e	1730			
CCSDTQ				
r_e	1.2749			
ω_e	1724			
Full CI				
r_e	1.2749			
ω_e	1724			
Experiment				
r_e	1.234			
ω_e	1865			
T_e	24111			

Table 5.3: Equilibrium geometries (in Å), harmonic vibrational frequencies (in cm^{-1}), and adiabatic exictation energies (in cm^{-1}) for the $^1\Sigma_u$ State of C_2

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
CCSD				
r_e	1.2905	1.2588	1.2541	1.2518
ω_e	1764	1805	1806	1814
T_e	47050	44934	44400	44211
CC3				
r_e	1.2750	1.2437	1.2394	1.2373
ω_e	1769	1843	1846	1855
T_e	45704	43529	43084	42924
CCSDT-3				
r_e	1.2800	1.2483	1.2440	1.2419
ω_e	1744	1811	1813	1822
T_e	46017	43963	43544	43401
Experiment				
r_e	1.238			
ω_e	1830			
T_e	43259			

Table 5.4: Equilibrium geometries (in Å), harmonic vibrational frequencies (in cm^{-1}), and adiabatic exictation energies (in cm^{-1}) for the $^1\Pi_u$ State of C_2

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
CCSD				
r_e	1.3481	1.3203	1.3175	1.3154
ω_e	1571	1632	1619	1626
T_e	9360	8952	8772	8747
CC3				
r_e	1.3522	1.3258	1.3238	1.3213
ω_e	1563	1632	1601	1609
T_e	8075	7924	7845	7865
CCSDT-3				
r_e	1.3490	1.3225	1.3200	1.3180
ω_e	1574	1617	1615	1621
T_e	8268	8073	7999	7902
Experiment				
r_e	1.318			
ω_e	1608			
T_e	8391			

Table 5.5: Equilibrium geometries (in Å), harmonic vibrational frequencies (in cm^{-1}), and adiabatic exictation energies (in cm^{-1}) for the $^1\Pi$ State of CO

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
CCSD				
r_e	1.2478	1.2297	1.2231	1.2196
ω_e	1554	1594	1605	1606
T_e	67073	66935	66858	66812
CC3				
r_e	1.2711	1.2522	1.2456	1.2421
ω_e	1378	1427	1439	1439
T_e	65316	65127	65001	64935
CCSDT-3				
r_e	1.2657	1.2472	1.2408	1.2374
ω_e	1425	1470	1481	1481
T_e	65629	65459	65342	65280
Experiment				
r_e	1.235			
ω_e	1518			
T_e	65076			

Table 5.6: Equilibrium geometries (in Å), harmonic vibrational frequencies (in cm^{-1}), and adiabatic exictation energies (in cm^{-1}) for the $^1\Pi_g$ State of N_2

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
CCSD				
r_e	1.2323	1.2155	1.2121	1.2102
ω_e	1760	1769	1775	1775
T_e	70494	71486	71517	71557
CC3				
r_e	1.2408	1.2252	1.2221	1.2204
ω_e	1685	1685	1690	1689
T_e	68736	69576	69529	69540
CCSDT-3				
r_e	1.2376	1.2219	1.2188	1.2171
ω_e	1717	1717	1721	1721
T_e	68945	69829	69791	69806
Experiment				
r_e	1.220			
ω_e	1694			
T_e	69283			

Table 5.7: Equilibrium geometries (in Å), harmonic vibrational frequencies (in cm^{-1}), and adiabatic exictation energies (in cm^{-1}) for the $^1\Sigma_u^-$ State of N_2

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
CCSD				
r_e	1.2852	1.2685	1.2663	1.2650
ω_e	1570	1593	1597	1597
T_e	71636	71565	71379	71390
CC3				
r_e	1.2964	1.2811	1.2793	1.2782
ω_e	1480	1496	1496	1497
T_e	68091	68354	68193	68211
CCSDT-3				
r_e	1.2892	1.2743	1.2726	1.2715
ω_e	1546	1555	1555	1555
T_e	68522	68765	68606	68626
Experiment				
r_e	1.276			
ω_e	1530			
T_e	68152			

CH^+ does not agree well with experiment while ω_e is reasonable with respect to the aforementioned error bounds. The FCI correction results in a much smaller difference between the bond distances and a comparable difference for ω_e. Another interesting feature of these two states evident from inspection of Tables 5.1 and 5.2 is that while the iterative triples methods show sigificant deviations (approximately .005 Å and 50 cm^{-1}) from the full CI limit, EOM-CCSDT is nearly completely converged. Although one would predict that the effect of quadruple and higher excitations on a six electron system to be small, it is somewhat surprising (and disappointing) that the approximate triples methods do not better approximate EOM-CCSDT in these examples.

As was mentioned earlier, the N_2 molecule has previously been studied in Ref. 15 with CCLRT and FCI using a cc-pVDZ basis set with the nitrogen 1s electrons frozen. The small differences between their CC3/cc-pVDZ results and ours (less than .0008 Ångstroms and 3 cm^{-1} in both cases for the excited state bond distances and harmonic vibrational frequencies) indicate that the frozen core assumption makes little difference here. While the cc-pVDZ bond distances using either CC3 or CCSDT-3 differ from experiment by .01-.02 Ångstroms, ω_e is much closer. For example, even though the FCI/cc-pVDZ bond distance of Ref. 15 differs by more than .02 Ångstroms from the experimental value, the harmonic vibrational frequency varies by less than 10 cm^{-1}. The results in this paper show only nominal differences for the two states of N_2 studied between the ω_e values with the cc-pVDZ and cc-pV5Z basis sets and CC3 or CCSDT-3 while the bond distance changes significantly. This feature is not preserved in the other systems, as ω_e changes by much larger amounts, and indicates cancellations associated with the reproduction of experimental frequencies for N_2 using a smallish basis set.

In all cases, the CC3 and CCSDT-3 methods appear to improve upon the EOM-CCSD results. Although it is difficult to make a general assessment of the amount of improvement associated with the upgrade from EOM-CCSD to the triples-corrected methods, the results we have obtained indicate that it is not insignificant. Thus, EOM-CCSDT-3 and EOM-CC3 are seen to offer improvement versus EOM-CCSD for the theoretical determination of excited state molecular properties and are therefore recommended in order to achieve high levels of accuracy.

5.5 Acknowledgements

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CHAPTER 6

THE GLOBAL MINIMUM STRUCTURE OF SiC_3: THE CONTROVERSY CONTINUES[1]

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[1] Kurt W. Sattelmeyer, Henry F. Schaefer, John F. Stanton. 2002. Journal of Chemical Physics. 116:9151-9153. Reprinted per conditions stated in the Transfer of Copyright Agreement with the American Institue of Physics.

6.1 ABSTRACT

The linear triplet structure of SiC_3 (with terminal Si) has been investigated using coupled cluster methods, including a perturbative treatment of triple excitations, and Dunning's correlation-consistent polarized core-valence quadrupole zeta basis set (CCSD(T)/cc-pCVQZ). Based on the demonstrated convergence with respect to correlation and the large basis set employed, this triplet isomer appears to be energetically less stable than the two ring isomers, which have either a C-C (**2s**) or a Si-C (**3s**) transannular bond, by 7.5 and 1.3 kcal/mole, respectively.

6.2 INTRODUCTION

Due to the early observation of the absorption spectrum of SiC_2[1], considerable effort has been given to the detection of silicon-containing carbon clusters in the interstellar medium (ISM). Indeed, the presence of SiC and SiC_2, for example, in high temperature silicon carbide vapors[2], points to a rich potential for chemistry. The next largest such cluster, SiC_3, is of special interest due to its similarity to the theoretically well-studied[3-17], yet spectroscopically elusive, C_4. As in C_4, one can imagine several competing structures, the energetically most favorable of which are the linear triplet (**1t**) (Fig. 1) and singlet rings with either a C-C (**2s**) or a Si-C (**3s**) transannular bond.

The first high-level theoretical attempt to determine the global minimum for SiC_3 was the work of Alberts, Grev, and Schaefer[18]. They used up to CISD+Q with a TZ2P basis set, finding structure **2s** to be more than 4 kcal/mole lower in energy than the other two isomers. However, the authors suggest that a better theoretical treatment, both with regard to correlation and basis set effects, would be necessary to provide a definitive ordering.

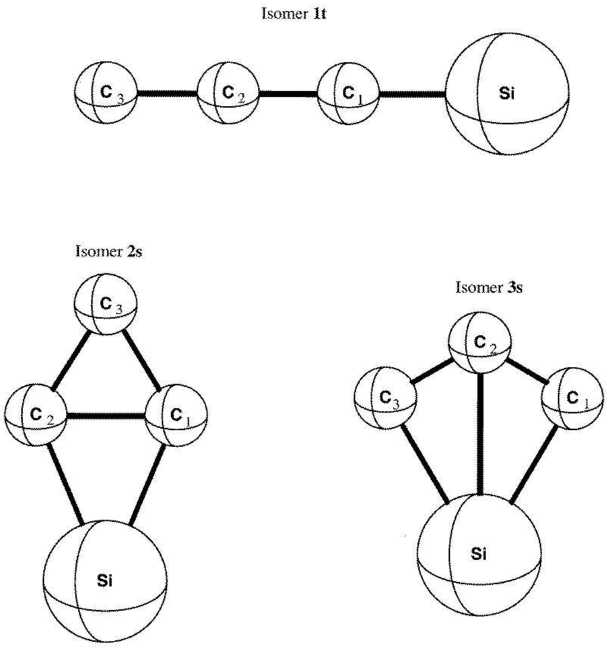

Figure 6.1: Structures of the three lowest lying isomers of SiC_3. Structure **1t** is linear while structures **2s** and **3s** have C_{2v} symmetry. Bond lengths are reported in Table 6.1.

More recently, the Fourier transform microwave spectra of the two cyclic isomers of SiC_3 were detected by the millimeter-wave group at Harvard [19, 20]. The first of these, **2s**, was found quickly thereafter in the interstellar medium (ISM) [21], making it the only four-membered ring so far observed in space. Not surprisingly, this finding has led to further study of the system.

A high-level *ab initio* study by Stanton, Gauss, and Christiansen[22] of the two ring isomers gives a similar qualitative and quantitative landscape as that of Alberts *et al.* for these two structures. At the highest level employed (CCSD(T)/cc-pCVQZ),

2s was found to be lower in energy than **3s** by 6.0 kcal/mole. A least squares fit of the aforementioned experimental geometry based on B_e and C_e constants obtained from CCSD(T)/cc-pVTZ quadratic and cubic force fields was found to agree with the CCSD(T)/cc-pCVQZ geometry quite well: no bond distances differ by more than 0.003 Å.

Concurrently, Rintelman and Gordon[23] found the linear triplet isomer to be the global minimum, with the **2s** and **3s** structures being 7.4 and 4.3 and kcal/mole less favorable, respectively. However, these energies were determined at MCSCF geometries, and the use of a second order perturbation multiconfigurational method (MCQDPT) with an active space consisting of 12 electrons in 11 orbitals (12 electrons in 10 orbitals for the linear case) showed a lack of basis set convergence (changes of up to over 3 kcal/mole) for the largest basis set, which was only aug-cc-pVDZ. Although experimental work by Lineberger *et al.*[24] appears to have shown the photoelectron transition of the linear anion to Isomer **1t** based on a comparison of calculated vibrational frequencies and electron affinities, no direct evidence of the ordering of the neutral states is offered.

It is the aim of this paper to use high-level coupled cluster theory with large basis sets for the linear triplet isomer to assign its relative energetic position definitively.

6.3 Computational Methods

The present optimized structure for the linear triplet isomer was determined at the CCSD(T) [25] level of theory using a cc-pCVQZ basis set[26], which for this system consists of 361 contracted Gaussian functions. An ROHF reference function was used, and all electrons were included in the correlation treatment. Reported relative energy values include a zero-point vibrational correction calculated at the CCSD(T)/cc-pVTZ level.

Due to the size of the system, gradients were computed numerically. All computations were performed with a local version of the ACESII program system [27].

6.4 Results and Discussion

Optimized geometries determined in this work are reported in Table 6.1, along with *ab initio* structures from Reference 22 and Reference 23 and those from least-squares fits to moments of inertia derived from empirical rotational constants reported in Reference 22. If one adopts the reasoning of Stanton *et al.* that the very good agreement in the two sets of quantities presented in Reference 22 for the ring isomers allows their structures to be determined with error bars no larger than ± 0.003 Å, it can only be concluded that likely error bars from Reference 23 would be at least *an order of magnitude* larger. It is our opinion that this is a valid deduction. Although some parameters from Reference 23 are quite close to the recommended values of Reference 22, others can vary by as much as 0.04 Å, such as the external Si-C bond length for **3s**. In this context, the structure of Isomer **1t** shows similar trends. As in **3s**, the FORS-MCSCF/6-31G(d) level tends to overestimate the Si-C bond length, in part due to the lack of tight d functions on Si, while providing more reasonable C-C distances.

Rintelman and Gordon[23] argue that multiconfigurational effects necessitate the use of a multi-reference scheme. Although this may be essential in some of the higher-lying isomers (such as the linear singlet, which includes important contributions from both the $\pi_{xz}^2 + \pi_{yz}^0$ and the $\pi_{xz}^0 + \pi_{yz}^2$ occupations), the species in question here show no such problem. As is the case for the closed-shell rings, the linear triplet is reasonably well-described by a single Slater determinant. The largest single and double excitation amplitudes at the CCSD level are 0.05 and 0.07, respectively. Further support for the quality of the calculations comes from the small difference found between

Table 6.1: Comparison of the r_e Structures of the Three Low-lying Isomers of SiC_3 Resultant from *Ab Initio* Methods and a Least-squares Fit of Experimental Rotational Constants

	Isomer **1t**	
	CCSD(T)/ cc-pCVQZ[a]	MCSCF/ 6-31G(d)[b]
$r_{\mathrm{Si-C_1}}$	1.7249	1.74
$r_{\mathrm{C_1-C_2}}$	1.2899	1.29
$r_{\mathrm{C_2-C_3}}$	1.3062	1.31

		Isomer **2s**	
	CCSD(T)/ cc-pCVQZ[d]	MCSCF/ 6-31G(d)[b]	Emp.[c]
$r_{\mathrm{Si-C_1}}$	1.8290	1.83	1.8282
$r_{\mathrm{C_1-C_2}}$	1.4342	1.43	1.4328
$r_{\mathrm{C_1-C_3}}$	1.4830	1.50	1.4831

		Isomer **3s**	
	CCSD(T)/ cc-pCVQZ[d]	MCSCF/ 6-31G(d)[b]	Emp.[c]
$r_{\mathrm{Si-C_1}}$	2.0213	2.06	2.0185
$r_{\mathrm{Si-C_2}}$	1.8857	1.89	1.8864
$r_{\mathrm{C_1-C_2}}$	1.3431	1.32	1.3426

[a] This work.

[b] Reference 23, Rintleman and Gordon.

[c] An empirical fit to experimental rotational constants from Reference 22.

[d] Reference 22, Stanton, Gauss, and Christiansen.

Table 6.2: Absolute Energies of SiC_3 Isomers: Optimized geometries were determined at the ROHF-CCSD(T)/cc-pCVQZ level. Energies reported here are at this geometry, using a cc-pCVQZ basis. Energies are given in hartrees.

Structure	HF	CCSD	CCSD(T)
1t[a]	-402.3538358	-403.4181711	-403.4629418
1t[b]	-402.3769397	-403.4200492	-403.4618068
2s[c]	-402.3619809	-403.4316845	-403.4748241
3s[c]	-402.3528564	-403.4205303	-403.4649815

[a] Using a ROHF reference wavefunction.
[b] Using an UHF reference wavefunction.
[c] Reference 22, Stanton, Gauss, and Christiansen.

relative energies calculated at the UHF-CCSD(T) and ROHF-CCSD(T) levels at the ROHF-CCSD(T) equilibrium geometry, namely, less than one kcal/mole.

Absoulte and relative energetics are reported in Tables 6.2 and 6.3, respectively, at the Hartree-Fock, CCSD, and CCSD(T) levels. One expects effects of electron correlation to lower the energy of singlets relative to triplets, and this trend is observed: the energy gap between Isomer **1t** and Isomer **2s** is larger at correlated levels than at the Hartree-Fock level. Based on the small change in relative energies when including partial connected triples effects and the aforementioned appropriateness of applying single determinant methods to the isomers in question here, we conclude that the singlet ring with a C-C transannular bond (**2s**) is the global minimum. Furthermore, given its increasing relative destabilization with added correlation, Isomer **1t** is predicted to be energetically less stable than Isomer **3s**.

Table 6.3: Relative Energies of SiC_3 Isomers: Optimized geometries were determined at the ROHF-CCSD(T)/cc-pCVQZ level. Relative energies reported here are at this geometry, using a cc-pCVQZ basis. Zero point vibrational energy corrections are computed at the CCSD(T)/cc-pVQZ level. Energies are given in kcal/mole, and values corrected for zero-point vibrational energy are in parentheses.

Structure	HF	CCSD	CCSD(T)
1t[a]	5.1	8.5	7.5(8.0)
1t[b]	-9.4	7.3	8.2(8.7)
2s[c]	0.0	0.0	0.0(0.0)
3s[c]	5.7	7.0	6.2(6.0)

[a] Using a ROHF reference wavefunction.
[b] Using an UHF reference wavefunction.
[c] Reference 22, Stanton, Gauss, and Christiansen.

6.5 Acknowledgements

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Chapter 7

The Equilibrium Structure of the Ammonium Radical Rydberg Ground State [1]

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[1] Kurt W. Sattelmeyer, Henry F. Schaefer, John F. Stanton. 2001. Journal of Chemical Physics. 114:9863-9865. Reprinted per conditions stated in the Transfer of Copyright Agreement with the American Institue of Physics.

7.1 ABSTRACT

The equilibrium structure of the ammonium radical is determined by an extrapolation procedure of large (up to CCSD(T)/aug-cc-pV5Z) coupled cluster calculations and analysis of experimental rotational constants corrected for effects of rotation-vibration interaction. These approaches yield r_e values of 1.0367 and 1.0363 Å, respectively. The small difference serves as a valuable internal consistency check and suggests that r_e in NH_4 lies in the range 1.0365 ± 0.0005 Å.

7.2 INTRODUCTION

Much of the intrigue of the ammonium radical rests in its classification as a Rydberg radical, as its ground state electronic structure consists of a closed shell NH_4^+ core and a single electron in a nominal $3s$ orbital [1, 2]. This makes it one of the simplest Rydberg radicals, along with the isoelectronic H_2F, H_3O, and CH_5.

Experimental studies of NH_4 date from observation of the Schüler bands, first observed in 1955 by Schüler, Michel, and Grün [3] in emission and not definitively assigned until 1981 by Herzberg [1]. These transitions give important spectroscopic information about the ammonium radical. While nearly fifty years have passed since its emission bands were observed in the laboratory, the ephemeral nature of NH_4 (with respect to dissociation into NH_3 and H [4]) has precluded detection of the corresponding absorption bands. However, after a series of assignments [1, 5, 6, 7], Alberti, Huber, and Watson have attributed the strongest emission band to the transition between the $3p$ ($^2T_2$) and $3s$ ($^2A_1$) states of the radical [8].

Nevertheless, a troublesome point of this work is that the rotational constants of both states cannot be determined independently, so the rotational constants of the $3s$ ($^2A_1$) state were fixed to those of Havriliak and King [6], who used an ad hoc model to estimate these.

Work by Signorell, Palm, and Merkt [9] using rotationally resolved zero-kinetic-energy (ZEKE) techniques to obtain a photoelectron spectrum of the perdeuterated ammonium radical has given further reason to question the theoretical results of Havriliak and King. The rotational constant they obtained ($B_0 = 2.8560$ cm^{-}1) differs from that of Ref. 6 ($B_0 = 3.0407$ cm^{-}1) by nearly seven percent.

Besides that of Havriliak and King, other theoretical attempts[11, 12, 13] have been made to determine the ground state structure of the ammonium radical, but none have been done at an exhaustive level of theory. In addition, Merkt and coworkers (unpublished) have carried out a series of NH_4 geometry optimizations, with inconclusive results. Therefore, this paper aims to establish definitively the ground-state equilibrium geometry of NH_4 using coupled cluster methods and large basis sets.

7.3 Computational Methods

In this study two levels of theory have been used to determine the ground state geometry of the ammonium radical. These include the coupled-cluster singles and doubles (CCSD) model [14] and CCSD augmented by a perturbative treatment of triple excitations (CCSD(T)) [15].

Optimizations at these levels of theory were performed in T_d symmetry (this point group having been verified as that of the equilibrium structure by harmonic vibrational frequency calculations), using a series of four Dunning correlation-consistent basis sets augmented with diffuse functions: aug-cc-pVXZ (X = D, T, Q, and 5)[16]. These four basis sets consist of 59, 138, 264, and 447 contracted Gaussian functions, respectively, for NH_4. In order to account properly for core correlation, optimizations were performed with the aug-cc-pCVXZ (X = D, T, and Q) basis sets (63, 151, and 293 contracted Gaussian functions). Additionally, higher correlation effects were included by an optimization with full inclusion of triples (CCSDT) with a small basis set. Vibrational corrections to rotational constants were obtained with analytic CC second derivative techniques [17], using previously established procedures [18].

All calculations were performed with a local version of the ACESII program system [19].

7.4 RESULTS

As can be seen from Table 7.1, the convergence of the NH bond length is smooth with respect to basis set expansion at both levels of theory. With both CCSD and CCSD(T), the change in bond distance when progressing from the aug-cc-pVQZ to the aug-cc-pV5Z basis set is less than eight ten-thousandths of an Ångstrom. All in all, the commonly observed trends in bond distance with respect to increases in basis set size and of correlation treatment are observed.

In order to exploit the smooth convergence, an infinite basis set extrapolation was performed. Choosing a reference NH bond distance of 1.038 Ångstroms and displacements of ± 0.005 Å, single point energies were calculated using the three largest basis sets. Using this data, an estimate of the infinite basis set HF energy at each point was obtained by fitting the energy to the simple exponential form[20]

$$E_{HF} = E_{\infty} + A * e^{-B*X},$$

where A and B fitting parameters and E_{∞} is the desired estimate of the infinite basis set energy. Similarly, the correlation energy was fit to the equation[21]

$$E_{corr} = E_{\infty} + \frac{B}{X^3}$$

as parametrized by the aug-cc-pVQZ and aug-cc-pV5Z values. The additive solutions were then used to estimate r_e by parabolic interpolation. The CCSD and CCSD(T)

Table 7.1: Structures and Energies of NH_4 Using the aug-cc-pVXZ Series

Theory	Basis Set	r_e(NH)	E
CCSD	aug-cc-pVDZ	1.04387	-56.9245022
CCSD	aug-cc-pVTZ	1.03501	-56.9933077
CCSD	aug-cc-pVQZ	1.03336	-57.0218005
CCSD	aug-cc-pV5Z	1.03259	-57.0325716
CCSD	infinite limit[a]	1.03180	-57.0432073
CCSD(T)	aug-cc-pVDZ	1.04673	-56.9307157
CCSD(T)	aug-cc-pVTZ	1.03835	-57.0023187
CCSD(T)	aug-cc-pVQZ	1.03678	-57.0315137
CCSD(T)	aug-cc-pV5Z	1.03608	-57.0425304
CCSD(T)	infinite limit[a]	1.03549	-57.0534134

[a] Values arrived at by extrapolation of all data as described in the text.
Bond lengths are in Ångstroms, and energies are in hartrees; the point group of the equilibrium structure is T_d.

values of r_e resulting from this fit are 1.03180 and 1.03549 Å, respectively, implying rotational constants (B_e) of 5.892 and 5.850 cm^{-1}. Relativistic corrections were found to effect the bond distance on the order of 10^{-7} Ångstroms and are not considered here.

However, due to the importance of core correlation with respect to molecular properties[22], we have performed optimizations using the aforementioned set of aug-cc-pCVXZ basis sets. Assuming that the recovery of core correlation effects from the aug-cc-pCVXZ series can be taken as additive corrections to the aug-cc-pVXZ series, we predict this correction to have an upper bound of +0.001 Å. This assessment is based on the aug-cc-pCVTZ and aug-cc-pCVQZ values given in Table 7.2. Furthermore, a CCSDT/aug-cc-pVDZ optimization showed a Δr_e of +0.0002

Table 7.2: Structures and Energies of NH_4 Using the aug-cc-pCVXZ Series

Theory	Basis Set	r(NH)	Δ r_e[a]
CCSD	aug-cc-pCVTZ	1.03628	+0.00127
CCSD	aug-cc-pCVQZ	1.03433	+0.00097
CCSD(T)	aug-cc-pCVTZ	1.03977	+0.00142
CCSD(T)	aug-cc-pCVQZ	1.03783	+0.00105

[a] As compared to the value using the comparable aug-cc-pVXZ basis set
Bond lengths are in Ångstroms, and energies are in hartrees; the point group of the equilibrium structure is T_d.

Å, as compared to CCSD(T). This correction will similarly be taken as an additive one, placing our final r_e at 1.0367 Å.

Therefore, the r_0 value (1.0515 Å) of Merkt et. al. is 15 thousandths of an Ångstrom larger than our extrapolated, corrected r_e. This discrepancy between r_e and r_0 is not outside the difference expected from experience. For example, r_0 - r_e for CH_4 is more than 0.02 Å[23]. However, in order to make a more straightforward comparison, we have performed a detailed analysis of the experimental rotational constants of Ref. 9 using calculated vibration-rotation interaction constants at the CCSD(T)/aug-cc-pVTZ level. This approach has previously been used by Stanton, Gauss, and coworkers for a number of polyatomic molecules [18]. The procedure leads to an r_e of 1.0363 Å, as seen in Table 7.3. The good agreement of the values arising from these independent methods is encouraging, and there is little doubt that r_e(NH) for the ammonium radical is 1.0365 Å, a conservative uncertainty being 0.001 Å.

Table 7.3: Comparison of r_e (in Ångstroms) As Determined by Analysis of Experimental Data Versus Theory

	empirical fit[a]	extrapolation[b]
r(NH)	1.0363	1.0367

[a] Determined from analysis of the experimental rotational constants [9] with calculated vibration-rotation interaction constants (CCSD(T)/aug-cc-pVTZ level)
[b] Based on CCSD(T) extrapolation of all calculated data assuming additivity of core correlation and full triples effects

7.5 Summary

The use of very accurate quantum chemical calculations and a reanalysis of experimental rotational constants supplemented by computed vibrational corrections allows the ground state structure of the ammonium radical to be determined. When extrapolation techniques are used to account for basis set deficiencies and estimates made for the full triples contribution to the correlation, the calculated r_e differs from that obtained by the procedure involving reanalysis of experimental work by just 0.0004 Å. Thus, we consider the ground state structure of the $3s\ ^2A_1$ ammonium radical to be solved to a high level of accuracy.

7.6 Acknowledgements

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