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The Theoretical Prediction of Molecular Radical Species: a Systematic Study of Equilibrium Geometries and Harmonic Vibrational Frequencies

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A systematic study of the accuracy of structures and frequencies of 33 small radical molecules is presented as predicted by Hartree−Fock (HF) theory, second-order Møller−Plesset (MP2) theory, coupled-cluster singles and doubles (CCSD) theory, coupled-cluster singles and doubles with perturbational triples correction [CCSD(T)] theory, and gradient-corrected density functional theory with 3-parameter exact exchange mixing (B3LYP). For all methods, calculations were carried out using the Pople 6-31G**, the correlation-consistent polarized valence double-ζ (cc-pVDZ), and the correlation-consistent polarized valence triple-ζ (cc-pVTZ) basis sets. While basis set effects were moderate, large differences in the performance of the different methods were found. Due primarily to artifactual symmetry breaking and orbital instabilities, both restricted and unrestricted HF and MP2 perform too erratically to be acceptable. CCSD with either restricted or unrestricted orbitals yields results in generally good agreement with experiment. However CCSD(T) geometries and frequencies exhibit a surprising lack of improvement and in many cases are less accurate than CCSD. The accuracy of B3LYP, however, is roughly comparable, or better, to CCSD and at much reduced computational cost and therefore is a good compromise between cost and accuracy for the routine study of molecular radicals. In addition, for several radicals significant discrepancies exist between the most reliable computational methods and existing experimental data for structures and frequencies.

I. Introduction

The ability to accurately predict molecular properties with ab initio calculations is dependent on both the size of the one-electron basis set and the correct description of electron correlation. By systematically improving the level of approximations made, one can continually improve the reliability of results. To determine how useful any theoretical method and basis set is, one must make comparisons to experiment. This study presents such a comparison, investigating the effectiveness of a variety of ab initio wave function methods, as well as one of the most popular density functional theory (DFT) approaches. We predict equilibrium geometries and harmonic vibrational frequencies for 33 doublet radical species consisting mostly of first-row atoms.

Through the efforts of Dunning and co-workers, the correlation consistent basis sets[1−4] have achieved a hierarchical progression toward the full basis set limit. With this well delineated series, comparison and improvement in results are easily obtained, and thus the correlation consistent polarized valence double-ζ (cc-pVDZ)[1] and correlation consistent polarized triple-ζ (cc-pVTZ)[1] basis sets are used in this study with all methods. The Pople 6-31G** basis set[5−7] is also included in this work because of its popularity and the fact that matrix element evaluation is more efficient than with the similar sized cc-pVDZ because of exponent sharing between valence s and p functions. For anionic species, the basis sets were augmented through the addition of diffuse functions.

One of the more successful multielectron wave function hierarchies in use today is based on coupled-cluster (CC) theory. This series typically consists of the Hartree−Fock (HF), second-order Møller−Plesset (MP2), as the first iteration of coupled-cluster singles and doubles, coupled-cluster singles and doubles (CCSD),[8−11] and CCSD with the perturbation triples correction [CCSD(T)].[12] The ability to systematically improve this hierarchy makes it quite attractive in studies of this nature. The cost of these calculations (at least for very small molecules) increases with the fourth, fifth, sixth, and seventh powers of the molecule size respectively, reflecting the consequences of increasingly sophisticated treatments of correlation.

In addition to the above models, we have included the density functional theory[13] B3LYP model (with the Vosko−Wilk−Nusair 5 (VWN5) correlation functional)[14,15] based on the Becke exchange functional[16] and the Lee−Yang−Parr correlation functional (LYP).[17] Although this theory does not fall within the coupled-cluster hierarchy, its growing predominance in the quantum chemistry community makes it a worthy addition to this study. The computational cost of B3LYP calculations scales similarly to HF theory with the size of the molecule, but unlike HF theory, electron correlation is accounted for.

Many previous investigations have inspected the reliability of a series of methods and basis sets on closed-shell molecules.[18−26] These works state the CCSD(T) method to be the most accurate for both equilibrium geometries and harmonic vibrational frequencies, with both rivaling experimental results. Previous studies also recommended the use of a triple-ζ basis set as a minimum starting basis set for high-accuracy predictions of closed-shell molecules. In addition there also exists literature on the performance of standard theoretical models for radicals. Farnell et al. inspected the ability of restricted open-shell and unrestricted Hartree−Fock and Møller−Plesset theory with small basis sets (the largest being the 6-31G* basis set) to predict

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the geometries of a series of small diatomic and triatomic molecules.[27] They found that the restricted open-shell and the unrestricted HF produced similar results with the 6-31G* basis set. Also, when UHF exhibited large spin contamination, the unrestricted Møller−Plesset results were usually quite poor. This is supported by the work of Tozer et al., who examined the geometries, frequencies, and reaction energies of 30 small open-shell molecules with ROHF, UHF, ROMP2, and UMP2 using the 6-31G* basis set.[28] Tozer and co-workers also found ROMP2 to be better in cases when the UHF reference had a significant amount of spin contamination. Otherwise, they found the two types of MP2 to yield similar geometries, while ROMP2 did not "...suffer from the gross errors sometimes observed in UMP2 calculations of vibrational frequencies." As shall be shown later, ROMP2 can also suffer from large errors in calculating frequencies, depending on the molecule and basis set.

The performance of these theories in computing geometries and frequencies plays an important role in their ability to accurately predict barrier heights, thermodynamic properties, and stabilization energies. Wong et al. found that the reaction barriers and enthalpies of radical addition to alkenes are sensitive to calculated geometries.[29] Comparing Hartree−Fock, Møller−Plesset theories, quadratic configuration interaction with singles and doubles (QCISD),[30] QCISD with perturbative triples [QCISD(T)],[30] CCSD(T), BLYP, and B3LYP for a series of radical additions to various alkenes, Wong and Radom found QCISD and B3LYP to yield good results for both geometries and zero-point vibrational energy corrections, while UHF and UMP2 both performed poorly. Wong and Radom also found that increasing the size of the basis usually improved the results by 1−2 kJ/mol for barrier heights and 2−4 kJ/mol for enthalpies.

While B3LYP performed well for the radical addition calculations, Parkinson et al. concluded that for radical stabilization energies, ROMP2, QCISD(T), or CCSD(T) are preferable theories compared to DFT.[31] Parkinson and co-workers inspected the stabilization energy of the cyanovinyl radical with a large selection of popular theoretical models and Pople basis sets and determined that unrestricted MP2 was a completely inappropriate model to describe such a reaction, and while B3LYP did not display as serious errors as UMP2, it did consistently overestimate the stabilization energy. Restricted open-shell MP2, QCISD, QCISD(T), and CCSD(T), however, all agreed well with their benchmark calculation.

The goal of this study is to investigate the accuracy of molecular geometries and harmonic vibrational frequencies using restricted open-shell and unrestricted HF, MP2, CCSD, CCSD(T), and unrestricted B3LYP and the 6-31G**, cc-pVDZ, and cc-pVTZ basis sets on the following 33 *radical* species: FH^+ ($^2\Pi$), NH^+ ($^2\Pi$), N_2^+ ($^2\Sigma_g^+$), BO ($^2\Sigma^+$), BH^+ ($^2\Sigma^+$), CF ($^2\Pi$), C_2^- ($^2\Sigma_g^-$), F_2^+ ($^2\Pi_g$), OF ($^2\Pi$), CO^+ ($^2\Sigma^+$), CH ($^2\Pi$), CN ($^2\Sigma^+$), NO ($^2\Pi$), OH ($^2\Pi$), O_2^+ ($^2\Pi_g$), CH_2^- ($^2B_1$), HO_2 ($^2A''$), HNF ($^2A''$), HCO ($^2A'$), BH_2 ($^2A_1$), NH_2 ($^2B_1$), H_2O^+ ($^2B_1$), CO_2^+ ($^2\Pi_g$), CH_3 ($^2A_2''$), HCC ($^2\Sigma^+$), N_3 ($^2\Pi_g$), HCP^+ ($^2\Pi$), CNC ($^2\Pi_g$), NCO ($^2\Pi$), CH_3O (^2E), $C_4H_2{}^+$ ($^2\Pi_g$), C_3H_5 ($^2A_2$), and CH_2CHO ($^2A''$). The 37 unique bond distances are listed in Table 1, while the 84 unique frequencies for the 33 molecules are in Table 2. Our analysis is similar to that of Helgaker et al.,[18] who presented a systematic study of ab initio predictions of equilibrium structures of 19 closed-shell molecules, although we also consider harmonic vibrational frequencies.

TABLE 1: Bond Lengths of 29 Molecules in Order of Increasing Experimental Lengths

	molecule	bond	exptl (pm)		molecule	bond	exptl (pm)
1	OH	R_{OH}	96.97[a]	22	HCO	R_{CO}	117.5[b]
2	HO_2	R_{OH}	97.7[b]	23	CO_2^+	R_{CO}	117.682[c]
3	H_2O^+	R_{OH}	100.1[c]	24	CO_2^+	R_{CO}	117.682[c]
4	FH^+	R_{FH}	100.1[a]	25	BH_2	R_{BH}	118.1[b]
5	NH_2	R_{NH}	102.5[c]	26	N_3	R_{NN}	118.15[e]
6	HNF	R_{HN}	103.5[d]	27	N_3	R_{NN}	118.15[e]
7	$C_4H_2^+$	R_{HC}	104.6[c]	28	BO	R_{BO}	120.5[a]
8	HCC	R_{HC}	104.653[c]	29	BH^+	R_{BH}	121.5[a]
9	NH^+	R_{NH}	107.[b]	30	HCC	R_{CC}	121.652[c]
10	HCP^+	R_{HC}	107.3[e]	31	$C_4H_2^+$	R_{CC}	123.4[c]
11	CH_3	R_{HC}	107.67[e]	32	CNC	R_{CN}	124.5[e]
12	CH_3	R_{HC}	107.67[e]	33	CNC	R_{CN}	124.5[e]
13	CH_3O	R_{HC}	109.58[c]	34	C_2^-	R_{CC}	126.8[a]
14	CH_3O	R_{HC}	109.58[c]	35	CF	R_{CF}	127.2[a]
15	O_2^+	R_{OO}	111.64[a]	36	F_2^+	R_{FF}	130.5 [f]
16	N_2^+	R_{NN}	111.642[a]	37	HO_2	R_{OO}	133.5[b]
17	CH	R_{HC}	111.99[a]	38	$C_4H_2^+$	R_{CC}	134.6[c]
18	HCO	R_{HC}	112.5[b]	39	OF	R_{OF}	135.4[g]
19	CO^+	R_{CO}	112.83[a]	40	CH_3O	R_{CO}	136.37[c]
20	NO	R_{NO}	115.08[a]	41	HNF	R_{NF}	137.3[d]
21	CN	R_{CN}	117.18[a]	42	HCP^+	R_{CP}	160.0[e]

[a] Reference 53. [b] Reference 54. [c] Reference 55. [d] Reference 56. [e] Reference 57. [f] Reference 58. [g] Reference 59.

II. Theoretical Approach

Calculations of the molecular equilibrium geometries and harmonic frequencies have been carried out using the HF, MP2, CCSD, and CCSD(T) methods with both restricted open-shell and unrestricted Hartree−Fock references and the B3LYP density functional theory with unrestricted orbitals. In all correlated wave function-based calculations, the core 1*s* orbitals have been frozen. For all levels of theory, the calculations have been performed using the Pople 6-31G** and the correlation consistent Dunning cc-pVDZ and cc-pVTZ basis sets. To properly account for the more diffuse electronic structure of anions, the 6-31++G**, aug-cc-pVDZ^2, and aug-cc-pVTZ^2 basis sets were used for the CH_2^- and C_2^- molecules. All basis sets used are present in the on-line EMSL basis set library.[32]

The HF and CCSD energies were converged to 10^{-10} and 10^{-8} hartrees. A grid of 100 radial points and 302 angular points per radial point was used for all integrals of the exchange-correlation functionals in the DFT calculations. Analytical gradient techniques were used to optimize the equilibrium molecular structures for all levels of theory to at least four decimal places. The Hartree−Fock vibrational frequencies were obtained from analytical second derivatives, while the DFT and all correlated harmonic frequencies were calculated from finite differences of corresponding analytical gradients. The b_2 modes of C_3H_5 using unrestricted CCSD(T) in the cc-pVTZ basis set were obtained by energy differences and not through gradients due to convergence difficulties. For the same molecule, we were unable to determine the b_2 modes in the cc-pVTZ basis set with restricted open-shell CCSD(T) because we could not converge the Hartree−Fock reference for either gradient or energy-difference steps.

For several of the molecules with degenerate point-group symmetry, real frequencies were unobtainable unless the symmetry was broken by allowing the molecule to relax to a different, lower symmetry, geometry. Calculations for these molecules were started with an initial broken-symmetry geometry. For several methods, the molecule recovered the true point-group symmetry to within convergence criteria. For the symmetry-broken molecules, there are multiple entries in Figures 1 and 2 for those bond distances or harmonic modes which are derived from the higher-symmetry solution. Additionally ROMP2/cc-pVDZ does not yield a stable minimum for F_2^+, and therefore this molecule is not a factor in all statistical data. Finally, three

TABLE 2: Frequencies of 33 Molecules in Order of Increasing Experimental Energies; Experimental Harmonic Frequencies Are Denoted with an *H*

	molecule	mode	exptl (cm^{-1})		molecule	mode	exptl (cm^{-1})
1	CNC	Π_u	321^a	48	HO_2	a'	1392^a
2	CNC	Π_u	321^a	49	CH_3	e'	1398^a
3	HCC	Π	372^a	50	H_2O^+	a_1	1408^a
4	CH_2CHO	a''	404^b	51	HNF	a'	1419^a
5	C_3H_5	a_1	427^a	52	CO_2^+	Σ_u^+	1423^a
6	$C_4H_2^+$	Π_g	432^a	53	CNC	Σ_u^+	1453^a
7	$C_4H_2^+$	Π_g	432^a	54	C_3H_5	b_2	1463^a
8	N_3	Π_u	457^a	55	CH_2CHO	a'	1486^b
9	N_3	Π_u	457^a	56	CH_3O	e	1487^a
10	CH_2CHO	a'	500^b	57	CH_3O	e	1487^a
11	CO_2^+	Π_u	511^a	58	C_3H_5	a_1	1488^a
12	CO_2^+	Π_u	511^a	59	NH_2	a_1	1497^a
13	C_3H_5	b_1	518^a	60	CH_2CHO	a'	1543^b
14	NCO	Π	535^a	61	N_3	Σ_u^+	1645^a
15	NCO	Π	535^a	62	C_2^-	Σ_g^+	1781^e H
16	C_3H_5	a_2	549^a	63	HCC	Σ^+	1841^a
17	CH_2CHO	a''	557^b	64	HCO	a'	1868^a
18	CH_3	a_2''	606^a	65	BO	Σ^+	1886^c H
19	HCP^+	Π	642^a	66	NO	Σ^+	1904^e H
20	HCP^+	Π	642^a	67	O_2^+	Σ_g^+	1905^e H
21	CH_3O	e	653^a	68	NCO	Σ^+	1921^a
22	CH_3O	e	653^a	69	CN	Σ^+	2069^e H
23	CH_2CHO	a''	703^b	70	CO^+	Σ^+	2170^e H
24	C_3H_5	b_1	802^a	71	$C_4H_2^+$	Σ_g^+	2177^a
25	CH_2CHO	a'	957^b	72	N_2^+	Σ_g^+	2207^c H
26	C_3H_5	b_1	968^a	73	HCO	a'	2434^a
27	$C_4H_2^+$	Σ_g^+	972^a	74	BH^+	Σ^+	2435^c
28	HNF	a'	1000^a	75	CH_3O	e	2774^a
29	BH_2	a_1	1030^c	76	CH_3O	e	2774^a
30	CH_3O	a_1	1047^a	77	CH_3O	a_1	2840^a
31	OF	Σ^+	1053^c H	78	CH	Σ^+	2858^d H
32	C_3H_5	a_1	1066^a	79	NH^+	Σ^+	2922^c
33	HCO	a'	1081^a	80	CH_3	a_1	3005^a
34	HO_2	a'	1098^a	81	C_3H_5	b_2	3016^a
35	F_2^+	Σ_g^+	1104^d H	82	C_3H_5	a_1	3048^a
36	CH_2CHO	a'	1143^b	83	FH^+	Σ^+	3090^c H
37	HCP^+	Σ^+	1147^a	84	C_3H_5	b_2	3105^a
38	C_3H_5	b_2	1182^a	85	HCP^+	Σ^+	3125^a
39	CH_2^-	a_1	1230^a	86	$C_4H_2^+$	Σ_g^+	3137^a
40	CO_2^+	Σ_g^+	1244^a	87	CH_3	e'	3161^a
41	C_3H_5	a_1	1245^a	88	H_2O^+	a_1	3213^a
42	NCO	Σ^+	1273^a	89	NH_2	a_1	3219^a
43	CF	Σ^+	1308^c H	90	H_2O^+	b_2	3259^a
44	N_3	Σ_g^+	1320^a	91	NH_2	b_2	3301^a
45	CH_3O	a_1	1362^a	92	HO_2	a'	3437^a
46	CH_2CHO	a'	1366^b	93	OH	Σ^+	3738^e H
47	C_3H_5	b_2	1389^a				

[a] Reference 60. [b] Reference 49. [c] Reference 61. [d] Reference 62. [e] Reference 53.

molecules in the data set (NCO, C_3H_5, and CH_2CHO) all lacked sufficiently accurate experimental geometries to compare against, and therefore these molecules were removed from consideration during the discussion of equilibrium geometries. They shall be inspected in greater detail at the end of section III B.

For B3LYP, calculations have been carried out with the Q-CHEM program.[33,34] All remaining calculations were performed with the ACESII program.[35] All calculated structures, energies, vibrational frequencies, and infrared intensities for the 33 molecules are available upon request from the authors.

III. Results and Discussion

A. Equilibrium Geometries. In Figures 1−4 we have plotted the error relative to experiment for each bond distance given in Table 1. Figures 1−2 contain each of the four theories based on either the ROHF or UHF reference (HF, MP2, CCSD, CCSD[T]) with the cc-pVTZ basis set. Inspection of these two figures gives an immediate overall impression of the relative performance of these four methods: clearly HF and MP2 are erratic and poor, while CCSD and CCSD(T) appear more satisfactory. The performance of unrestricted B3LYP is illustrated in Figure 3 for each of the three basis sets. It is evident that its performance is generally quite satisfactory. Additionally the basis set dependence of the unrestricted CCSD results are shown in Figure 4.

The statistical performance of each level of theory with each basis set is shown in Tables 3, 4, and 5 (each table summarizing a different basis set). We shall briefly discuss the overall performance of the different theories below, before considering specific cases in more detail in the following subsection.

Both Hartree−Fock methods perform quite poorly, but clearly UHF is the preferred Hartree−Fock approach, as ROHF yields mean absolute errors and standard deviations that are typically 40−50% larger. The deviations are slightly larger in the larger cc-pVTZ basis than in the 6-31G** basis, indicating that there is little advantage in employing larger basis sets when the intrinsic errors of the theory are clearly dominant. As is well-known, HF systematically underestimates bond lengths.

For closed-shell molecules, the accuracy of second-order Møller−Plesset theory is usually adequate for geometries. Wong et al. (and others), however, have shown that MP2 can be an unreliable method for open-shell systems.[36] Our results in Tables 3−5 are certainly consistent with this conclusion. Indeed on a statistical basis, it appears that there is no advantage to employing UMP2 relative to UHF, and little advantage to employing ROMP2 relative to ROHF. This is primarily due to large outliers, as is evident in Figures 1 and 2, and therefore in many *individual* cases MP2 results are improved relative to HF. Clearly MP2 for radicals must be used with caution, if at all.

With the extreme sensitivity of MP2 to the reference wave function, we turn next to CCSD as a potentially more robust wave function method. By all measures, restricted and unrestricted CCSD perform quite similarly. This illustrates the ability of CCSD to correct for errors in the reference. Mean absolute and standard deviations for CCSD relative to those for experiment are typically a factor of 2−3 smaller than for MP2 or HF, and all of the large outliers are eliminated. These are quite encouraging results, which are quite comparable to what is expected for closed-shell systems. For example, unrestricted CCSD/cc-pVTZ yields an overall mean absolute error of 0.56 pm, which is actually slightly smaller than the 0.72 pm error seen with the same method and basis set for closed-shell molecules.[18]. There is a noticeable basis set effect for CCSD: in going from 6-31G** to cc-pVTZ, the mean absolute error decreases by approximately 0.3 pm, as is also visually evident in Figure 4.

CCSD(T) has proven to perform extremely well for closed-shell molecules, substantially improving on CCSD results.[18] Unfortunately, our results for radicals are quite different, as can be seen by comparing CCSD and CCSD(T) in Table 5 for example. ROCCSD(T) only marginally improves upon ROCCSD, while UCCSD(T) is statistically inferior to UCCSD, the solution it is trying to correct. These results mirror the performance of MP2 relative to that of HF theory discussed above. From inspection of the figures it can be seen that this is again a result of large outliers in CCSD(T) relative to CCSD. It is striking to compare our lowest open shell CCSD(T) standard deviation (0.70 pm) for ROCCSD(T)/cc-pVTZ with the 0.32 pm deviation of CCSD(T)/cc-pVTZ for closed-shell molecules.[18]

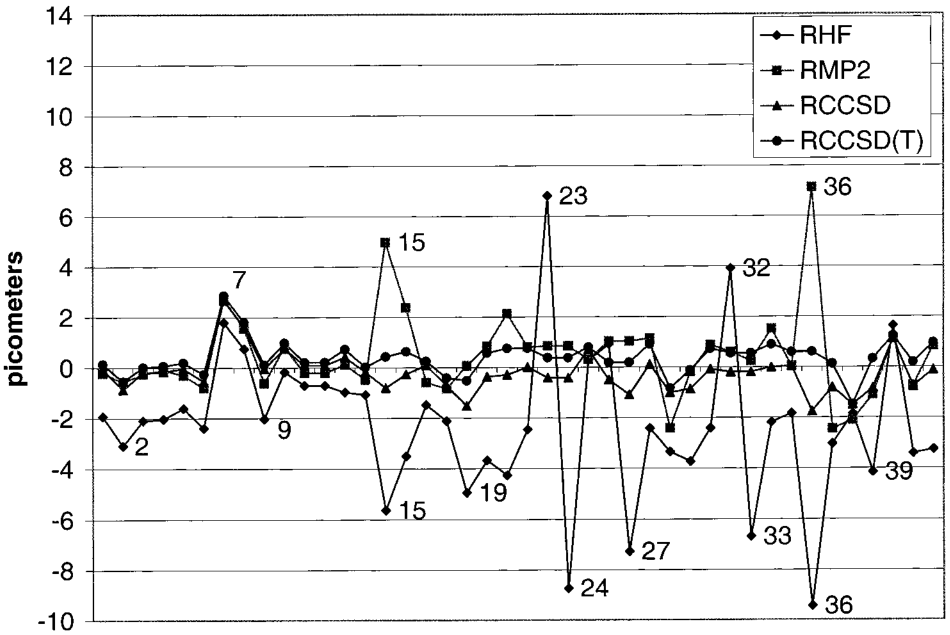

Figure 1. Restricted reference bond distance errors as a function of correlation treatment. For each of the 42 bond lengths listed in Table 1, given as a list along the *x* axis, the deviations in calculated HF, MP2, CCSD, and CCSD(T) bond lengths relative to experiment are plotted as the *y* value. These calculated values all use restricted (ROHF) orbitals and the largest basis set used in this study, the cc-pVTZ basis.

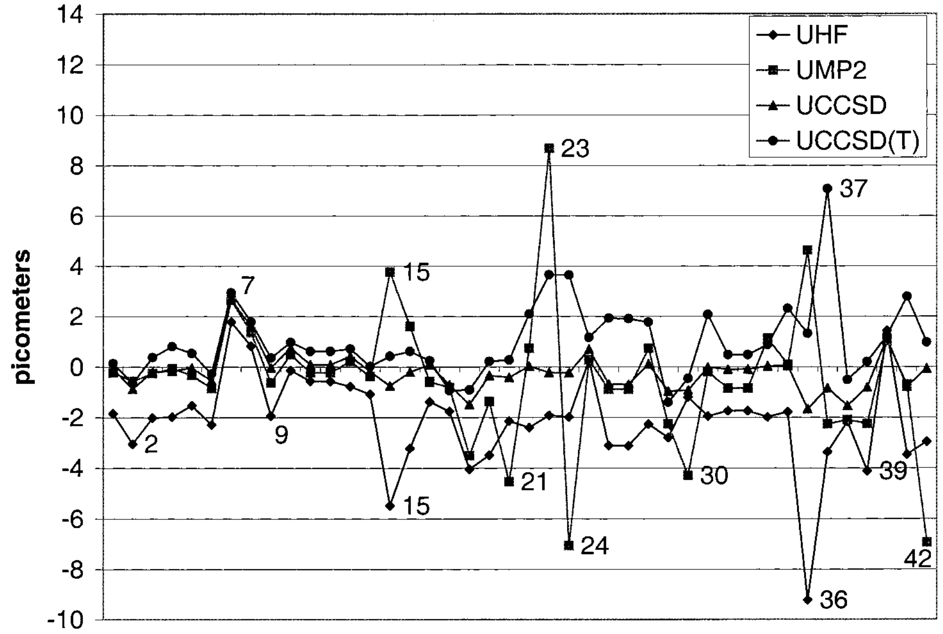

Figure 2. Unrestricted reference bond distance errors as a function of correlation treatment. The deviations that result when unrestricted (UHF) orbitals are used with the cc-pVTZ basis are in the same format as that of Figure 1.

We next consider the computationally inexpensive B3LYP flavor of density functional theory. As can be seen from Tables 3, 4, and 5, and Figure 3 the performance of B3LYP is very satisfactory indeed. On a statistical basis, B3LYP results are essentially comparable to those for CCSD and CCSD(T), and are substantially better than those of MP2 or HF theory. There are no large outliers, which makes the method suitable for routine application. Compared to the 0.3 pm decrease in mean absolute error in going from the CCSD/6-31G** to CCSD/cc-pVTZ, for B3LYP the mean absolute error only decreases by 0.02 pm, reflecting the more demanding basis set requirements of CCSD relative to those of B3LYP. The most dramatic basis set effect in Figure 3 is the much poorer performance of cc-pVDZ relative to that of 6-31G** despite both sets being the same size.

Finally we note that with a great many diatomics and linear triatomics in this study, and a lack of experimental data, there is little that we can say on the subject of interatomic angles. For most of the molecules, the mean absolute errors are all within 1 to 2°, with little differentiation between basis sets or theory. To keep the size of the paper manageable, we have not included these data.

B. Equilibrium Geometries: Details. The major failure in the prediction of molecular geometries is that in some cases the correct molecular point group was not obtained. This symmetry breaking is a generally an artifact resulting from the use of an approximate wave function (or density functional) and is therefore most acute in the lower-level theories (HF and MP2 in particular). For CH_3, restricted open-shell Hartree−Fock, for the 6-31G** and cc-pVDZ basis sets, does not result in a

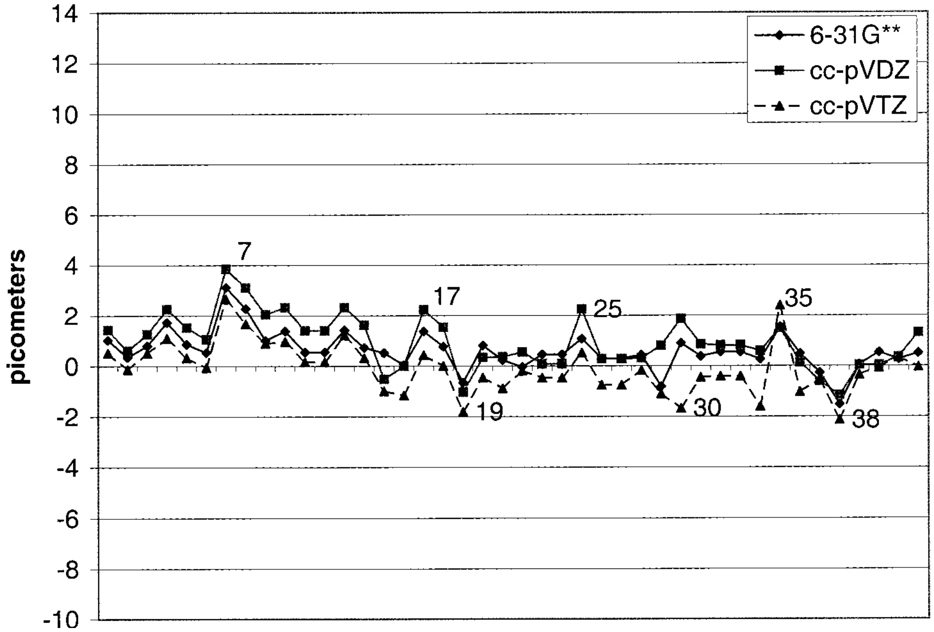

Figure 3. B3LYP bond distance errors as a function of basis set. The calculated deviations in bond lengths for B3LYP relative to experiment are in the same format as that of Figure 1.

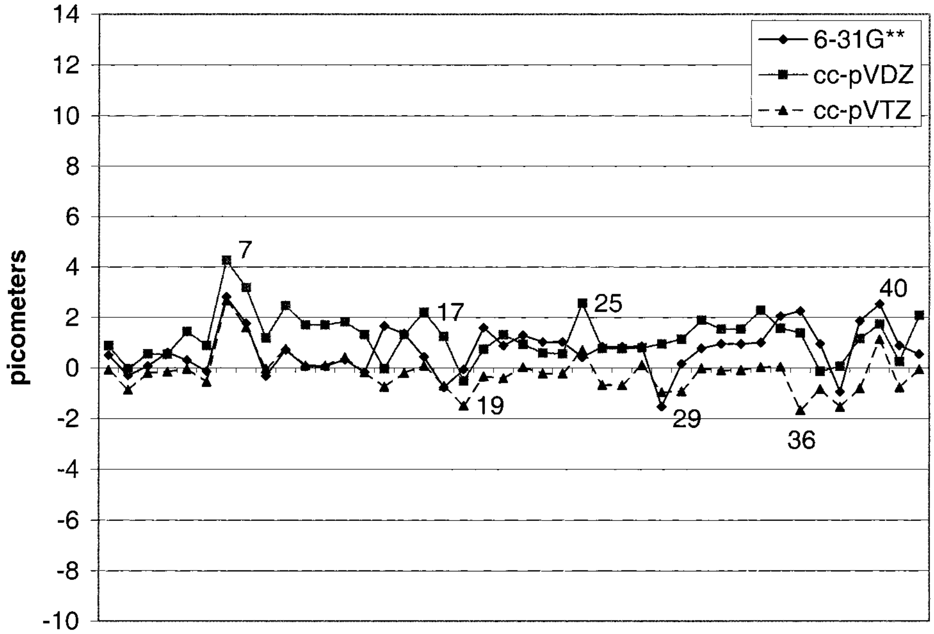

Figure 4. UCCSD bond distance errors as a function of basis set. The calculated deviations in bond lengths for unrestricted CCSD relative to experiment are in the same format as that of Figure 1.

planar D_{3h} structure, but rather a C_{3v} structure, with improper torsion angles of 169 and 191°, respectively. B3LYP also fails to obtain the correct geometry for HCC with the 6-31G** and cc-pVDZ basis sets, with calculations yielding a bent structure instead of linear, with angles of 163 and 162°, respectively. All attempts at converging to the correct point groups resulted in imaginary frequencies, demonstrating the geometry was not the minimum, but rather a saddle point.

Other cases of incorrect point group solutions are seen in the $D_{\infty h}$ molecules: CNC, CO_2^+, and N_3. Restricted open-shell Hartree−Fock for all basis sets yielded a $C_{\infty v}$ geometry for each of these molecules, as does UHF, although the distortion is much smaller than that seen for ROHF. Unrestricted MP2 and CCSD also exhibit this symmetry breaking for the CO_2^+ molecule, while ROCCSD has symmetry breaking for N_3 and results in a $C_{\infty v}$ solution. All other methods result in the correct point-group symmetry for these molecules to within convergence criteria.

TABLE 3: Mean ($\bar{\Delta}$), Absolute Mean ($\bar{\Delta}_{abs}$) Deviations, Standard Deviations, and Maximum Errors Relative to Experiment in Calculated (pm) Bond Distances with the 6-31G Basis Set**

	$\bar{\Delta}$	$\bar{\Delta}_{abs}$	std dev	max error
ROHF	−1.70	2.63	2.84	−7.96
UHF	−1.53	1.79	1.57	−7.30
ROMP2	1.34	1.78	2.63	13.22
UMP2	0.35	1.90	3.18	10.56
ROCCSD	0.68	0.88	0.90	2.81
UCCSD	0.71	0.92	0.90	2.81
ROCCSD(T)	1.17	1.32	1.13	4.32
UCCSD(T)	1.53	1.64	1.44	4.62
UB3LYP	0.61	0.77	0.78	3.12

TABLE 4: Mean ($\bar{\Delta}$), Absolute Mean ($\bar{\Delta}_{abs}$) Deviations, Standard Deviations, and Maximum Errors Relative to Experiment in Calculated (pm) Bond Distances with the cc-pVDZ Basis Set

	$\bar{\Delta}$	$\bar{\Delta}_{abs}$	std dev	max error
ROHF	−1.46	2.64	3.03	−8.66
UHF	−1.29	1.90	1.95	−8.48
ROMP2	1.54[a]	1.93[a]	1.49[a]	5.96[a]
UMP2	0.91	2.30	3.22	13.32
ROCCSD	1.21	1.46	0.94	4.26
UCCSD	1.24	1.49	0.93	4.26
ROCCSD(T)	1.75	1.95	0.96	4.42
UCCSD(T)	2.26	2.52	1.38	5.47
UB3LYP	0.95	1.26	1.08	3.86

[a] F_2^+ (36) nonconvergent.

TABLE 5: Mean ($\bar{\Delta}$), Absolute Mean ($\bar{\Delta}_{abs}$) Deviations, Standard Deviations, and Maximum Errors Relative to Experiment in Calculated (pm) Bond Distances with the cc-pVTZ Basis Set

	$\bar{\Delta}$	$\bar{\Delta}_{abs}$	std dev	max error
ROHF	−2.26	3.02	3.00	−9.44
UHF	−2.11	2.32	1.83	−9.22
ROMP2	0.46	1.15	1.71	7.13
UMP2	−0.45	1.76	2.69	8.68
ROCCSD	−0.22	0.59	0.81	2.67
UCCSD	−0.20	0.56	0.80	2.67
ROCCSD(T)	0.38	0.58	0.70	2.86
UCCSD(T)	1.01	1.25	1.50	7.07
UB3LYP	−0.01	0.75	1.00	2.65

A very different case in which the calculated point group does not agree with experiment is the CH_3O radical. For all methods and all basis sets, the calculations yielded a C_s geometry of $^2A'$ symmetry, instead of the correct C_{3v} point-group symmetry. In all computations, the oxygen lay canted toward one of the hydrogens, with that hydrogen−carbon bond length longer than the other two hydrogen−carbon distances. For this molecule, the availability of a Jahn−Teller distortion to lower the energy yields a real, and not artifactual, effect. Due to this Jahn−Teller coupling of the *e* vibrations and the ^2E ground state, the gradient determined in the vibrational degrees of freedom is nonzero; therefore, the electronic degeneracy is lifted, stablizing the molecule. Proper description of methoxy is beyond the scope of this paper; some references for this purpose are the papers of Barckholtz et al.[37] and Höper et al.[38]

We would now like to turn to a case where there is a systematic deviation between the best calculated values we have obtained, and existing experimentally derived information. The R_{HC} distance (distance 7) in $C_4H_2^+$ is always overestimated by approximately 3 pm for every theory in this study. It is possible that the experimentally derived value for this parameter should be reexamined.

Additionally the NCO, C_3H_5, and CH_2CHO molecules were originally included in the statistical data. Upon closer inspection of the data, we noticed a consistent error for CH_2CHO, where the carbon−carbon distances were always too long by approximately 3−5 pm, while the oxygen−carbon distances were too short by 4 pm on average. For C_3H_5, the carbon−carbon lengths were always too short by 5 pm relative to experiment. For NCO, the computed bond distances were always reversed in which is longest when compared to experiment. These systematic errors demand closer inspection of the original experimental analysis.

For the CH_2CHO molecule, both laser-induced fluorescence[39] and microwave[40] studies have been performed, and a microwave study inspecting the deuterated species was done by Endo and Hirota in 1988.[41] However, to determine the carbon−hydrogen bond distances and the CCH angles, all of these studies have used the theoretical work of Dupuis et al. who used multiconfigurational Hartree−Fock with the STO-3G and 3-21G basis sets.[42] In the experimental studies, these bonds and angles were assumed to be the same as the calculated values. It would be of interest to look at the experimental data using the data generated in this study and see if there is better agreement between the experimental and calculated backbone structure.

There were several reasons why the experiment results obtained with electron diffraction for C_3H_5 were unsuitable for this study.[43] This experiment used electron diffraction, which normally has a resolution of approximately 10 pm due to thermal equilibration, was run at a rather high temperature of 960 °C. Not only will this increase the error in the experiment, but it will also move the molecule further from its equilibrium geometry, which we are computing. Similar to studies for CH_2-CHO, the use of small basis set, uncorrelated multiconfigurational Hartree−Fock structures to set the carbon−hydrogen bond distances influenced the carbon backbone structure values.[44] Further experimental measurements on this molecule with more accurate techniques would aid in correctly determining the equilibrium geometry.

Experimental evidence on the structure of NCO is scarce, with the most recent study performed by Misra et al.[45] While Misra did examine both ^{14}NCO and ^{15}NCO using flash photolysis, the lack of microwave data on ^{15}NCO necessitated the use of certain molecular constants from ^{14}NCO in the Hamiltonian. The transferability of these constants in the Hamiltonian is obviously not exact, and could introduce too many errors to make the experimental geometry applicable for this study. Also, it would be preferable if microwave studies could be done using all combinations of isotopic substitution for the most accuracy possible. In contrast to the experimental data analytic UCCSD-(T) second derivative geometries and frequencies of NCO are in good agreement with our theoretical data.[46]

C. Harmonic Vibrational Frequencies. In Figures 5−8, we have plotted the error relative to experiment for each harmonic frequency, with the *x* ordinate corresponding to the entries in Table 2, which are sorted in order of increasing energy. From inspection of these figures, a general impression of the results for vibrational frequency calculations for radicals emerges that is similar to what we saw previously for geometries. Both restricted open-shell and unrestricted HF calculations and restricted open-shell and unrestricted MP2 calculations are noisy and quite erratic. CCSD and B3LYP appear to eliminate virtually all of the outliers, while a few remain with CCSD(T). Basis set effects in B3LYP and CCSD appear for the most part to be smaller than the main remaining deviations between calculation and experiment.

Statistical characterizations of our frequency results are given in Tables 6−8, which we will now discuss. These characterizations are calculated in two ways: first as absolute values (in cm^{-1}) and expressed as percentages to illustrate the magnitude of the error relative to the size of the frequency. It is immediately clear from Tables 6 through 8 that, due to large outliers in most methods, these percentage values are very large. An example of how large these incorrect frequencies can be is the Σ_u^+ stretching mode of N_3 (number 61 in Table 2), where ROMP2/cc-pVTZ results in a frequency of 32803 wavenumbers!

Therefore, to get an indication of how such methods perform in cases where they do not break down, we have also computed "corrected" statistics after removing these unphysical frequencies, as noted in Tables 6−8. We have somewhat arbitrarily

TABLE 6: Mean $\bar{\Delta}$ (cm^{-1}), Mean Percent $\bar{\Delta}_{\%}$ Deviations, Mean Absolute Deviations ($\bar{\Delta}_{abs}$) (cm^{-1}), Mean Absolute Percent Deviations ($\bar{\Delta}_{abs\%}$), Standard Deviations (Δ_{std}) (cm^{-1}), and Standard Percent Deviations ($\Delta_{std\%}$) Relative to Experiment in Calculated Harmonic Vibrational Frequencies with the 6-31G Basis Set**

	$\bar{\Delta}$		$\bar{\Delta}_{\%}$		$\bar{\Delta}_{abs}$		$\bar{\Delta}_{abs\%}$		Δ_{std}		$\Delta_{std\%}$	
ROHF	280	234^a	20.4	16.5^a	292	247^a	22.4	18.5^a	486	199^a	42.1	18.4^a
UHF	175		12.4		198		15.0		171		15.2	
ROMP2	559	80^b	38.3	5.1^b	599	121^b	41.6	8.5^b	2805	155^b	188.0	11.5^b
UMP2	270	145^c	18.5	11.0^c	299	174^c	21.4	14.0^c	940	195^c	58.6	19.1^c
ROCCSD	109	94^a	7.0	5.7^a	121	106^a	9.2	8.0^a	176	106^a	16.1	10.5^a
UCCSD	88		5.3		104		8.1		108		10.8	
ROCCSD(T)	153	70^d	8.8	3.3^d	176	94^d	12.8	7.5^d	689	113^d	43.8	11.8^d
UCCSD(T)	38		1.4		102		9.3		130		14.5	
UB3LYP	64		5.1		83		7.3		88		11.0	

[a] Removing frequency C_3H_5 b_2 (38). [b] Removing frequencies 38, CO_2^+ Σ_u^+ (52), CNC Σ_u^+ (53), N_3 Σ_u^+ (61). [c] Removing frequencies 52, 61, NO (66). [d] Removing frequencies 38, 61.

TABLE 7: Mean $\bar{\Delta}$ (cm^{-1}), Mean Percent $\bar{\Delta}_{\%}$ Deviations, Mean Absolute Deviations ($\bar{\Delta}_{Abs}$) (cm^{-1}), Mean Absolute Percent Deviations ($\bar{\Delta}_{abs\%}$), Standard Deviations (Δ_{std}) (cm^{-1}), and Standard Percent Deviations ($\delta_{std\%}$) Relative to Experiment in Calculated Harmonic Vibrational Frequencies with the cc-pVDZ Basis Set

	$\bar{\Delta}$		$\bar{\Delta}_{\%}$		$\bar{\Delta}_{abs}$		$\bar{\Delta}_{abs\%}$		Δ_{std}		$\Delta_{std\%}$	
ROHF	280	221^a	20.4	15.3^a	292	233^a	22.6	17.6^a	601	197^a	51.6	18.0^a
UHF	165		11.6		188		14.4		168		15.0	
ROMP2	550^b	64^c	37.7^b	4.1^c	593^b	110^c	42.5^b	9.2^c	2837^b	151^c	189.7^b	16.5^c
UMP2	192	150^d	13.6	11.0^d	226	184^d	17.1	14.6^d	495	281^d	33.1	22.3^d
ROCCSD	83	68^a	5.1	3.9^a	103	89^a	8.4	7.2^a	171	100^a	16.2	11.0^a
UCCSD	61		3.3		83		6.8		97		10.8	
ROCCSD(T)	190	42^e	11.5	0.8^e	230	83^e	18.5	7.9^e	1012	113^e	74.7	14.6^e
UCCSD(T)	23		1.7		89		7.3		121		11.9	
UB3LYP	44		3.9		73		6.6		89		10.6	

[a] Removing frequency C_3H_5 b_2 (38). [b] Unable to obtain frequency F_2^+ Σ_g^+ (35). [c] Unable to obtain 35 and removing frequencies CO_2^+ Σ_u^+ (52), CNC Σ_u^+ (53), N_3 Σ_u^+ (61). [d] Removing frequency 61. [e] Removing frequencies 38, 61.

TABLE 8: Mean $\bar{\Delta}$ (cm^{-1}), Mean Percent $\bar{\Delta}_{\%}$ Deviations, Mean Absolute Deviations ($\bar{\Delta}_{abs}$) (cm^{-1}), Mean Absolute Percent Deviations ($\bar{\Delta}_{Abs\%}$), Standard Deviations (Δ_{std}) (cm^{-1}), and Standard Percent Deviations ($\Delta_{std\%}$) Relative to Experiment in Calculated Harmonic Vibrational Frequencies with the cc-pVTZ Basis set

	$\bar{\Delta}$		$\bar{\Delta}_{\%}$		$\bar{\Delta}_{abs}$		$\bar{\Delta}_{abs\%}$		Δ_{std}		$\Delta_{std\%}$	
ROHF	331	223^a	25.0	15.9^a	346	238^a	27.5	18.3^a	1061	195^a	90.5	19.1^a
UHF	170		12.6		193		15.1		168		15.7	
ROMP2	683^a	74^b	37.2^a	5.0^b	716^a	108^b	40.0^a	7.8^b	3743^a	140^b	208.0^a	11.0^b
UMP2	152		11.3		183		14.5		265		22.0	
ROCCSD	112^a	96^c	7.0^a	6.6^c	127^a	111^c	9.4^a	9.0^c	210^a	145^c	13.5^a	12.8^c
UCCSD	82		6.1		97		8.5		94		11.8	
ROCCSD(T)	82^d	57^{d,e}	4.7^d	3.2^{d,e}	110^d	85^{d,e}	9.5^d	8.0^{d,e}	253^d	99^{d,e}	18.7^d	12.2^{d,e}
UCCSD(T)	31		1.0		92		8.2		124		12.8	
UB3LYP	58		4.6		73		6.5		76		9.8	

[a] Removing frequency C_3H_5 b_2 (38). [b] Removing frequencies 38, CO_2^+ Σ_u^+ (52), CNC Σ_u^+ (53), N_3 Σ_u^+ (61), C_3H_5 b_2 (84). [c] Removing frequencies 38, 84. [d] Unable to obtain all C_3H_5 b_2 frequencies (38, 47, 54, 81, 84). [e] Removing frequency 61.

defined these unphysical frequencies as those which are over 120% in error. These corrected statistics are most emphatically not any measure of overall robustness. The most robust methods are those for which no such correction was needed, such as B3LYP, UCCSD, and UCCSD(T).

Looking to the HF data in Figures 5 and 6, as we proceed to higher energies, it is possible to envision a noisy linear increase in error, which is similar to what one sees for closed-shell molecules, where the vibrational frequencies are normally scaled by 0.893.[47] The similarity between mean percentage and mean absolute percentage errors corroborates this observation. UHF is consistently better than its restricted open-shell counterpart. The restricted open-shell percent mean, percent absolute mean, and percent standard deviations are consistently worse by approximately 3% than the unrestricted method.

Turning to correlated corrections to HF theory, we find that, statistically, unrestricted MP2 has little or no value as a correction to UHF, while the corrected ROMP2 statistics do improve upon the ROHF starting point. However, given the very large outliers that have been removed, one must certainly be very cautious in applying either MP2 method. These statistics are dominated by the outliers, and thus one can see from Figures 5 and 6 that many MP2 results are improved over their HF references.

Figures 5 and 6 illustrate how the coupled-cluster wave function damps the errors seen in the lower-level theories, with just a few exceptions (three of the b_2 C_3H_5 frequencies for ROCCSD/cc-pVTZ). Overall the CCSD results are satisfactorily smooth with low errors. It is interesting that UCCSD is consistently better than ROCCSD, regardless of basis set. This is surprising, considering how closely these methods mimicked each other for equilibrium geometries. The basis set dependence of UCCSD is shown in Figure 8, and from both this figure and from the statistics in the tables, one can see that results with the larger cc-pVTZ basis are not improved over the smaller basis sets. This does not reflect good basis set convergence; rather it

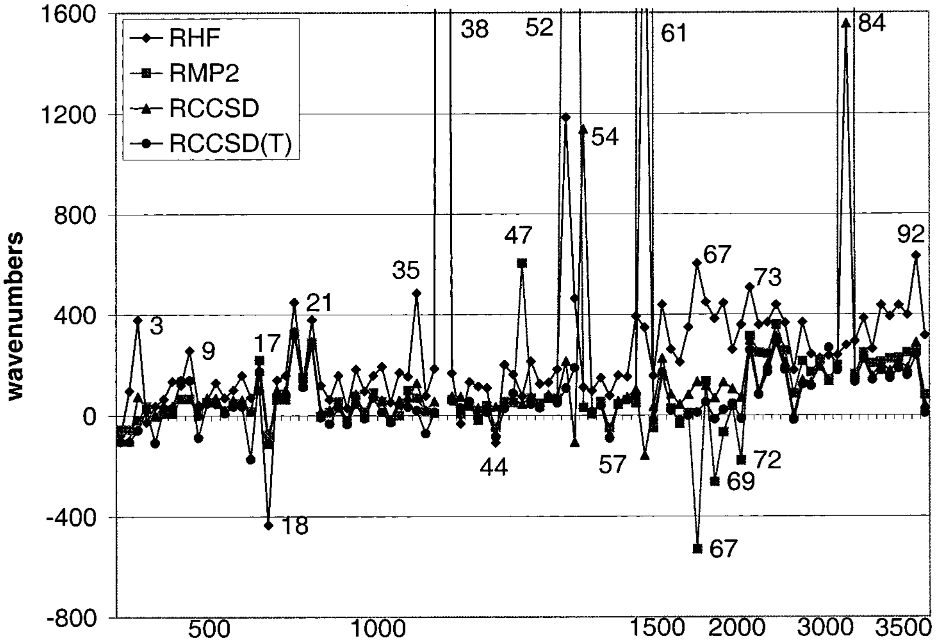

Figure 5. Restricted reference vibrational frequency errors as a function of correlation treatment. For each of the 93 vibrational frequencies listed in Table 2, given as a list along the *x* axis, the deviations in calculated HF, MP2, CCSD, and CCSD(T) bond lengths relative to experiment are plotted as the *y* value. These calculated values all use restricted (ROHF) orbitals and the largest basis set used in this study, the cc-pVTZ basis. Note also that the frequencies in Table 2 are ordered by increasing frequency, and therefore to guide the eye, we have labeled the *x*-axis in (unequally spaced) multiples of 500 cm^{-1}.

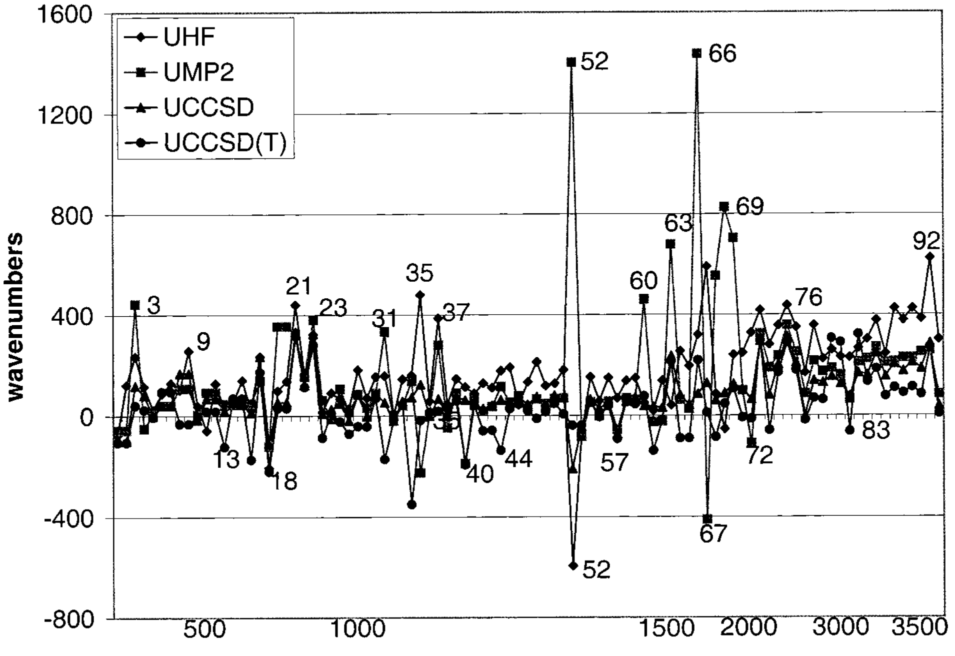

Figure 6. Unrestricted reference vibrational frequency errors as a function of correlation treatment. The deviations that result when unrestricted (UHF) orbitals are used with the cc-pVTZ basis are in the same format as that of Figure 5.

suggests that the main deviations between UCCSD and experiment are not basis-set related.

For UCCSD, the overall statistics we have obtained are considerably inferior to what has been reported previously for simple closed-shell molecules. We find UCCSD yields absolute percent errors of 7−9%, while Thomas et al.[23] found CCSD/DZP yields an average absolute percent error of 1.7% for small closed-shell molecules. Although the UCCSD percent standard deviations of 11−12% are lower than those for the other wave function methods, they are still some 12 times larger than the 0.9% standard deviation for closed-shell CCSD/DZP.[23] Thomas et al. were making comparisons to experimental harmonic frequencies, while we are making comparisons to harmonic and fundamental frequencies, which can explain part but certainly not all of this difference. At the end of this section, we will present a quantitative examination of this question.

The CCSD(T) results are an overall disappointment for frequencies much as they were for predicting geometries. UCCSD(T) does not improve upon UCCSD. ROCCSD(T) improves upon ROCCSD only after removing outliers, which suggests that its use will not always be routine. These results mirror the behavior of MP2, just as they did for geometries. The contrast between our CCSD and CCSD(T) results is

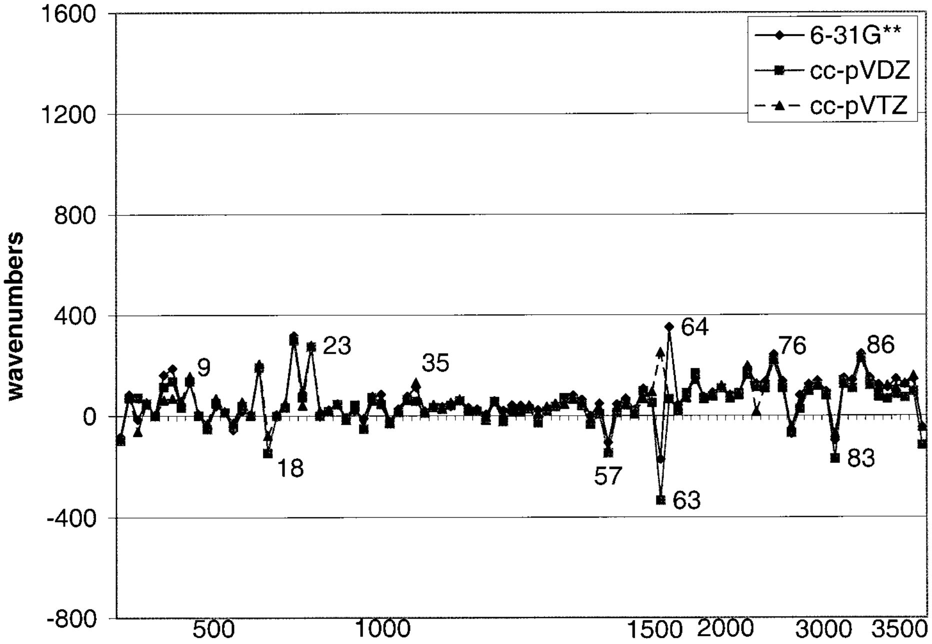

Figure 7. B3LYP vibrational frequency errors as a function of basis set. The calculated deviations in vibrational frequencies for B3LYP relative to experiment are in the same format as that of Figure 5.

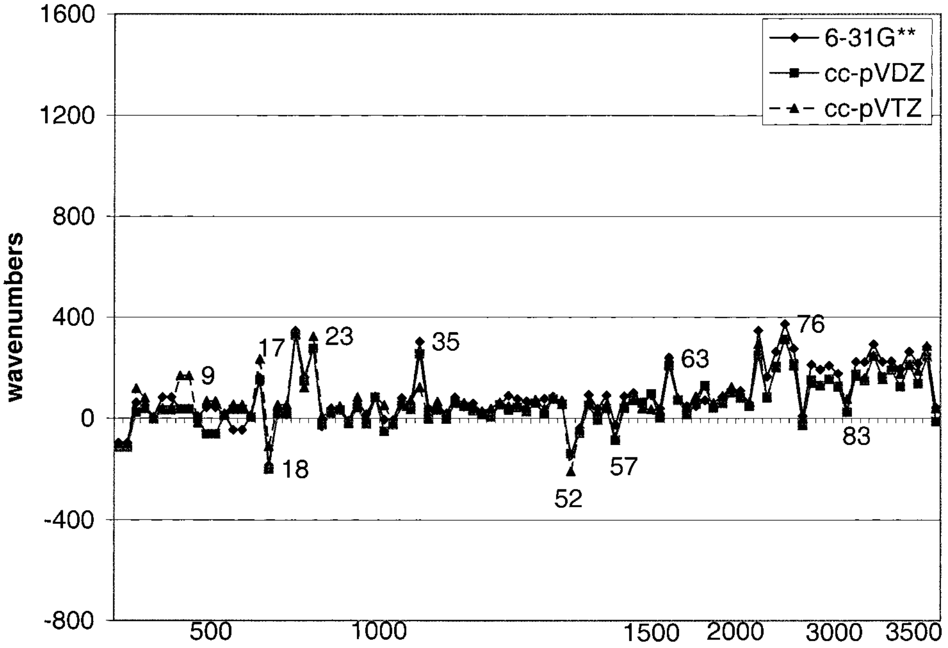

Figure 8. UCCSD vibrational frequency errors as a function of basis set. The calculated deviations in vibrational frequencies for unrestricted CCSD relative to experiment are in the same format as that of Figure 5.

sharpened further by recalling the improvement of CCSD(T) over CCSD in closed-shell systems.[24]

Figure 7 reveals how similar the B3LYP density functional theory results are to the CCSD methods. There are no large outliers relative to HF, MP2, and even CCSD(T), and statistically the uncorrected B3LYP results are the best in each of the three basis sets studied. There is a small but distinct improvement in the quality of the calculated frequencies upon going from the 6-31G* and cc-pVDZ basis sets to the larger cc-pVTZ basis. It is clear that B3LYP is the best compromise between computational cost and overall reliability for vibrational frequencies.

The comparison we have presented thus far is not strictly a direct one. The experimental frequencies are a mixture of harmonic values (e.g., for the diatomics) and measurements of fundamentals and in some cases even overtones. This gives rise to some systematic deviations between the calculations and experiment, as already alluded to earlier. For example, visual inspection of Figure 8 for UCCSD shows that calculated high-frequency values are mostly too high. This deviation is in large part due to anharmonicity in the experimental values versus calculated harmonic values.

To address how the calculated (harmonic) frequencies compare with experimentally derived harmonic frequencies, Table 9 and Figure 9 contains statistics for cc-pVTZ calculations for just those entries from Table 2 for which experimentally derived harmonic frequencies are available. This reduced dataset also eliminates most of the other problem cases to be discussed

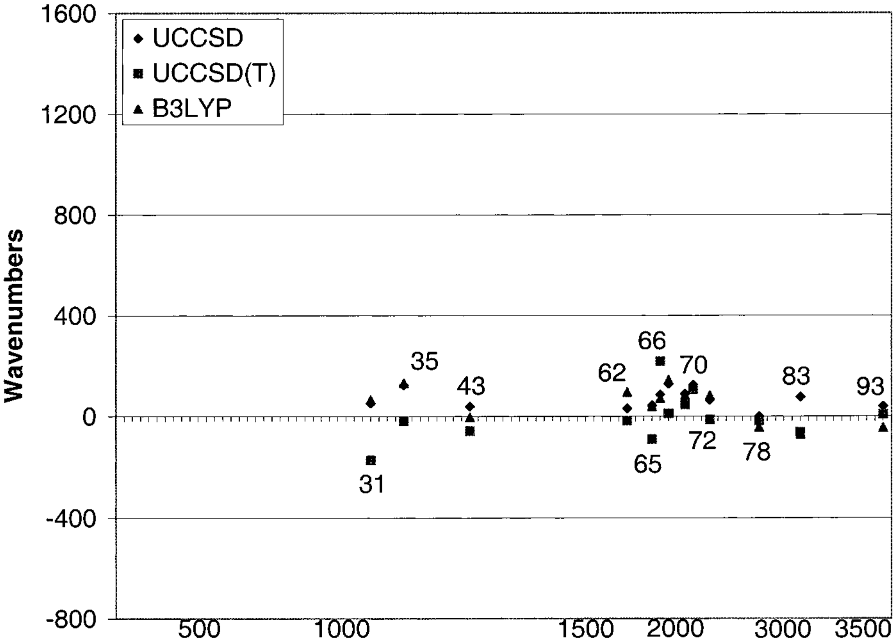

Figure 9. UCCSD, UCCSD(T), and B3LYP vibrational frequency errors in the cc-pVTZ basis set compared to experimental harmonic frequencies as noted in Table 2. The calculated deviations in vibrational frequencies for these methods relative to experiment are in the same format as that of Figure 5.

TABLE 9: Mean $\bar{\Delta}$ (cm^{-1}), Mean Percent $\bar{\Delta}$ Deviations, Mean Absolute Deviations ($\bar{\Delta}_{abs}$) (cm^{-1}), Mean Absolute Percent Deviations ($\bar{\Delta}_{abs\%}$), Standard Deviations (Δ_{std}) (cm^{-1}), and Standard Percent Deviations ($\Delta_{std\%}$) Relative to Experimental Harmonic Frequencies in Calculated Harmonic Vibrational Frequencies with the cc-pVTZ Basis Set

	$\bar{\Delta}$	$\bar{\Delta}_{\%}$	$\bar{\Delta}_{abs}$	$\bar{\Delta}_{abs\%}$	Δ_{std}	$\Delta_{std\%}$
ROHF	310	16.8	310	16.8	146	10.8
UHF	246	13.6	255	14.0	165	11.8
ROMP2	−46	−2.3	128	6.4	188	9.5
UMP2	217	10.9	335	18.4	499	26.9
ROCCSD	79	4.3	79	4.3	54	3.0
UCCSD	69	3.9	69	3.9	40	2.9
ROCCSD(T)	13	0.5	27	1.2	52	1.8
UCCSD(T)	−5	−0.9	64	3.9	94	6.2
UB3LYP	46	3.1	71	3.9	70	4.1

in the next section (Jahn−Teller distortions, etc). Comparing Table 9 and Table 8 it is evident that substantially better performance is attained with the direct comparison of harmonic-only values. The coupled cluster methods emerge as slightly more accurate than B3LYP, although UCCSD(T) is still a poor performer due to outliers for NO and OF. Unfortunately, experimentally derived harmonic frequencies are not usually available, and theoretical calculation of anharmonic effects is not yet generally feasible; therefore, this direct comparison is not usually possible for polyatomics.

D. Harmonic Vibrational Frequencies: Details. One of the modes for which all methods get incorrect results is the a_2'' mode of CH_3 (frequency 18). Initially, one might think that this underestimation is due to the lack of higher angular momentum functions in the basis sets.[48] Using the cc-pVQZ[1] and cc-pV5Z[1] basis sets with UCCSD, we computed the new geometries and a_2'' mode for this molecule. The cc-pVQZ basis set increased this frequency from the cc-pVTZ result of 496 to 506 cm^{-1}, while the cc-pV5Z basis set increased this mode to 511 cm^{-1}. We conclude that this underestimation is not due to basis set effects, but rather anharmonic effects. Due to the symmetry of the molecule, there should be no first-order anharmonic correction, but rather the leading term should be of second order. It is possible that this correction is positive and would increase the calculated frequencies. We believe this large anharmonic contribution is the basis for the consistent underestimation of this vibrational mode. However, other molecules within this sub-1000 cm^{-1} regime have errors due to other reasons entirely.

One of these molecules is the aforementioned CH_3O, which displayed symmetry breaking upon geometry optimization due to Jahn−Teller distortions for all methods. This error in the geometry obviously carries over to the frequencies, with the largest relative error apparent for mode 21 (*e*). This vibrational mode is continuously overestimated, irrelevant of method or basis set. The other degenerate modes of this molecule (numbers 56−57, 75−76) are also consistently in error but not to the same extent as the low frequency mode. This broken-symmetry surface is not harmonic and cannot be easily described by the harmonic approximation, nor by higher order corrections, and therefore we should not be surprised by the inability of these theories to predict vibrational modes of this molecule.[37]

Anharmonic corrections, broken-symmetry solutions, and incorrect geometries are only a few of the sources of error in this study. Experimental error is also a potential source of error, with several of the vibrational modes lending themselves to this explanation. For example, two of the CH_2CHO a'' vibrational modes (modes 17 and 23) are incorrect for all methods and basis sets, with both modes always too high. While it is possible that the errors in the geometry are responsible for these modes, it could also be an experimental error. These frequencies were not observed directly, but rather as overtones in fluorescence spectra.[49]

Finally, we offer an explanation for the most catastrophic failures seen in this study. The Σ_u^+ mode (52) of CO_2^+, the Σ_u^+ mode (53) of CNC, the Σ_u^+ mode (61) of N_3 and either many or all of the b_2 modes (38, 47, 54, 81, 84) of C_3H_5 all exhibit excessive errors which appear to derive from the same fundamental source, namely the poor choice of Hartree−Fock as a reference for calculations on radical species. For mode 52, we see a breakdown in the Hartree−Fock and MP2 theories, while mode 61 fails for every perturbative method except for UCCSD-

(T). Restricted open-shell Hartree−Fock and ROMP2 both yield incorrect results for mode 53, while the b_2 modes of C_3H_5 are plagued with difficulty for any correlated method based on the ROHF reference.

Commonly stated reasons for breakdowns in perturbation theories, for both the MP series and the perturbative triples correction to coupled-cluster theory, are either spin contamination or a small HOMO−LUMO gap. However, many of the systems listed above are based on the ROHF reference, which by definition has zero-spin contamination. We inspected many of the most serious failures and found the HOMO−LUMO gap to never be smaller than 9 eV, and often in excess of 11 eV. While this is not as large as the 20 eV gap found in water, it is not small enough to be a reasonable source of error in the perturbation series. Rather, what seems to be occurring is a rapid varying of the Hartree−Fock orbitals, as reported in the work of Crawford et al.,[50] who reported on an “instability volcano” in the vicinity of symmetry breaking orbital instabilities. For many of these molecules, it would be better to think of the failures as being due not to a symmetry breaking problem, but rather to an orbital instability problem, which can potentially occur in unsymmetric as well as symmetric systems.

IV. Conclusions

We have carried out calculations on 33 small radicals using the coupled-cluster based hierarchy of HF, MP2, CCSD, and CCSD(T) starting with both the restricted open-shell and unrestricted references. In the coupled-cluster series, the computational scalings go formally as n^4, n^5, n^6, and n^7, with n being the number of electrons. We have also included the B3LYP density functional theory, which scales the same as HF. The Dunning cc-pVDZ and cc-pVTZ basis sets were employed as well as the Pople 6-31G** basis set. Our main conclusions are the following:

(1) In the tradeoff between accuracy and computational cost, the best compromise is clearly B3LYP. While there are undoubtedly small remaining deficiencies in calculations at this level of theory, it performed very satisfactorily across all the molecules considered here for both geometries and vibrational frequencies. B3LYP results were systematically improved with the larger cc-pVTZ basis relative to 6-31G**.

(2) CCSD methods offer a reliable wave function-based alternative to density functional theory, but at dramatically greater computational cost. Additionally converging the reference Hartree−Fock orbitals was often problematical (see item (4) below). The accuracy of CCSD for these radicals was somewhat lower than seen for simple closed-shell molecules.

(3) CCSD(T) does not offer the same systematic improvement over CCSD that is observed in closed shell calculations apparently because of problems with the Hartree−Fock orbitals (see item 4 below). We suspect that the use of Bruckner type orbitals[51,52] or even Kohn−Sham orbitals might largely alleviate this problem, but that is beyond the scope of this study.

(4) Hartree−Fock and MP2 methods are both too erratic to be recommended for general use. This seems to arise primarily from artifactual symmetry breaking and orbital instabilities in the HF equations for radicals. These same difficulties make the HF equations difficult to converge. They also appear to partly account for the relative performance of CCSD(T) compared to CCSD itself.

(5) We have identified systematic discrepancies between the best calculations reported here (i.e., both CCSD and B3LYP) and existing experimental data for several molecules. For bond lengths, this includes NCO, C_3H_5, and CH_2CHO, as well as $C_4H_2^+$. For frequencies this includes CH_2CHO. In most of these cases, based on both the reliability of the best computational methods and examination of the specific experiments, we believe the experimentally derived values should be reevaluated.

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