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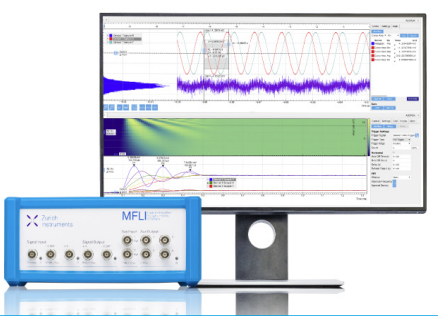

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The balance between theoretical method and basis set quality: A systematic study of equilibrium geometries, dipole moments, harmonic vibrational frequencies, and infrared intensities

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Analytic gradient methods have been used to predict the equilibrium geometries, dipole moments, harmonic vibrational frequencies, and infrared (IR) intensities of HCN, HNC, CO_2, CH_4, NH_4^+, HCCH, H_2O, H_2CO, NH_3, and FCCH at the self-consistent-field (SCF), the single and double excitations configuration interaction (CISD), the single and double excitations coupled-cluster (CCSD), and the single, double, and perturbative triple excitations coupled-cluster [CCSD(T)] levels of theory. All studies were performed using a triple zeta plus double polarization (TZ2P) basis set and a TZ2P basis set augmented with one set of higher angular momentum functions [TZ (2*df*,2*pd*)]. The predicted equilibrium geometries, dipole moments, harmonic vibrational frequencies, and IR intensities were compared to available experimental values. The geometries were predicted accurately at the highest levels of theory. Most of the dipole moments were found to agree favorably with experiment. With the TZ2P basis set, the average absolute errors in harmonic vibrational frequencies with respect to experiment were 9.9%, 3.8%, 1.5%, and 2.3% for the SCF, CISD, CCSD, and CCSD(T) methods, respectively. With the TZ(2*df*,2*pd*) basis set, the four methodologies yielded average absolute errors of 10.3%, 6.3%, 3.7%, and 2.2%, respectively. When the absolute errors for bending modes of triply bonded molecules and the a_1 umbrella mode of NH_3 were excluded from the previous two sets of averages, the TZ2P average errors became 7.3% (SCF), 3.0% (CISD), 1.1% (CCSD), and 1.1% [CCSD(T)], and the TZ(2*df*,2*pd*) average errors became 7.4% (SCF), 3.5% (CISD), 1.5% (CCSD), and 0.6% [CCSD(T)]. Theoretical IR intensities were generally close to given experimental values. Among the eight methodologies investigated in this research, the TZ2P CCSD and the TZ(2*df*,2*pd*) CCSD(T) methods exhibited the best balance between theoretical method and basis set quality. This "balance" was evident in the *simultaneous* prediction of the most accurate values overall for the molecular properties compared.

INTRODUCTION

The single, double, and perturbative triple excitations coupled-cluster [CCSD(T)] method was first developed by Raghavachari *et al.*[1] as a computationally inexpensive way to incorporate the effects of connected triple excitations in the coupled-cluster procedure. The CCSD(T) method is therefore an approximation to the full single, double, and triple excitations coupled-cluster (CCSDT) method. The full CCSDT method was initially developed and implemented by Noga and Bartlett[2] and later by Scuseria and Schaefer.[3] More recently, Rendell, Lee, and Komornicki[4] employed a parallel vectorized algorithm to determine the triples contribution to the CCSD(T) energy. Numerous studies[5–10] have shown the usefulness of the CCSD(T) method. The CCSD(T) method is less expensive than the CCSDT method because connected T_3 terms are not included directly in the exponential wave function. Instead, the CCSD(T) method approximates the effects of connected triples terms with a perturbative energy correction, $E_{(T)}$, which is simply added to the single and double excitations coupled-cluster (CCSD) energy to obtain the CCSD(T) energy. This correction is obtained using the converged single- and double-excitation amplitudes from a CCSD wave function. Therefore, the CCSD(T) procedure partially accounts for both interactions between single and triple excitations and interactions between double and triple excitations. Analytic CCSD(T) gradients are determined using the method of analytic CCSD gradients with the addition of the derivative of the perturbative triples correction to the energy. For a more detailed discussion, the reader may refer to earlier papers on the formulation of the closed-shell[9] and open-shell[11] CCSD(T) energy and the closed-shell gradient[12] techniques.

The present research utilizes analytic closed-shell CCSD(T) gradient techniques in a systematic study of the equilibrium geometries, dipole moments, harmonic vibrational frequencies, and infrared (IR) intensities of the HCN, HNC, CO_2, CH_4, NH_4^+, HCCH, H_2O, H_2CO, NH_3, and FCCH molecules with a triple zeta plus double polarization functions (TZ2P) basis set and a TZ2P basis set augmented with one set of higher angular momentum polarization functions on all atoms [TZ(2*df*,2*pd*)]. This

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type of study has been performed previously in this laboratory for the self-consistent-field (SCF) and single and double excitations configuration interaction (CISD) methods,[13] the CCSD method,[14] and the CCSD(T) method[15] using a double-zeta plus polarization (DZP) basis set. These earlier studies have proven useful because they give reasonable general estimates of the systematic errors involved in theoretically predicted values for a basis set relative to experimental values. This information is particularly valuable when applying the theoretical methods in question to molecules or physical properties of molecules that have not yet been experimentally observed. For example, accurate theoretical harmonic vibrational frequencies are very desirable since anharmonicity corrections and associated theoretical errors are an order of magnitude smaller than the harmonic frequencies themselves.[16–19] Therefore, much more reliable theoretical fundamentals can be predicted if the harmonic frequencies are accurate. The accurate theoretical prediction of thermodynamic properties also requires a knowledge of reliable harmonic frequencies.[20]

Systematic studies of this type also illustrate problems that can arise if a proper balance is not kept between the quality of basis sets employed and improvements in the method for treating electron correlation. For example, it has recently been shown that a marginal improvement in theoretically predicted harmonic vibrational frequencies when switching from the DZP CCSD to the DZP CCSD(T) methodology is accompanied by a noticeable worsening in the theoretically predicted equilibrium geometries.[15] It was expected that the use of larger basis sets than the DZP basis sets employed in our previous studies would produce more accurate results when used in conjunction with the CCSD and CCSD(T) methods. A logical choice to achieve this improvement is a TZ2P basis. It has been shown[21,22] that a further step in improving basis set quality beyond that of TZ2P is *not* toward saturation of the *spd* space but rather the inclusion of higher angular momentum functions in the basis set. Thus, a TZ(2*df*,2*pd*) basis set is preferable to a quadruple zeta plus three sets of polarization functions (QZ3P) basis.

The present research includes all electrons in the various correlation procedures utilized here in order to directly compare with the previous systematic studies using the DZP basis set.[13–15] We realize that many recent theoretical studies in correlated levels of theory have frozen the core electrons of heavy atoms. The inclusion of these core electrons may create a problem because the basis set size used in the current study may not be large enough to adequately include core–core and core–valence correlation.[23]

THEORETICAL DETAILS

The *ab initio* methods employed in this work were essentially the same as those used in the previous studies.[13–15] Rather than the DZP basis set of the earlier studies, larger TZ2P and TZ(2*df*,2*pd*) basis sets of contracted Gaussian functions were used. The present research included all nine of the previously studied molecules, as well as FCCH. The TZ2P basis sets consisted of Huzinaga's[24] (10*s*6*p*) primitive sets for heavy atoms (C,N,O,F) and (5*s*) primitive set for H contracted by Dunning[25] to (5*s*3*p*) for the C,N,O, and F atoms and (3*s*) for H. These were augmented with two sets of polarization functions with orbital exponents $\alpha_d(\mathrm{C})=1.50$, 0.375, $\alpha_d(\mathrm{N})=1.60$, 0.40, $\alpha_d(\mathrm{O})=1.70$, 0.425, $\alpha_d(\mathrm{F})=2.00$, 0.50, and $\alpha_p(\mathrm{H})=1.50$, 0.375. The orbital exponents for the polarization functions were deduced from the suggestions of Frisch, Pople, and Binkley.[26] Therefore, the complete contraction scheme for the TZ2P basis set is (10*s*6*p*2*d*/5*s*3*p*2*d*) for all heavy atoms (C,N,O,F) and (5*s*2*p*/3*s*2*p*) for H. The TZ(2*df*,2*pd*) basis set was obtained by augmenting the TZ2P basis with one set of higher angular momentum polarization functions for all atoms. Thus, the complete contraction scheme for the TZ(2*df*,2*pd*) basis set is (10*s*6*p*2*d*1*f*/5*s*3*p*2*d*1*f*) for all heavy atoms and (5*s*2*p*1*d*/3*s*2*p*1*d*) for H. The orbital exponents for the higher angular momentum polarization functions were $\alpha_f(\mathrm{C})=0.80$, $\alpha_f(\mathrm{N})=1.00$, $\alpha_f(\mathrm{O})=1.40$, $\alpha_f(\mathrm{F})=1.85$, and $\alpha_d(\mathrm{H})=1.00$. Sets of six Cartesian *d*-like and ten Cartesian *f*-like Gaussian functions were used throughout.

Analytic restricted Hartree–Fock SCF,[27,28] CISD,[29–32] CCSD,[33] and CCSD(T) [12] closed-shell gradient techniques were used to fully optimize all structures. All residual Cartesian and internal coordinate gradients were less than 10^{-6} atomic units. The SCF harmonic vibrational frequencies were obtained from analytic SCF second derivatives of the energy.[34,35] SCF IR intensities were evaluated analytically[36] within the double harmonic approximation (i.e., neglect of the anharmonicity of the potential energy surface and of the nonlinear relationship of the dipole moment to the normal coordinates).

The CISD wave functions were determined with the shape-driven graphical unitary group approach.[37] The number of single and double excitations for each molecule in the various symmetries required to perform the optimizations and finite differences displacements with the TZ2P basis set were as follows: 39 761 (D_{2h}) and 79 118 (C_{2v}) for CO_2; 15 172 (C_{2v}) and 54 391 (C_s) for HCCH; 21 925 (C_{2v}) and 39 760 (C_s) for HCN and HNC; 10 381 (D_{2h}) and 41 041 (C_1) for NH_4^+ and CH_4; 15 103 (C_s) for NH_3; 35 570 (C_{2v}) and 69 141 (C_s) for H_2CO; 5423 (C_{2v}) and 10 543 (C_s) for H_2O; and 102 570 (C_{2v}) and 189 841 (C_s) for FCCH. For the TZ(2*df*,2*pd*) basis set, the number of configurations for the various molecular symmetries were as follows: 79 451 (D_{2h}) and 158 339 (C_{2v}) for CO_2; 32 456 (C_{2v}) for HCCH; 45 399 (C_{2v}) and 84 661 (C_s) for HCN and HNC; 26 226 (D_2), 27 666 (C_{2v}), and 52 216 (C_2) for NH_4^+ and CH_4; 37 237 (C_s) for NH_3; 78 336 (C_{2v}) and 153 901 (C_s) for H_2CO; 12 726 (C_{2v}) and 25 006 (C_s) for H_2O; and 212 580 (C_{2v}) and 402 445 (C_s) for FCCH.

The correlated frequencies were obtained by the method of central finite differences of CISD, CCSD, and CCSD(T) gradients with the exception of the TZ(2*df*,2*pd*) CCSD and the TZ2P and TZ(2*df*,2*pd*) CCSD(T) FCCH frequencies. These frequencies were found from finite differences of energies because of the extreme computational cost of evaluating the gradients. At

correlated levels of theory, IR intensities were also determined using the double (mechanical and electrical) harmonic approximation. All electrons and all orbitals were included in the correlated wave functions. The CI [38,30] and CC [33] dipole moments were evaluated as energy derivatives with respect to an external electric field, and dipole moment derivatives were obtained through the finite differences procedure.

RESULTS AND DISCUSSION

Tables I–X report the total energies, equilibrium bond lengths (r_e), bond angles (θ_e), dipole moments (μ_e), harmonic vibrational frequencies (ω_e), and infrared intensities (I) for the ten molecules at the SCF, CISD, CCSD, and CCSD(T) levels of theory with the TZ2P and TZ(2*df*,2*pd*) basis sets, as well as available experimental values. Table XI reports the average error between the theoretical and experimental equilibrium bond lengths and the standard deviation at the various levels of theory for the two basis sets. Table XII contains the percentage errors between the theoretical and experimental equilibrium bond angles. Table XIII gives the percentage errors between theoretical and experimental dipole moments. Table XIV presents the average error between the theoretical and experimental harmonic frequencies and the standard deviation. Table XV summarizes the average absolute errors in equilibrium bond lengths and harmonic vibrational frequencies for all eight methodologies employed in this study. The present results obtained with the TZ2P and TZ(2*df*,2*pd*) basis sets will be the primary focus of this discussion. For detailed discussion of the DZP results, refer to the earlier papers by Yamaguchi and Schaefer,[13] Besler *et al.*,[14] and Thomas *et al.*[15] The following discussion is separated into sections that compare the results for both basis sets for the specified zeroth-, first-, and second-order molecular properties.

Equilibrium geometries

Results presented in Table XI show that the accuracy of the TZ2P and TZ(2*df*,2*pd*) CCSD and CCSD(T) equilibrium bond lengths improved drastically relative to the previously reported DZP results.[14,15] The average absolute error for the 13 bond lengths compared in this study is 0.21% for TZ2P CCSD(T), while the TZ2P CCSD average error is only 0.15%. The main difference between the errors in bond lengths for the two methods lies in the direction of the error. The TZ2P CCSD method *underestimates* 11 of the 13 experimental bond lengths, whereas TZ2P CCSD(T) *overestimates* 10 of 13. The TZ(2*df*,2*pd*) results show that the CCSD error is 0.21% whereas that of CCSD(T) is 0.17%. The TZ2P CCSD and CCSD(T) results confirm the importance of maintaining a balance between basis set and method. Note that the TZ2P CCSD and TZ(2*df*,2*pd*) CCSD(T) methods give the smallest absolute average errors in bond lengths. Comparison with the larger absolute errors for the TZ2P CCSD(T) and TZ(2*df*,2*pd*) CCSD methodologies again confirms the importance of maintaining a balance between the quality of basis and theoretical methodology. Table XII shows that the predicted bond angles at the TZ2P and TZ(2*df*,2*pd*) CCSD(T) levels are also in good agreement with the experimental values.

It should be noted that experimental equilibrium geometrical variables are only as reliable as the uncertainty inherent in the procedure used to derive these values from the experimentally observed spectrum and by the approximations used in the model potential employed in fitting the experimental data.[39–41]

Dipole moments

Generally, experimentally determined dipole moments are not equilibrium values (μ_e) but are actually μ_0 values. Furthermore, the state for which the dipole moment is experimentally reported often is not the rotational ground state. This is because experimental dipole moments are usually measured from Stark shifts and require a transition from one rotational state to another (rotational dependence is needed in the state being studied). For these reasons, a direct comparison between theoretical and experimental dipole moments is only useful on an approximate level. *Quantitative* agreement between theory and experiment does not explicitly imply accuracy of the theoretical predictions.

With these points in mind, Table XIII shows that the most reasonable dipole moments are predicted for both basis sets at correlated levels of theory. As expected, CCSD(T) dipole moments, in general, lie closer to experimental values than for any of the other three levels of theory studied presently. However, it is worth noting that the CCSD(T) dipole moments are not *always* the closest to experimental values (i.e., CISD gives the closest value for HNC).

Harmonic vibrational frequencies

The three previous systematic studies[13–15] reported the average error in theoretical DZP harmonic vibrational frequencies with respect to experiment as 9.1% for SCF, 3.7% for CISD, 2.3% for CCSD, and 2.4% for CCSD(T) for seven of the eight molecules (FCCH was previously excluded) studied in this work. The present research found the average error for the TZ2P SCF, CISD, CCSD, and CCSD(T) methods to be 8.9%, 3.2%, 1.6%, and 2.0%, respectively, for the same seven molecules (HNC and NH_4^+ had no reliable experimental harmonic frequencies for comparison with theoretical results). The TZ(2*df*,2*pd*) averages were 8.2%, 4.2%, 2.1%, and 1.2%, respectively. A direct comparison of the average absolute errors given above with the previously reported DZP results[13–15] shows the favorable effect of larger basis sets on the harmonic frequencies.

The present study also includes the results for the FCCH molecule for a total comparison of 33 vibrational modes (out of a total of 40 possible). For all eight molecules, the average absolute errors in frequencies for the SCF, CISD, CCSD, and CCSD(T) methods with the

TABLE I. Comparison of theoretical predictions with experimental values for molecular properties of HCN. All theoretical parameters are evaluated at the equilibrium geometry. All experimental parameters are equilibrium values unless indicated otherwise. The bond lengths used to determine the percent differences in Table XI were taken from footnote a and the harmonic frequencies used to compute the percent differences in Table XIV were taken from footnote e.

	SCF		CISD		CCSD		CCSD(T)					
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.			
E (hartrees)	−92.909 87	−92.913 00	−93.241 83	−93.271 21	−93.268 72	−93.300 26	−93.285 37	−93.318 50				
r_e(C–H) (Å)	1.0571	1.0569	1.0616	1.0582	1.0659	1.0621	1.0680	1.0639	1.065 49 ± 0.000 24[a]			
									1.065 01 ± 0.000 08[b]			
r_e(C–N) (Å)	1.1236	1.1241	1.1417	1.1406	1.1498	1.1488	1.1569	1.1560	1.153 21 ± 0.000 05[a]			
									1.153 24 ± 0.000 02[b]			
μ_e(D)	3.262	3.261	3.080	3.088	3.026	3.034	2.985	2.990	μ_0 = 2.985[c]			
Harmonic vibrational frequencies (cm^{-1})												
$\omega_1(\sigma^+)$	3610	3613	3501	3556	3437	3498	3408	3470	3442[d]	3440[e]	3442[f]	3444[g]
$\omega_2(\pi)$	862	883	750	849	710	817	679	791	727[d]	727[e]	727[f]	725[g]
$\omega_3(\sigma^+)$	2406	2409	2248	2266	2173	2193	2109	2128	2129[d]	2128[e]	2127[f]	2130[g]
Infrared intensities (km mol^{-1})												
I_1	73	71	68	71	64	66	61	64	54[h]			
I_2	71	70	70	69	71	70	72	71	46[h]			
I_3	9.9	10.4	1.8	1.9	0.3	0.6	0.01	0.06	0.1[h]			

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TABLE II. Comparison of theoretical predictions with experimental values for molecular properties of HNC. All theoretical parameters are evaluated at the equilibrium geometry. All experimental parameters are equilibrium values unless indicated otherwise.

	SCF		CISD		CCSD		CCSD(T)		
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.
E (hartrees)	−92.892 44	−92.896 48	−93.219 37	−93.248 23	−93.244 95	−93.275 81	−93.261 00	−93.293 37	
r_e(N–H) (Å)	0.9814	0.9820	0.9889	0.9887	0.9932	0.9930	0.9957	0.9956	0.9941[a]
r_e(C–N) (Å)	1.1442	1.1451	1.1590	1.1582	1.1658	1.1649	1.1728	1.1719	1.1689[a]
μ_e(D)	2.964	2.944	3.084	3.072	3.099	3.086	3.104	3.092	$\mu_0=3.05\pm0.1$[b]
Harmonic vibrational frequencies (cm^{-1})									
$\omega_1(\sigma^+)$	4052	4054	3915	3940	3847	3873	3809	3835	$\nu_1=3653$[c,d]
$\omega_2(\pi)$	484	553	453	570	431	552	404	529	$\nu_2=464$[c]
$\omega_3(\sigma^+)$	2283	2284	2157	2174	2101	2119	2037	2055	$\nu_3=2024$[c]
Infrared intensities (km mol^{-1})									
I_1	373	371	346	292	256	262	233	239	
I_2	318	322	279	282	271	274	268	270	
I_3	97	100	63	67	58	59	54	54	

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TZ2P basis were 9.9%, 3.8%, 1.5%, and 2.3%, respectively. For the TZ(2*df*,2*pd*) basis, the average errors were 10.3%, 6.3%, 3.7%, and 2.2%.

Table XIV shows that excluding the bending modes of the triply bonded molecules (HCN π mode, HCCH π_u and π_g modes, and both FCCH π modes) as well as the NH_3 a_1 umbrella mode from the TZ2P and TZ(2*df*,2*pd*) average absolute errors led to further improvement in those values. The SCF, CISD, CCSD, and CCSD(T) averages after exclusion of the aforementioned modes were 7.3%, 3.0%, 1.1%, and 1.1%, respectively, for the TZ2P basis and 7.4%, 3.5%, 1.5%, and 0.6% for the TZ(2*df*,2*pd*) basis. The greatest improvement from the exclusion of these modes was seen for the CCSD(T) method, in which the average absolute errors for both basis sets decreased by more than a factor of 2. The bending mode problem has been attributed to basis set incompleteness. Simandiras *et al.* showed[21] that when basis sets were increased by saturating only the *spd* space, the bending frequencies of HCCH became progressively smaller in magnitude, thus underestimating the experimental values by larger amounts. The conclusion drawn from their studies was that the *d* and *f* functions must be kept "in balance." Specifically, it was found that one set of *f* functions complemented two sets of *d* functions and that two sets of *f* functions complemented three sets of *d* functions. In this manner, a TZ(2*df*,2*pd*) basis should be a balanced extension of the TZ2P basis set. For more information on basis set inadequacies with respect to the aforementioned excluded modes, refer to the discussion in our earlier paper[15] or to earlier papers concerning the NH_3,[42–44] HCCH,[21] and FCCH [45] molecules, specifically.

TABLE III. Comparison of theoretical predictions with experimental values for molecular properties of CO_2. All theoretical properties are evaluated at the equilibrium geometry. All experimental parameters are equilibrium values.

	SCF		CISD		CCSD		CCSD(T)		
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.
E (hartrees)	−187.708 85	−187.717 99	−188.242 28	−188.303 32	−188.299 81	−188.366 91	−188.325 95	−188.395 90	
r_e(C–O) (Å)	1.1351	1.1349	1.1491	1.1467	1.1582	1.1558	1.1655	1.1629	1.160[a,b]
Harmonic vibrational frequencies (cm^{-1})									
$\omega_1(\sigma_g^+)$	1505	1513	1429	1442	1376	1389	1332	1345	1354[c]
$\omega_2(\pi_u)$	767	779	700	729	668	697	643	672	573[c]
$\omega_3(\sigma_u^+)$	2538	2556	2452	2502	2380	2432	2340	2391	2397[c]
Infrared intensities (km mol^{-1})									
I_2	123	128	81	87	65	70	55	59	48[d]
I_3	1057	1071	834	849	738	749	624	634	548[e]

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TABLE IV. Comparison of theoretical predictions with experimental values for molecular properties of CH_4. All theoretical properties are evaluated at the equilibrium geometry. All experimental parameters are equilibrium values unless indicated otherwise. The bond lengths used to calculate the percent differences in Table XI were taken from footnote a.

	SCF		CISD		CCSD		CCSD(T)		
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.
E (hartrees)	−40.213 72	−40.214 14	−40.423 90	−40.442 73	−40.433 89	−40.453 72	−40.439 46	−40.460 21	
r_e(C–H) (Å)	1.0813	1.0818	1.0827	1.0829	1.0852	1.0854	1.0865	1.0867	1.0858±0.0010[a] 1.0862±0.0024[b] 1.0870±0.0007[c]
Harmonic vibrational frequencies (cm^{-1})									
$\omega_1(a_1)$	3161	3150	3078	3077	3046	3044	3028	3027	3026[a]
$\omega_2(e)$	1675	1668	1608	1599	1592	1583	1583	1571	1583[a]
$\omega_3(t_2)$	3259	3249	3191	3195	3159	3162	3143	3147	3157[a]
$\omega_4(t_2)$	1459	1455	1386	1378	1372	1363	1361	1351	1367[a]
Infrared intensities (kcal mol^{-1})									
I_3	115	116	74	66	74	66	73	64	69±3,[d] 72±11,[e] 70±3[f]
I_4	29	29	30	33	29	32	29	32	29±1,[d] 41±6[e]

[a]D. L. Gray and A. G. Robiette, Mol. Phys. **37**, 1901 (1979).
[b]L. S. Bartell and K. Kuchitsu, J. Chem. Phys. **68**, 1213 (1978).
[c]E. Hirota, J. Mol. Spectrosc. **77**, 213 (1979).
[d]R. E. Hiller and J. W. Straley, J. Mol. Spectrosc. **5**, 24 (1960).
[e]D. E. Burch and D. Williams, Appl. Opt. **1**, 587 (1962).
[f]P. Varanasi, L. A. Pugh, and B. R. P. Bangaru, J. Quant. Spectrosc. Radiat. Transfer **14**, 829 (1974).

At the SCF level of theory, all theoretical frequencies are overestimated and all theoretical equilibrium bond lengths are shorter than the experimental ones. By the time the TZ2P and TZ(2*df*,2*pd*) CCSD(T) levels of theory are reached, almost all of the theoretical frequencies have either just slightly overestimated or have underestimated the experimental values. In all cases, the frequencies decrease and the bonds elongate with improved correlation. This trend for frequencies to decrease as the bond lengths elongate is expected from Badger's rule.[46,47]

Of all the methodologies studied, TZ2P CCSD, TZ2P CCSD(T), and TZ(2*df*,2*pd*) CCSD(T) prove to be the most accurate in predicting the harmonic vibrational frequencies and the equilibrium bond lengths. Clearly, the TZ(2*df*,2*pd*) CCSD(T) method is the most accurate of the three with respect to predicted harmonic frequencies. As seen in Table XIV, over a third (12) of the 33 harmonic frequencies differ by no more than 0.5% (absolute error) with this method. Also, over two-thirds (25) of this method's predicted frequencies differ by no more than 1.2%. The only modes greater than 3% are the troublesome π modes and the NH_3 a_1 umbrella mode. This distribution clearly demonstrates the expected superiority of the TZ(2*df*,2*pd*) CCSD(T) method in accurately reproducing harmonic frequencies compared to the other methodologies employed in the current research.

Martin, Lee, and Taylor[48] recently used the CCSD(T) method to predict the harmonic vibrational frequencies and the quartic force field of NH_3 with two large correlation-consistent basis sets[49] denoted cc-pVTZP

TABLE V. Comparison of theoretical predictions with experimental values for molecular properties of NH_4^+. All theoretical properties are evaluated at the equilibrium geometry.

	SCF		CISD		CCSD		CCSD(T)		
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.
E (hartrees)	−56.565 53	−56.566 17	−56.798 63	−56.818 59	−56.808 67	−56.829 59	−56.814 51	−56.836 31	
r_e(N–H) (Å)	1.0096	1.0098	1.0164	1.0173	1.0191	1.0202	1.0206	1.0219	r_0=1.028 73±0.000 02[a] r_e=1.0208±0.0020[a] (Estimated)
Harmonic vibrational frequencies (cm^{-1})									
$\omega_1(a_1)$	3582	3571	3469	3442	3429	3400	3407	3377	
$\omega_2(e)$	1860	1848	1795	1767	1780	1752	1771	1741	
$\omega_3(t_2)$	3693	3686	3576	3559	3538	3519	3519	3498	ν_3=3343[b]
$\omega_4(t_2)$	1610	1603	1539	1520	1525	1504	1514	1492	
Infrared intensities (km mol^{-1})									
I_3	580	587	532	551	514	533	507	526	
I_4	465	459	427	428	420	420	415	416	

[a]M. W. Crofton and T. Oka, J. Chem. Phys. **86**, 5983 (1987).
[b]E. Schäfer, R. J. Saykally, and A. G. Robiette, J. Chem. Phys. **80**, 3969 (1984).

TABLE VI. Comparison of SCF, CISD, CCSD, and CCSD(T) theoretical results for the TZ2P and TZ(2*df*,2*pd*) basis sets with experimental values for molecular properties of HCCH. All theoretical properties are reported at the equilibrium geometry. All experimental properties are equilibrium values unless indicated otherwise.

	SCF		CISD		CCSD		CCSD(T)		
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.
E (hartrees)	−76.849 39	−76.852 64	−77.158 40	−77.189 63	−77.183 97	−77.217 52	−77.199 20	−77.234 43	
r_e(C–C) (Å)	1.1797	1.1799	1.1934	1.1907	1.2009	1.1980	1.2073	1.2042	1.202 57 ± 0.000 09[a]
r_e(C–H) (Å)	1.0536	1.0542	1.0564	1.0559	1.0601	1.0595	1.0618	1.0611	1.062 15 ± 0.000 17[a]
Harmonic vibrational frequencies (cm^{-1})									
$\omega_1(\sigma_g^+)$	3671	3668	3590	3613	3533	3560	3508	3536	3495[b]
$\omega_2(\sigma_g^+)$	2208	2210	2098	2131	2039	2078	1991	2032	2008[b]
$\omega_3(\sigma_u^+)$	3556	3556	3462	3503	3408	3453	3386	3434	3415[b]
$\omega_4(\pi_g)$	785	813	635	788	578	752	528	716	624[b]
$\omega_5(\pi_u)$	855	870	787	839	755	813	734	794	747[b]
Infrared intensities ($km\ mol^{-1}$)									
I_3	97	95	84	90	77	83	75	81	71 ± 2[c]
I_5	236	231	199	194	191	186	186	182	175 ± 5[c]

[a]A. Baldacci, S. Ghersetti, S. C. Hurlock, and K. N. Rao, J. Mol. Spectrosc. **59**, 116 (1976).
[b]G. Strey and I. M. Mills, J. Mol. Spectrosc. **59**, 103 (1976).
[c]T. Koops, W. M. A. Smit, and T. Visser, J. Mol. Struct. **112**, 285 (1984).

[(4*s*3*p*2*d*1*f*) for N, (3*s*2*p*1*d*) for H] and ccVQZ [(5*s*4*p*3*d*2*f*1*g*) for N, (4*s*3*p*2*d*1*f*) for H]. They concluded that their theoretical harmonic vibrational frequencies ω_1, ω_3, and ω_4 (3472, 3598, and 1688 cm^{-1} for cc-pVTZ and 3481, 3609, and 1680 cm^{-1} for cc-pVQZ) supported the two recently measured sets of experimental vibrational frequencies by Lehmann and Coy[50,51] over the accepted values of Duncan and Mills[52] for these three fundamentals. Lehmann and Coy did not report a value for the highly anharmonic a_1 umbrella mode, ω_2. However, Martin and Lee hypothesized that Duncan and Mills' experimental ω_2 value of 1022 cm^{-1} was too small by at least 20 to 30 cm^{-1}. If this is so, then their predicted theoretical values of 1109 cm^{-1} (cc-pVTZ) and 1084 cm^{-1} (cc-pVQZ) are in good agreement with the "true value." They attributed this underestimation to the experimentalists' neglect of higher than quartic anharmonicity in determination of the harmonics from the fundamentals. Higher orders of anharmonicity are needed to correctly describe the motion that results from a small inversion barrier and a high upper level for the ν_2 fundamental.

The present results tend to support Martin and Lee's

TABLE VII. Comparison of theoretical predictions with experimental values for molecular properties of H_2O. All theoretical properties are evaluated at the equilibrium geometry. All experimental parameters are equilibrium values unless indicated otherwise. The r_e value used to compute the average error in bond lengths in Table XI was taken from footnote a.

	SCF		CISD		CCSD		CCSD(T)		
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.
E (hartrees)	−76.061 35	−76.062 90	−76.311 69	−76.337 74	−76.322 57	−76.349 70	−76.329 39	−76.357 72	
r_e(O–H) (Å)	0.9400	0.9402	0.9523	0.9530	0.9558	0.9568	0.9582	0.9594	0.9572 ± 0.0003[a] 0.9578[b]
θ_e(HOH) (deg)	106.3	106.4	104.9	104.8	104.7	104.5	104.4	104.2	104.5[a,b]
μ_e(D)	1.988	1.984	1.940	1.939	1.932	1.931	1.922	1.920	$^0\mu_x$ = 1.8473 ± 0.0010[c]
Harmonic vibrational frequencies (cm^{-1})									
$\omega_1(a_1)$	4139	4134	3943	3937	3883	3874	3845	3835	3832[a]
$\omega_2(a_1)$	1764	1745	1702	1676	1690	1662	1679	1650	1649[a]
$\omega_3(b_2)$	4238	4235	4042	4039	3987	3981	3951	3944	3943[a]
Infrared intensities ($km\ mol^{-1}$)									
I_1	14.8	16.5	6.2	8.4	4.4	6.2	3.2	4.7	2.2,[c] 2.2,[d] 2.2,[e] 2.5[f]
I_2	96.4	96.5	75.7	76.3	72.1	72.6	69.2	69.5	53.6,[c] 63.9,[d] 66.6,[e] 71.9[f]
I_3	80.7	85.4	53.6	60.3	47.2	52.9	42.9	48.4	44.6,[c] 48.2,[d] 39.8[e]

[a]A. R. Hoy, I. M. Mills, and G. Strey, Mol. Phys. **24**, 1265 (1972).
[b]A. R. Hoy and P. R. Bunker, J. Mol. Spectrosc. **74**, 1 (1979).
[c]S. A. Clough, Y. Beers, G. P. Klein, and L. S. Rothman, J. Chem. Phys. **59**, 2254 (1973).
[d]R. A. McClatchey, W. S. Benedict, S. A. Clough, D. E. Burch, R. F. Calfee, K. Fox, L. S. Rothman, and J. S. Garing "Atmospheric Absorption Line Parameters Compilation," Air Force Cambridge Research Laboratory Tecnical Report 73-0096, 1973.
[e]D. J. Swanton, G. B. Backsay, and N. S. Hush, J. Chem. Phys. **84**, 5715 (1986).
[f]C. W. von Rosenberg, N. H. Pratt, and K.N.C. Bray, J. Quant. Spectrosc. Radiat. Transfer **10**, 1155 (1970).

TABLE VIII. Comparison of theoretical predictions with experimental values for the molecular properties of H_2CO. All properties are evaluated at the equilibrium geometry. All experimental parameters are equilibrium values unless indicated otherwise. Experimental frequencies from footnotes g and h are used to compute the percent differences in Table XIV. The experimental equilibrium structure used to compute errors in Tables XI and XII was taken from footnote a.

	SCF		CISD		CCSD		CCSD(T)				
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.		
E (hartrees)	−113.913 88	−113.917 95	−114.289 02	−114.328 15	−114.320 01	−114.362 20	−114.335 13	−114.379 21			
r_e(C–O) (Å)	1.1778	1.1769	1.1949	1.1924	1.2033	1.2008	1.2101	1.2075	1.203±0.003,[a] 1.2033[b]		
r_e(C–H) (Å)	1.0911	1.0925	1.0929	1.0939	1.0974	1.0987	1.0994	1.1008	1.099±0.009,[a] 1.1005[b]		
θ_e(HCH) (deg)	116.2	116.0	116.4	116.2	116.4	116.3	116.5	116.3	116.5±1.2,[a] 116.18[b]		
μ_e(D)	2.698	2.692	2.450	2.464	2.377	2.391	2.331	2.341	$\mu_{1_{10}}$ = 2.323 ± 0.015,[c] 2.331[d]		
Harmonic vibrational frequencies (cm^{-1})											
$\omega_1(a_1)$	3102	3088	3024	3019	2962	2955	2933	2926	2944[e]	2944[f]	2978[g,h]
$\omega_2(a_1)$	1987	1998	1865	1888	1805	1827	1756	1776	1764[e]	1761[f]	1778[g,h]
$\omega_3(a_1)$	1655	1652	1592	1591	1561	1559	1543	1541	1563[e]	1517[f]	1529[g,h]
$\omega_4(b_1)$	1342	1341	1255	1260	1216	1220	1193	1197	1191[e]	1187[f]	1191[g,h]
$\omega_5(b_2)$	3175	3159	3097	3092	3033	3026	3003	2996	3009[e]	3033[f]	2997[g,h]
$\omega_6(b_2)$	1374	1371	1321	1315	1296	1289	1280	1272	1288[e]	1282[f]	1299[g,h]
Infrared intensities (km mol^{-1})											
I_1	63.9	64.3	60.8	57.3	61.3	57.1	64.2	59.4	75.5±7.1[i]		
I_2	155.0	159.5	100.2	104.1	82.2	85.4	71.7	74.5	74.0±5.3[i]		
I_3	19.1	17.7	12.2	11.5	11.4	10.5	12.2	10.6	11.2±1.0[i]		
I_4	2.1	2.0	3.5	3.5	4.1	4.1	4.3	4.4	6.5±0.6[i]		
I_5	107.5	109.7	105.2	99.7	108.0	102.1	115.1	108.4	87.6±8.0[i]		
I_6	22.0	22.2	15.4	15.2	13.6	13.4	12.2	12.0	9.9±1.0[i]		

[a]K. Yamada, T. Nakagawa, K. Kuchitsu, and Y. Morino, J. Mol. Spectrosc. **38**, 70 (1971).
[b]J. L. Duncan, Mol. Phys. **28**, 1177 (1974).
[c]K. Kondo and T. Oka, J. Phys. Soc. Jpn. **15**, 307 (1960).
[d]B. Fabricant, D. Krieger, and J. S. Muenter, J. Chem. Phys. **67**, 1576 (1977).
[e]J. L. Duncan and P. D. Mallinson, Chem. Phys. Lett. **23**, 597 (1973).
[f]Y. Tanaka and K. Machida, J. Mol. Spectrosc. **64**, 429 (1977).
[g]D. E. Reisner, R. W. Field, J. L. Kinsey, and H.-L. Dai, J. Chem. Phys. **80**, 5968 (1984).
[h]M. W. Wohar and P. W. Jadgodzinski, J. Mol. Spectrosc. **148**, 13 (1991).
[i]T. Nakanaga, S. Kondo, and S. Saëki, J. Chem. Phys. **76**, 3860 (1982). Intensities include overlapped combination bands.

TABLE IX. Comparison of theoretical predictions with experimental values for molecular properties of NH_3. All properties are evaluated at the equilibrium geometry. All experimental parameters are equilibrium values unless indicated otherwise. The frequencies from footnote d were used to calculate errors in Table XIV.

	SCF		CISD		CCSD		CCSD(T)		
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.
E (hartrees)	−56.220 26	−56.221 26	−56.455 93	−56.476 53	−56.467 03	−56.488 62	−56.473 95	−56.496 57	
r_e(N-H) (Å)	0.9984	0.9984	1.0064	1.0066	1.0098	1.0102	1.0120	1.0125	1.0124[a]
θ_e(HNH)(deg)	107.7	108.1	106.6	107.0	106.4	106.7	106.1	106.4	106.7[a]
μ_e(D)	1.619	1.592	1.626	1.601	1.628	1.604	1.628	1.603	$\mu_{1_{10}}=1.472$[b] $\mu_0=1.472$[c]
Harmonic vibrational frequencies (cm^{-1})									
$\omega_1(a_1)$	3699	3692	3568	3554	3519	3502	3488	3471	3506,[d] 3485,[e] 3478[f]
$\omega_2(a_1)$	1130	1103	1112	1079	1110	1077	1110	1076	1022[d]
$\omega_3(e)$	3817	3817	3685	3681	3637	3630	3608	3600	3577,[d] 3624,[e] 3597[f]
$\omega_4(e)$	1803	1790	1736	1708	1720	1692	1709	1679	1691,[d] 1678,[e] 1684[f]
Infrared intensities (km mol^{-1})									
I_1	0.6	0.4	1.7	1.0	2.5	1.6	3.3	2.3	7.6±0.9[g]
I_2	192	194	158	162	150	154	143	147	138±6[g]
I_3	7.3	10.2	3.9	7.6	2.4	5.2	1.4	3.8	3.8±0.8[g]
I_4	40	41	33	34	31	32	29	31	28.2±0.5[g]

[a]W. S. Benedict and E. K. Plyler, Can. J. Phys. **35**, 1235 (1957).
[b]M. D. Marshall and J. S. Muenter, J. Mol. Spectrosc. **85**, 322 (1981).
[c]K. Tanaka, H. Ito, and T. Tanaka, J. Chem. Phys. **87**, 1557 (1987).
[d]J. L. Duncan and I. M. Mills, Spectrochim. Acta. **20**, 523 (1964).
[e]S. L. Coy and K. K. Lehmann, Spectrochim. Acta. A **45**, 47 (1989).
[f]K. K. Lehmann and S. L. Coy, J. Chem. Soc. Faraday Trans. 2 **84**, 1389 (1988).
[g]T. Koops, T. Visser, and W. M. A. Smit, J. Mol. Struct. **96**, 203 (1983).

conclusions. The TZ(2*df*,2*pd*) CCSD(T) ω_1, ω_3, and ω_4 frequencies for NH_3 are 3471, 3600, and 1679 cm^{-1}, respectively. All three of these frequencies are more consistent with the experimental values reported by Lehmann and Coy[50,51] than with those of Duncan and Mills.[52] The theoretical ω_1 and ω_3 values agree better with the first set[50] of frequencies reported by Lehmann and Coy. For ω_4, the agreement is very good for both sets[50,51] of frequencies they

TABLE X. Comparison of theoretical predictions with experimental values for molecular constants of FCCH. All theoretical properties are reported at the equilibrium geometry. All experimental properties are equilibrium values unless indicated otherwise. The asterisks indicate that IR intensities were not found due to the method used to calculate the harmonic vibrational frequencies. See the text of the methods section for a more detailed explanation.

	SCF		CISD		CCSD		CCSD(T)			
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	Expt.	
E (hartrees)	−175.714 76	−175.721 87	−176.217 76	−176.276 53	−176.274 35	−176.339 03	−176.296 16	−176.363 67		
									r_s[a]	r_e[b,c]
r_e(C–C)(Å)	1.1714	1.1717	1.1826	1.1797	1.1934	1.1902	1.2002	1.1968	1.198	1.1980∼1.2060
r_e(C–F)(Å)	1.2598	1.2566	1.2732	1.2664	1.2836	1.2761	1.2878	1.2802	1.279	1.2806∼1.2734
r_e(C–H)(Å)	1.0519	1.0522	1.0527	1.0514	1.0582	1.0566	1.0598	1.0582	1.053	1.0625
μ_e(D)	0.781	0.760	0.746	0.718	0.763	0.729	0.724	0.690	0.7207±0.0003[a]	
Harmonic vibrational frequencies (cm^{-1})										
$\omega_1(\sigma^+)$	3634	3634	3571	3611	3490	3537	3467	3515	3500[b]	
$\omega_2(\sigma^+)$	2485	2494	2386	2429	2302	2350	2250	2300	2284[b]	
$\omega_3(\sigma^+)$	1161	1171	1105	1130	1062	1088	1042	1069	1076[b]	
$\omega_4(\pi)$	746	767	657	750	595	700	559	666	597[b]	
$\omega_5(\pi)$	503	514	442	482	383	439	342	412	375[b]	
Infrared intensities (km mol^{-1})										
I_1	107.6	105	96.0	98.3	83.9	*	*	*		
I_2	154.0	159	128.7	134.7	112.1	*	*	*		
I_3	97.5	98	85.5	86.9	78.3	*	*	*		
I_4	127.2	125	*	*	*	*	*	*		
I_5	0.004	0.03	*	*	*	*	*	*		

[a]J. K. Tyler and J. Sheridan, Trans. Faraday Soc. **59**, 2661 (1963).
[b]J. K. Holland, D. A. Newnham, and I. M. Mills, Mol. Phys. **70**, 319 (1990).
[c]These r_e values were obtained by fixing r_e(C–H)=1.0625 in order to calculate consistent values of r_e(C–F) and r_e(C–C) in footnote a.

TABLE XI. Percentage errors for theoretical equilibrium bond lengths (r_e). A negative sign means that the theoretical value is less than the experimental one.

Molecule		SCF		CISD		CCSD		CCSD(T)	
		TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)
HCN	r_e(C–H)	−0.79	−0.81	−0.37	−0.68	0.04	−0.32	0.24	−0.15
	r_e(C–N)	−2.57	−2.52	−1.00	−1.09	−0.30	−0.38	0.32	0.24
HNC	r_e(N–H)	−1.28	−1.22	−0.52	−0.54	−0.09	−0.11	0.16	0.15
	r_e(N–C)	−2.11	−2.04	−0.85	−0.92	−0.27	−0.34	0.33	0.26
CO_2	r_e(C–O)	−2.15	−2.16	−0.94	−1.15	−0.16	−0.36	0.47	0.25
CH_4	r_e(C–H)	−0.41	−0.37	−0.29	−0.27	−0.06	−0.04	0.06	0.08
NH_4^+	r_e(N–H)	−1.10	−1.08	−0.43	−0.34	−0.17	−0.06	−0.02	0.11
HCCH	r_e(C–H)	−1.90	−1.89	−0.76	−0.99	−0.14	−0.38	0.39	0.14
	r_e(C–C)	−0.80	−0.75	−0.54	−0.59	−0.19	−0.25	−0.03	−0.10
H_2O	r_e(O–H)	−1.80	−1.78	−0.51	−0.44	−0.15	−0.04	0.10	0.23
H_2CO	r_e(C–O)	−2.09	−2.17	−0.67	−0.88	0.02	−0.18	0.59	0.37
	r_e(C–H)	−0.72	−0.59	−0.56	−0.46	−0.15	−0.03	0.04	0.16
NH_3	r_e(N–H)	−1.38	−1.38	−0.59	−0.57	−0.26	−0.22	−0.04	0.01
Average error		−1.47%	−1.44%	−0.62%	−0.69%	−0.14%	−0.21%	+0.20%	+0.13%
Average absolute error		1.47%	1.44%	0.62%	0.69%	0.15%	0.21%	0.21%	0.17%
Standard deviation for absolute errors		0.68	0.70	0.22	0.29	0.10	0.14	0.19	0.10

reported. The TZ(2*df*,2*pd*) CCSD(T) ω_2 frequency of 1076 cm^{-1} also suggests that Duncan and Mill's experimental ω_2 might be underestimating the "true" value as was hypothesized in Martin and Lee's earlier work. If the values reported by Lehmann and Coy are closer to the "true" harmonic frequencies, then the absolute average errors given in Table XIV will be reduced due to better agreement between theory and the revised experimental values for NH_3. The percent differences for NH_3 given in Table XIV are relative to the harmonic frequencies reported by Duncan and Mills[52] and not those of Lehmann and Coy[50,51] because it was difficult to determine which set of values reported by Lehmann and Coy are the most reliable.

An interesting point concerning the linear molecule bending modes arises from the earlier results of Lee and Rendell[53] for the HCN molecule. They reproduced the experimental π bending frequency of 727 cm^{-1} quite accurately at the CCSD(T) level of theory when they improved the basis set from TZ2P (677 cm^{-1}, −6.9% error) to TZ2P+*f* (729 cm^{-1}, 0.3% error). These results were surprising considering the present coupled-cluster HCN π frequencies were 2.3% (TZ2P CCSD) in error when compared to the experimental value, and the larger TZ(2*df*,2*pd*) basis set gave errors of 12.4% and 8.8% at the CCSD and CCSD(T) levels, respectively. Several factors in the present research differ from that performed by Lee and Rendell. Their TZ2P+*f* basis set only included higher angular momentum functions on the heavy atoms (i.e., *f* functions on C and N), whereas the present research used the TZ(2*df*,2*pd*) basis set which included higher angular momentum functions on all atoms (the same as TZ2P+*f* with the addition of *d* functions on the H atom). In addition, Lee and Rendell used different (correlation optimized) polarization function exponents given by Dunning[49] [α_d(C)=1.097, 0.318, α_f(C)=0.761, α_d(N)=1.654, 0.469, α_f(N)=1.093, and α_p(H)=1.407, 0.388]. They also scaled their H *s* functions by 1.49. Finally, Lee and Rendell froze the core 1*s*-like and virtual 1*s**-like molecular orbitals of HCN in the correlation procedures, whereas the present research included all orbitals and electrons in the correlated procedures.

Infrared intensities

The effect of correlation on the IR intensities is the least evident of all the theoretical molecular properties reported and compared in this paper. Comparison of theo-

TABLE XII. Percentage errors for theoretical equilibrium bond angles (θ_e). A negative sign means that the theoretical value is below the experimental one.

Molecule		SCF		CISD		CCSD		CCSD(T)	
		TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)
H_2O	θ_e(H–O–H)	1.7	1.8	0.4	0.3	0.2	0.0	−0.1	−0.3
H_2CO	θ_e(H–C–H)	−0.3	−0.4	−0.1	−0.3	−0.1	−0.2	0.0	−0.2
NH_3	θ_e(H–N–H)	0.9	1.3	−0.1	0.3	−0.3	0.0	−0.6	−0.3

TABLE XIII. Percentage errors for theoretical equilibrium dipole moments (μ_e) from experimental dipole moments (μ_0). A negative sign means that the theoretical value is below the experimental one.

	SCF		CISD		CCSD		CCSD(T)	
Molecule	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)
HCN	9.3	9.2	3.2	3.5	1.4	1.6	0.0	0.2
HNC	−2.8	−3.5	1.1	0.7	1.6	1.2	1.8	1.4
H_2O	7.6	7.4	5.0	5.0	4.6	4.5	4.0	3.9
H_2CO	15.7	15.5	5.1	5.7	2.0	2.6	0.0	0.4
NH_3	10.0	8.1	10.5	8.8	10.6	8.9	10.6	8.9
FCCH	8.4	5.5	3.5	−0.4	5.9	1.2	0.5	−4.3

TABLE XIV. Percentage errors for theoretical harmonic vibrational frequencies relative to experimental harmonic vibrational frequencies. A negative sign means that the theoretical frequency is below the experimental one.

	SCF		CISD		CCSD		CCSD(T)	
Molecule and mode	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)
HCN $\omega_1(\sigma^+)$	4.9	5.0	1.8	3.4	−0.1	1.7	−0.9	0.9
$\omega_2(\pi)$	18.6	21.5	3.2	16.8	−2.3	12.4	−6.6	8.8
$\omega_3(\sigma^+)$	13.1	13.2	5.6	6.5	2.1	3.1	−0.9	0.0
CO_2 $\omega_1(\sigma_g^+)$	11.2	11.7	5.5	6.5	1.6	2.6	−1.6	−0.7
$\omega_2(\pi_u)$	14.0	15.8	4.0	8.3	−0.7	3.6	−4.5	−0.1
$\omega_3(\sigma_u^+)$	5.9	6.6	2.3	4.4	−0.7	1.5	−2.4	−0.3
CH_4 $\omega_1(a_1)$	4.5	4.1	1.7	1.7	0.7	0.6	0.1	0.1
$\omega_2(e)$	5.8	5.4	1.6	1.0	0.6	0.0	0.0	−0.8
$\omega_3(t_2)$	3.2	2.9	1.1	1.2	0.1	0.2	−0.4	−0.3
$\omega_4(t_2)$	6.7	6.4	1.4	0.8	0.4	−0.3	−0.4	−1.2
HCCH $\omega_1(\sigma_g^+)$	5.0	4.9	2.7	3.4	1.1	1.9	0.4	1.2
$\omega_2(\sigma_g^+)$	10.0	10.1	4.5	6.1	1.5	3.5	−0.8	1.2
$\omega_3(\sigma_u^+)$	4.1	4.1	1.4	2.6	−0.2	1.1	−0.8	0.6
$\omega_4(\pi_g)$	25.8	30.3	1.8	26.3	−7.4	20.5	−15.4	14.7
$\omega_5(\pi_u)$	14.5	16.5	5.4	12.3	1.1	8.8	−1.7	6.3
H_2O $\omega_1(a_1)$	8.0	7.9	2.9	2.7	1.3	1.1	0.3	0.1
$\omega_2(a_1)$	7.0	5.8	3.2	1.6	2.5	0.8	1.8	0.1
$\omega_3(b_2)$	7.5	7.4	2.5	2.4	1.1	1.0	0.2	0.03
H_2CO $\omega_1(a_1)$	4.2	3.7	1.5	1.4	−0.5	−0.8	−1.5	−1.7
$\omega_2(a_1)$	11.8	12.4	4.9	6.2	1.5	2.8	−1.2	−0.1
$\omega_3(a_1)$	8.2	8.0	4.1	4.1	2.1	2.0	0.9	0.8
$\omega_4(b_1)$	12.7	12.6	5.4	5.8	2.1	2.4	0.2	0.5
$\omega_5(b_2)$	5.9	5.4	3.3	3.2	1.2	1.0	0.2	−0.3
$\omega_6(b_2)$	5.8	5.5	1.7	1.2	−0.2	−0.8	−1.5	−2.1
NH_3 $\omega_1(a_1)$	5.5	5.3	1.8	1.4	0.4	−0.1	−0.5	−1.0
$\omega_2(a_1)$	10.6	7.9	8.8	5.6	8.6	5.4	8.6	5.3
$\omega_3(e)$	6.7	6.7	3.0	2.9	1.7	1.5	0.9	0.6
$\omega_4(e)$	6.6	5.9	2.7	1.0	1.7	0.1	1.1	−0.7
FCCH $\omega_1(\sigma^+)$	3.8	3.8	2.0	3.2	−0.3	1.1	−0.9	0.4
$\omega_2(\sigma^+)$	8.8	9.2	4.5	6.3	0.8	2.9	−1.5	0.7
$\omega_3(\sigma^+)$	7.9	8.8	2.7	5.0	−1.3	1.1	−3.2	−0.7
$\omega_4(\pi)$	25.0	28.4	10.1	25.6	−0.3	17.3	−6.4	11.6
$\omega_5(\pi)$	34.1	37.1	17.9	28.5	2.1	17.1	−8.8	9.9
Average absolute error	9.9% (7.3%)[a]	10.3% (7.4%)[a]	3.8% (3.0%)[a]	6.3% (3.5%)[a]	1.5% (1.1%)[a]	3.7% (1.5%)[a]	2.3% (1.1%)[a]	2.2% (0.6%)[a]
Standard deviation for absolute errors	7.0 (3.0)[a]	8.2 (3.3)[a]	3.3 (1.4)[a]	7.4 (2.2)[a]	2.0 (0.7)[a]	5.3 (1.1)[a]	3.3 (1.0)[a]	3.7 (0.5)[a]

[a]The average absolute errors and standard deviations given in parentheses exclude the bending modes of all the triply bonded molecules (the HCN π mode, the HCCH π_g, π_u modes, and both of the doubly degenerate π modes of FCCH) and the NH_3 a_1 umbrella mode.

TABLE XV. Comparison of SCF, CISD, CCSD, and CCSD(T) theoretical average absolute errors in equilibrium bond lengths and harmonic vibrational frequencies for the TZ2P and TZ(2*df*,2*pd*) basis sets.

	SCF		CISD		CCSD		CCSD(T)	
	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)	TZ2P	TZ(2*df*,2*pd*)
Bond lengths	1.47%	1.44%	0.62%	0.69%	0.15%	0.21%	0.21%	0.17%
Harmonic frequencies	9.9% (7.3%)[a]	10.3% (7.4%)[a]	3.8% (3.0%)[a]	6.3% (3.5%)[a]	1.5% (1.1%)[a]	3.7% (1.5%)[a]	2.3% (1.1%)[a]	2.2% (0.6%)[a]

[a]The average absolute errors and standard deviations given in parentheses exclude the bending modes of all the triply bonded molecules (the HCN π mode, the HCCH π_g, π_u modes, and both of the π modes of FCCH) and the NH_3 a_1 umbrella mode.

retical and experimental intensities leads to several *general* conclusions. First, the theoretical intensities converge toward the experimental values with increasing correlation. Second, increasing the correlation causes the theoretical intensities to agree with the experimental intensities in terms of ordering by magnitudes. This feature was also seen in the previous research with the DZP basis set.[13–15] The ability of a basis set of DZP quality to yield correct *qualitative* information has been previously established.[36] Larger basis sets are expected to give better *quantitative* agreement, and this is observed with our TZ2P and TZ(2*df*,2*pd*) results. Several TZ2P and TZ(2*df*,2*pd*) CCSD(T) intensities were found to lie within the ranges of experimental error for the measured intensities. The majority of the intensities are found to lie very close (within a few km mol^{-1}) of the experimental values. Unfortunately, uncertainties do not accompany *all* of the reported experimental intensities listed here. The magnitudes of experimental uncertainties are usually at least 10%. Also, it should be kept in mind that the experimental intensities are those of the fundamentals and not the harmonics (experimental intensities include anharmonic and overlap effects, whereas the theoretical intensities do not), and that the experimental accuracy for modes with weak intensities may be poorer than for strong modes.

Oddly, the ordering of the modes with respect to magnitude for H_2CO does not agree with experiment as correlation or basis set size is increased. This discrepancy between theory and experiment was discussed by Willets *et al.*[54] in their study of theoretical anharmonic corrections to IR vibrational intensities. They noted that the I_1 and I_5 intensities are not well established experimentally because several weaker overlapping bands lie in the same spectral region. The theoretical anharmonic correction was found to be quite large ($\sim$39 km mol^{-1}) for I_5 due to Fermi resonance between ν_5 and two combination bands, $\nu_2+\nu_6$ and $\nu_3+\nu_6$, neither of which is predicted to have intensity within the double harmonic approximation used here. Theoretical refinement of the method used to predict the intensities was made by Willets *et al.*[54] to give a reduced value of 67 km mol^{-1} for the intensity of ν_5 alone. Two comparable experimental values of 69 km/mol[55,56] (this value was determined in Ref. 54 from the experimental data reported in Refs. 56 and 57) and $\geqslant$59 km/mol[57,58] for this intensity have been reported. The TZ(2*df*,2*pd*) CCSD(T) I_5 value is 108 km mol^{-1}, so an anharmonic correction of approximately the same size as above would give a value of $\sim$70 km mol^{-1}, in good agreement with experiment.

The trend for IR intensities to decrease with improved treatment of electron correlation effects may be simply justified. In general, as a bond is elongated, the electron density becomes less sensitive to infinitesimal nuclear motions. Therefore, smaller changes in the dipole moment should occur when a molecule vibrates, and this will lead to smaller IR intensities. This tendency is observed in the present research with the use of TZ2P and TZ(2*df*,2*pd*) basis sets. The bond lengths became elongated at higher correlated levels, and the intensities decreased. It should be noted that the previous DZP results did *not* display this tendency. This was because the DZP basis was too small to provide sufficient balance with the amount of correlation included in the CCSD and CCSD(T) procedures.

CONCLUDING REMARKS

Although our study of ten polyatomic molecules in no way establishes a completely reliable average error (especially since we are only comparing molecules with closed-shell ground states), availability of additional experimental data will enable theoreticians to easily improve upon the average errors presented here. As can be seen for the harmonic frequencies in Table XV, a balance seems to exist between the TZ2P basis and the level of excitations included in the CCSD method. The same is observed for the TZ(2*df*,2*pd*) CCSD(T) methodology. A similar balance was seen in our previous studies[13–15] between the DZP basis and the CISD procedure. The DZP CCSD and CCSD(T) vibrational *frequencies* showed apparent greater accuracy, but this was achieved at the expense of the accuracy of the predicted *geometries*. In the present research, the TZ2P CCSD method gave the best overall agreement of the four TZ2P methodologies with respect to *both geometries and frequencies*. The TZ(2*df*,2*pd*) CCSD(T) method gave geometries that were in as good agreement with experiment as the TZ2P CCSD results. Overall, however, the TZ(2*df*,2*pd*) CCSD(T) frequencies disagreed more with experiment due to *overestimation* of the bending modes of the various π-bonded linear molecules. Exclusion of these problematic bending modes from the average error showed that TZ(2*df*,2*pd*) CCSD(T) frequencies were slightly more accurate than any other methodology. In the present study, the TZ(2*df*,2*pd*) CCSD(T) results were found to give the most reliable predictions with respect to

equilibrium bond lengths and harmonic vibrational frequencies. Although TZ2P CCSD equilibrium bond lengths were the most accurate on the average, the slight improvement in accuracy [only 0.02% better than TZ(2*df*,2*pd*)] does not outweigh the more accurately predicted TZ(2*df*,2*pd*) CCSD(T) harmonic vibrational frequencies. Also, it should be kept in mind when making these types of comparisons that experimental harmonic and anharmonic vibrational frequencies may have some inherent uncertainty from the procedure used to extract them from experimentally observed data.

This study shows the importance of keeping a balance between the basis set quality and theoretical method. An appropriate balance allows the correct prediction of *both* the shape *and* the position of the potential energy well on a molecule's potential energy hypersurface. The effect of an "imbalanced" methodology can be seen in the DZP CCSD(T) results reported previously.[15] Specifically, the *shape* of the potential wells were accurately predicted (as can be seen from the extremely accurate frequencies) at the expense of the incorrect *position* of the wells (reflected in the geometry errors). The present study found that the TZ2P CCSD and TZ(2*df*,2*pd*) CCSD(T) methodologies are properly balanced and *simultaneously* reproduced accurate molecular properties. As mentioned in the Introduction, another systematic study on the effect of frozen core approximations in predicting molecular properties is underway in this laboratory and the results will be presented in a forthcoming paper.

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