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Basis Set Limit CCSD(T) Harmonic Vibrational Frequencies[†]

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Benchmark, frozen-core CCSD(T) equilibrium harmonic vibrational frequencies of 12 closed-shell and five open-shell molecules are computed to within 1 cm^{-1} of the basis set limit using the explicitly correlated CCSD(T)-R12 method. The convergence of the standard CCSD(T) method with the one-particle basis sets of Dunning and co-workers is examined and found to be slow, with mean and maximum absolute errors of 1.3 and 3.5 cm^{-1} remaining at the cc-pV6Z level. Finite basis set effects do not appear to introduce systematic errors in equilibrium harmonic frequencies, and mean absolute errors reduce by a factor of 2 for each basis set cardinal number increment. The convergence of individual equilibrium harmonic frequencies is not guaranteed to be monotonic due to the associated shift in the equilibrium structure. The inclusion of computed scalar relativistic effects and previously available corrections for core-valence correlation and higher-order excitations in the cluster operator results in an agreement with experimentally derived harmonic frequencies of 0.1, 0.3, and −0.4 cm^{-1} for HF, N_2, and CO, respectively. F_2 continues to present a challenge to computational chemistry with an error of 3.2 cm^{-1}, primarily resulting from the high basis set dependence of the quadruples contribution.

1. Introduction

One of the fundamental questions that theoretical chemists face is: which level of approximation to the exact solution of the quantum mechanical wave equation is required for a given accuracy relative to experimental observations? Or, equivalently: how accurate is a particular computational method? In the absence of any useful a priori error estimates, it is only possible for quantum chemists to base their assessment of the various methods on the performance of previous applications of the theory. Careful convergence studies, reducing errors by systematically improving the level of approximation, therefore play an important role, providing definitive error bars for a given method over a set of test systems, which may then be used to guide the general application and development of quantum chemical methods.[1]

The convergence of the popular coupled-cluster methods is in two directions: the level of excitation in the cluster operator that defines the wave function and the size of the one-particle basis in which the wave function is expanded. Benchmark reference data, either from full configuration interaction (FCI) or basis set limit calculations, form a vital part of any convergence studies for the coupled-cluster class of methods. The truncation of the cluster operator at successively higher levels of excitation forms a natural, physically motivated, hierarchy of approximations[2] that converges to the FCI limit. Similarly, the carefully constructed correlation-consistent basis sets of Dunning and co-workers form sequences that reduce finite basis errors in a systematic manner.[3−5]

Because of the availability of optimized basis sets for first and second row elements with cardinal numbers 2 through 6[3,6] and coupled-cluster implementations to arbitrary level of excitation,[7,8] many careful studies have been performed for the convergence of the energy to the basis set limit FCI value.[9−11] The convergence with respect to the level of excitation included in the cluster operator is rapid, provided that the state is dominated by a single Hartree−Fock reference determinant. The convergence with the one-particle basis is notoriously slow due to the ineffectual representation of the electron cusp.[12−15] Methods that include the interelectronic distance explicitly in the form of the wave function are required to obtain near basis set limit values for total energies. Because of the systematic way the Dunning basis sets are constructed, the basis set error may also be reduced through extrapolation techniques.[3,16]

For relative energies, such as atomization energies, an accuracy of 1 kcal mol^{-1} relative to experiment may be generally obtained by extrapolating frozen-core (fc) CCSD(T) energies to close to the basis set limit and using all-electron (ae) calculations to include an approximate treatment of core-valence correlation.[17] For molecules containing second row atoms, scalar relativistic effects must also be included to maintain an accuracy of 1 kcal mol^{-1}. To improve agreement with experiment to within 1 kJ mol^{-1}, many post-CCSD(T) contributions must be considered because they are of similar magnitude. In particular, a full treatment of triple and quadruple excitations together with more accurate treatments of relativistic effects, and core-valence correlation is required.[10,11,18]

A number of convergence studies focusing on molecular geometries and vibrational frequencies have begun to appear in the literature.[19−24] Such studies are important because there is no guarantee that an identical convergence behavior will be

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observed for properties as for the energy. However, most of these investigations are fairly limited in the extent of systems considered. Recently, some of us have examined the convergence of energy gradients in the context of predicting equilibrium geometries for a set of 17 small molecules.[25−27] In accordance with the conclusions of other researchers, we found that basis set limit fc-CCSD(T) was generally sufficient for an accuracy of 0.1 to 0.2 pm and that the mean absolute deviations from the basis set limit when using Dunning's quintuple-ζ and sextuple-ζ basis sets are 0.033 and 0.021 pm respectively. The effect of including quadruples (at the level of a double-ζ basis) led to changes in the geometry of around 0.1 pm for multiply bonded systems and 0.4 pm for the challenging case of F_2. Treatment of the core-valence correlation at the CCSD(T) level was also necessary to obtain a final agreement with experiment to within 0.05 pm.

Ruden et al. have recently performed a comprehensive study of the convergence of the coupled-cluster harmonic frequencies of HF, N_2, F_2, and CO to experimentally derived values.[24] They find that the fc-CCSD(T) method predicts high-quality harmonic frequencies with mean and maximum absolute errors of 6.4 and 14.4 cm^{-1}, respectively. They also find that the close agreement with experiment arises from a high degree of error cancellation between the approximate treatment of triples, the missing core-valence correlation, and the missing contributions from higher-order excitations. Indeed, the effect of including quadruple excitations is as much as 19 cm^{-1} for N_2. After examining the basis set dependence of these post-CCSD(T) contributions, and including scalar relativistic and diagonal Born−Oppenheimer corrections, Ruden et al. report mean and maximum absolute errors of 1.1 and 2.3 cm^{-1}, respectively.

Following the excellent work of Ruden et al. and our previous study of equilibrium geometries, we intend to provide a benchmark study of harmonic frequencies for the set of 17 small molecules. In this article, we are primarily concerned with the fc-CCSD(T) method, important both in its own right and also as a rung in the ladder of the many additivity schemes that aim to converge to the exact solution to the Schrödinger equation.[9−11,28−30] CCSD(T) is also used as a standard tool for computing potential energy surfaces and is important for many applications concerning assignments and interpretation of the various experimental spectra that exhibit ro-vibrational band structure.

In Section 2, we present near basis set limit fc-CCSD(T)-R12 harmonic vibrational frequencies for the set of 12 open and five closed-shell molecules that were used as a reference set in our geometry study. In Section 3, we examine the basis set convergence of the fc-CCSD(T) harmonic frequencies with the correlation-consistent basis sets of Dunning and co-workers. In Section 4, we use the corrections due to core-valence correlation and from higher excitations in the cluster operator, computed by Ruden et al.,[24] and also corrections from scalar relativistic effects, to assess the accuracy of our benchmark data through comparison with experimentally derived values.

2. Basis Set Limit CCSD(T)-R12 Harmonic Frequencies

In this section, we present the results of benchmark near basis set limit fc-CCSD(T) calculations using the CCSD(T)-R12 method.[31−35] Our test set of molecules includes the 12 closed-shell systems HF, H_2O, CH_2 ($^1A_1$), NH_3, CH_4, CO, N_2, F_2, HCN, HNC, C_2H_2, and CO_2, and the five open-shell molecules OH ($^2\Pi$), CN ($^2\Sigma^+$), NH_2 ($^2B_1$), CH_2 ($^3B_1$), NO ($^2\Pi$). CCSD(T)-R12 calculations were performed using the DIRCCR12-OS program.[36] For the open-shell systems, spin-orbital based coupled-cluster calculations were performed using a restricted Hartree−Fock reference. A 19s14p8d6f4g3h2i basis (9s6p4d3f2g for H) of ref 37 was used for both the orbital basis and the auxiliary basis for the resolution of the identity employed to approximate the many electron integrals, with approximation B for the matrix elements of the geminal functions over the Fock operator.

TABLE 1: Frozen-Core CCSD(T)-R12 Harmonic Frequencies[a]

	reference geometry			
molecule	parameter	a_0 and deg	mode	ω_e
HF	r(HF)	1.7332866	σ	4142.53
H_2O	r(OH)	1.8108074	a_1 (bend)	1649.39
	∠(HOH)	104.46268	a_1 (s-str)	3835.89
			b_2 (a-str)	3946.65
NH_3	r(NH)	1.9124265	a_1 (s-bend)	1056.98
	∠(HNH)	106.61367	e (a-bend)	1674.71
			a_1 (s-str)	3480.64
			e (a-str)	3612.77
CH_2 ($^1A_1$)	r(CH)	2.0937614	a_1 (bend)	1400.55
	∠(HCH)	102.06377	a_1 (s-str)	2925.61
			b_2 (a-str)	3000.66
CH_4	r(CH)	2.0550266	t_2 (bend)	1344.63
			e (bend)	1570.29
			a_1 (s-str)	3035.75
			t_2 (a-str)	3158.02
F_2	r(FF)	2.6628448	σ_g	931.86
N_2	r(NN)	2.0764499	σ_g	2363.36
CO	r(CO)	2.1356878	σ	2167.29
HCN	r(CN)	2.1825841	π (bend)	728.33
	r(CH)	2.0155145	σ (CN str)	2128.01
			σ (CH str)	3438.10
HNC	r(NC)	2.2123750	π (bend)	463.23
	r(NH)	1.8828294	σ (NC str)	2055.93
			σ (NH str)	3813.66
CO_2	r(CO)	2.1949257	π_u (bend)	673.92
			σ_g^+ (s-str)	1354.04
			σ_u^- (a-str)	2396.17
C_2H_2	r(CC)	2.2773187	π_g (bend)	620.45
	r(CH)	2.0087522	π_u (bend)	748.65
			σ_g^+ (CC str)	2009.41
			σ_u^- (a-str)	3412.09
			σ_g^+ (s-str)	3503.86
OH	r(OH)	1.8330586	σ	3800.58
NO	r(NO)	2.1754467	σ	1915.28
CN	r(CN)	2.2167925	σ	2071.41
NH_2	r(NH)	1.9363363	a_1 (bend)	1601.21
	∠(HNH)	103.04851	a_1 (s-str)	3402.99
			b_2 (a-str)	3474.44
CH_2 ($^3B_1$)	r(CH)	2.0348581	a_1 (bend)	1093.38
	∠(HCH)	133.72363	a_1 (s-str)	3144.13
			b_2 (a-str)	3373.61

[a] In cm^{-1}, using the energy conversion factor $E_h = 219474.6313705$ cm^{-1}.

Because analytic derivatives are not yet available, the equilibrium geometries were optimized by computing a number of grid points (at least 5 per degree of freedom) around the analytically optimized fc-CCSD(T)/cc-pV6Z equilibrium geometries taken from previous work.[25,26] The optimized fc-CCSD(T)-R12 internal coordinates are reported in Table 1. We do not claim basis set limit accuracy to the eight significant figures quoted, but present the definition of the reference structures used for the subsequent frequency calculations. Taking the deviation of the R12 values from structures optimized on a 56 extrapolated surface (using the two-point formula of ref 16 with the cc-pV5Z and cc-pV6Z basis sets) as a conservative estimate of the accuracy, we expect the values in Table 1 to be within 0.005 pm of the basis set limit.

TABLE 2: Frozen-Core CCSD(T) Harmonic Frequencies in cm^{-1}, Computed Using cc-pV*XZ* Orbital Basis Sets and Benchmark CCSD(T)-R12 Calculations

molecule	ω_e	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z	R12
HF	σ	4177.39	4162.26	4151.01	4145.51	4142.53
H_2O	a_1 (bend)	1668.88	1659.29	1653.37	1651.28	1649.39
	a_1 (s-str)	3840.92	3844.46	3840.06	3837.27	3835.89
	b_2 (a-str)	3945.53	3951.41	3949.33	3947.22	3946.65
NH_3	a_1 (s-bend)	1109.21	1084.01	1067.53	1060.51	1056.98
	e (a-bend)	1687.93	1679.63	1677.87	1676.11	1674.71
	a_1 (s-str)	3471.91	3480.47	3481.89	3481.07	3480.64
	e (a-str)	3597.53	3608.78	3612.64	3612.64	3612.77
CH_2 ($^1A_1$)	a_1 (bend)	1406.57	1402.91	1400.99	1400.10	1400.55
	a_1 (s-str)	2912.05	2922.04	2925.02	2924.97	2925.61
	b_2 (a-str)	2983.11	2996.15	2999.37	2999.81	3000.66
F_2	σ_g	919.95	921.09	926.53	928.48	931.86
N_2	σ_g	2345.98	2356.21	2359.83	2361.05	2363.36
CO	σ	2153.73	2164.41	2165.15	2165.78	2167.29
HCN	π (bend)	716.02	721.77	725.17	727.19	728.33
	σ (CN str)	2111.38	2123.12	2125.23	2126.13	2128.01
	σ (CH str)	3443.43	3435.51	3437.54	3437.77	3438.10
HNC	π (bend)	472.56	466.60	464.25	464.14	463.23
	σ (NC str)	2045.42	2054.35	2054.32	2054.58	2055.93
	σ (NH str)	3824.46	3820.64	3816.71	3814.29	3813.66
CO_2	π_u (bend)	660.30	670.52	672.19	673.42	673.92
	σ_g^+ (s-str)	1346.19	1351.92	1352.64	1352.98	1354.04
	σ_u^- (a-str)	2396.26	2396.41	2394.44	2394.87	2396.17

We have used the 2002 CODATA recommended values of the fundamental physical constants,[38] with $E_h = 4.35974417 \times 10^{-18}$ J, $a_0 = 0.5291772108 \times 10^{-10}$ m, and $m_e = 9.1093826 \times 10^{-31}$ kg. We have furthermore used the atomic mass constant $m_u = 1.66053886 \times 10^{-27}$ kg and the relative atomic masses 1.0078250321 (H), 12.0 (^{12}C), 14.0030740052 (^{14}N), 15.9949146221 (^{16}O), and 18.99840320 (^{19}F).

The basis set limit projected Hessian matrix was evaluated by finite difference, centered at the optimized basis set limit geometries in Table 1 and using Hartree−Fock vibrational normal modes l_k as a coordinate system. Off-diagonal elements of the Hessian matrix were computed by evaluating the second derivative along the vector $(l_k + l_l)/\sqrt{2}$ and subtracting the (dominant) diagonal contributions. To reduce the finite difference error, all second derivatives were computed with a seven-point formula using the points 0, $\pm h$, $\pm 2h$, and $\pm 3h$. The step size h was chosen such that the Cartesian displacement vector $hm_i^{-1/2}l_{k,i\alpha}$ has a magnitude 0.05 a_0. The associated error in second derivatives is $\mathcal{O}(h^6)$, and the random error associated with the energy convergence criteria is negligible. It later emerged that, had we computed the points 0, $\pm h$, $\pm 2h$, and $\pm 4h$, utilizing the Richardson extrapolation would then be equivalent to a nine-point formula, with an associated error $\mathcal{O}(h^8)$. However, this was of no consequence because the resulting finite difference error in the harmonic frequencies computed using the seven-point formula is already below 0.01 cm^{-1}.

The resulting fc-CCSD(T)-R12 harmonic frequencies are presented in Table 1. It is not possible to give definite error bars for the deviation of the R12 frequencies from the true basis set limit, but considering the deviation between the cc-pV6Z and R12 values, and the discussions in Sections 3 and 4, we expect that the computed fc-CCSD(T)-R12 harmonic frequencies are within 1 cm^{-1} of the basis set limit.

For reference, the MP2-R12, CCSD(R12), CCSD-R12, CCSD(T)(R12), CCSD(T)-R12, CCSD[T](R12), and CCSD[T]-R12 energies[39,40] of the 17 molecules at the reference equilibrium geometries have been included as Supporting Information in Tables S1−S6. The corresponding orbital-only values are also tabulated.

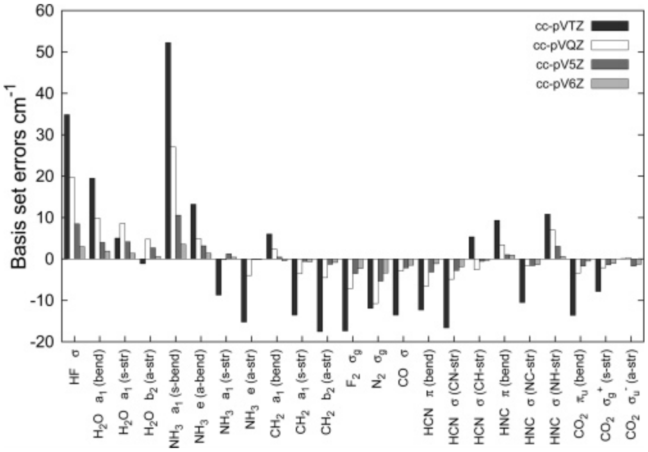
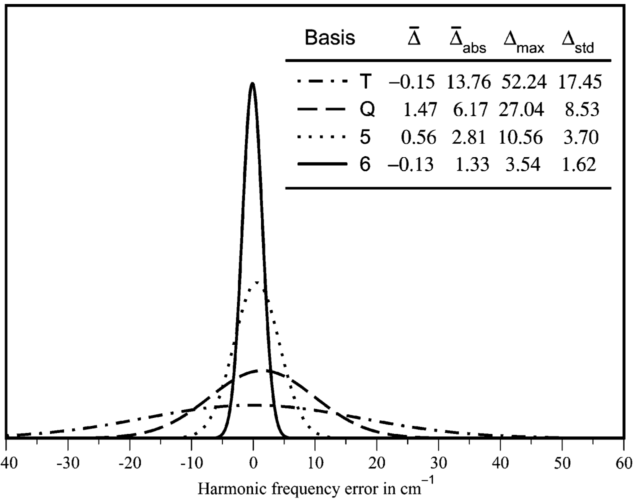


Figure 1. Basis set errors in fc-CCSD(T) harmonic frequencies (cm^{-1}) computed using cc-pV*XZ* basis sets with X = T, Q, 5, and 6 relative to the fc-CCSD(T)-R12 values.



Basis	$\bar{\Delta}$	$\bar{\Delta}_{abs}$	Δ_{max}	Δ_{std}
T	–0.15	13.76	52.24	17.45
Q	1.47	6.17	27.04	8.53
5	0.56	2.81	10.56	3.70
6	–0.13	1.33	3.54	1.62

Figure 2. Basis set error distributions for harmonic frequencies (cm^{-1}) computed using cc-pV*XZ* basis sets with X = T, Q, 5, and 6.

3. Convergence to the Basis Set Limit

In this section, we discuss the basis set convergence of fc-CCSD(T) harmonic frequencies. Because of the large computational requirement of second derivative calculations, we only consider a subset of the molecules included in our geometry convergence studies. We only include closed-shell systems, and also exclude CH_4 and C_2H_2.

Analytic second derivative calculations[41] were performed using the ACES2 program[42] for the cc-pV*XZ* correlation-consistent basis sets with $X = T, Q, 5, 6$. Each Hessian was evaluated at the equilibrium geometry consistent with the basis set used for the calculation. All of the analytically optimized $X = T, Q, 5, 6$ geometries are available from previous work.[25,26] The resulting harmonic frequencies are detailed in Table 2, and the deviations from the CCSD(T)-R12 values are depicted in Figure 1. The mean and standard deviation (s_N) of the basis set errors are summarized in Figure 2, together with the mean absolute and maximum errors. It is clear that the R12 harmonic frequencies are in complete agreement with the frequencies computed analytically using orbital-only basis sets.

For the cc-pVTZ basis, the mean absolute error is 13.8 cm^{-1} and the standard deviation is 17.5 cm^{-1}. These quantities are approximately halved upon each increment in the cardinal number and are 1.3 and 1.6 cm^{-1}, respectively, for the cc-pV6Z basis. Using standard methods, spectroscopic accuracy of 1 cm^{-1}

either requires basis sets larger than cc-pV6Z or extrapolation of the geometry and Hessian matrix toward the basis set limit. The NH_3 umbrella motion converges particularly slowly and is consistently responsible for the maximum error, which is 52.2 cm^{-1} for the cc-pVTZ basis and 3.5 cm^{-1} for the cc-pV6Z basis set. HF and F_2 also give large errors, with cc-pV6Z deviations of 3.0 and 3.4 cm^{-1}, respectively. We recall that the equilibrium geometries of fluorine-containing molecules are also observed to converge slowly, primarily due to the lack of diffuse functions in the fluorine basis.[26]

Figure 2 shows that no systematic basis set error is observed. For our test set, the mean error in the harmonic frequencies is small for all basis sets, at most 1.5 cm^{-1}. An inspection of the individual errors did not reveal any discernible pattern, with positive and negative errors spread over bends and stretches, singly bonded and multiply bonded systems. The statistics indicate that the general convergence of the computed CCSD(T) second derivatives to the basis set limit behaves similarly to that of the energy, and is slow, but steady. This is in full accord with the conclusions of Pawłowski et al., who performed a similar study on five diatomics at the MP2 and CCSD levels of theory.[43]

Inspection of Figure 1 reveals that the convergence of individual harmonic frequencies is not always smooth. For 5 of the 23 frequencies studied, the error changes sign as the basis set is increased from $X = T$ to $X = 6$. Simplified extrapolation methods involving only the eigenvalues of the equilibrium Hessian matrix are therefore unlikely to be successful.

For a one-dimensional case (diatomics), the convergence scheme used to obtain the equilibrium harmonic frequencies in Table 2 corresponds to expressing the potential curve as

$$E(x) = \frac{1}{2}kx^2 + \frac{1}{6}\phi x^3 + \mathcal{O}(x^4) \qquad (1)$$

where $x = r - r_e$, and the spectroscopic quantities k, ϕ, and r_e depend on the basis set. This is useful because the observed convergence of these quantities relates directly to the quality of the potential surface that would be obtained with a given basis. It is observed that a potential energy curve may be represented by[16]

$$E(r) = E_\infty(r) + A(r)X^{-3} + \mathcal{O}(X^{-4}), \qquad (2)$$

where $E_\infty(r)$ is the basis set limit and the curve $A(r)$ is the leading term in the basis set error. Note that, in this equation, and for the rest of this section, X denotes the cardinal number of the basis. The dependence of the basis set error $A(r)$ on r adds a bias to the potential, with the first derivative $A'(r)$ primarily responsible for the shift in the position of the minimum and the second derivative $A''(r)$ affecting the force constant. Expanding $A(r)$ as a Taylor series to second order in $x = r - (r_e)_\infty$ and writing $E_\infty(r)$ in the form of eq 1, one finds that the second derivative at the minimum of $E(r)$ as a function of X is given by

$$k^2 = k_\infty^2 + \left(A''X^{-3} + k_\infty - \frac{A'\phi_\infty}{A''}\right)^2 - \left(k_\infty - \frac{A'\phi_\infty}{A''}\right)^2 \qquad (3)$$

Clearly, the observed error of k for a given basis depends strongly on the magnitude of the anharmonicity in the surface, i.e., the change in the second derivative due to each new equilibrium geometry. In fact, eq 3 is sufficient to rationalize the patterns of convergence displayed in Table 2. Neglecting anharmonicity, the sign of the observed error depends on the sign of A''. However, the quadratic equation $k^2 - k_\infty^2$ has one root at $X^{-3} = 0$ and one at $X^{-3} = k_\infty - A'\phi_\infty/A''$. If the second root falls within the range of X considered, then the observed error in k changes sign. For polyatomic molecules, there is the additional complication that the normal coordinates at the minimum also vary with X.

TABLE 3: Convergence of fc-CCSD(T) Harmonic Frequencies (in cm^{-1}) of the Diatomic Closed-Shell Molecules HF, N_2, F_2, and CO at the Reference Geometries in Table 1

basis	HF	N_2	F_2	CO
cc-pVTZ	4177.79	2388.74	942.93	2196.38
cc-pVQZ	4147.08	2369.00	934.03	2173.95
cc-pV5Z	4143.94	2365.25	933.01	2169.57
cc-pV6Z	4142.83	2364.30	932.27	2168.40
56[a]	4141.97	2363.18	931.53	2167.26
R12	4142.53	2363.36	931.86	2167.29

[a] Extrapolated using cc-pV5Z and cc-pV6Z in eq 4.

In contrast to the error in the equilibrium force constant, one would expect the second derivative at a fixed geometry to converge monotonically with basis set because the convergence behavior is simply obtained by differentiation of eq 2. We have tested this for the closed-shell diatomic molecules HF, N_2, F_2, and CO. Using the cc-pVXZ basis sets of Dunning and coworkers, we have evaluated the fc-CCSD(T) second derivative at the reference geometries in Table 1 for $X = T$, Q, 5, and 6. The corresponding harmonic frequencies are presented in Table 3, together with the R12 values. The convergence is indeed smooth and is from above for all four molecules. Furthermore, we have performed an extrapolation of the second derivatives using the cc-pV5Z and cc-pV6Z basis sets. Subtracting the Hartree−Fock contribution to the force constant, we extrapolated the correlation contribution k^c using the formula[16]

$$k_\infty^c \approx \frac{X^3 k^c(X) - Y^3 k^c(Y)}{X^3 - Y^3} \qquad (4)$$

where X and Y are the cardinal numbers of the two basis sets. The final 56 extrapolated second derivative is taken as the sum of the extrapolated k^c and the cc-pV6Z Hartree−Fock value. The corresponding harmonic frequencies are also presented in Table 3. The differences between the 56 extrapolation and the R12 values are −0.6, −0.2, −0.3, and 0.0 cm^{-1} for HF, N_2, F_2, and CO, respectively. The extrapolated values tend to slightly overshoot the R12 values and the largest deviations are for HF and F_2, for which diffuse functions are known to be important. This is convincing evidence that our R12 values for these molecules are very close to the basis set limit. We expect that our benchmark, basis set limit predictions for the remaining molecules in Table 1 are similarly accurate.

4. Comparison with Experiment

Harmonic frequencies are not experimentally observed quantities. To compare with experiment, it is necessary either to compute fundamental frequencies directly or to fit the parameters of a model Hamiltonian to the observed spectrum and extract the harmonic vibrational contribution. The computation of fundamental frequencies requires a quantum treatment of the ro-vibrational nuclear motion on a potential energy surface, which must include an adequate treatment of anharmonicity so that the comparison with the observed fundamentals reflects the quality of the harmonic frequencies. We therefore choose to restrict our discussion to the closed-shell diatomic molecules

TABLE 4: Relativistic Effects on the Harmonic Vibrational Frequencies (cm^{-1}) of the Diatomics HF, N_2, F_2 and CO[a]

molecule	nonrel	+ DPT	+ DPT + Breit
HF	4142.53	4139.75	4139.12
N_2	2363.36	2362.55	2362.08
F_2	931.86	931.47	931.21
CO	2167.29	2166.41	2165.98

[a] The relativistic corrections to the harmonic vibrational frequencies were obtained by adding first-order direct perturbation theory (DPT) and Breit interaction corrections (obtained at the ae-CCSD(T)/aug-cc-pCVQZ level) to the fc-CCSD(T)-R12 energies.

HF, N_2, F_2, and CO, for which highly accurate spectroscopic constants are available and a direct comparison of harmonic frequencies is possible.[44]

It is clear that a correlation treatment beyond the fc-CCSD(T) method is essential for accurate predictions of vibrational frequencies.[19,24,45] Sufficiently converged corrections due to these higher-order effects must be included if the quality of the dominant fc-CCSD(T)-R12 harmonic frequencies is to be assessed by comparison with those derived from experiment. Taking the same set of diatomics, Ruden et al. performed calculations of the harmonic frequencies, correcting for core-valence correlation and up to connected quintuple excitations in the cluster operator. They make the assumption that the successive corrections to the harmonic frequencies are additive. Taking the fc-CCSD-R12 value as the starting point, they determine a correction for perturbative triples by computing the fc-CCSD and fc-CCSD(T) potential curves with an aug-cc-pV6Z basis. The correction to the harmonic frequency is taken to be the difference between the harmonic frequencies at the different minima on the two surfaces. Proceeding in this way, they compute corrections due to ae-CCSD(T)/aug-cc-pCV5Z, fc-CCSDTQ/cc-pVTZ, and fc-CCSDTQ5/cc-pVDZ.

Additionally, we have computed relativistic corrections at the ae-CCSD(T) level in the aug-cc-pCVQZ basis.[3−5] At each point used to compute the CCSD(T)-R12 frequencies, we used the Dalton program package[46] to compute the relativistic effects arising from first-order direct perturbation theory (DPT)[47−50] and those from the Breit interaction.[51] Adding these corrections to the fc-CCSD(T)-R12 curve defines a new surface upon which the new equilibrium geometry and harmonic frequency may be evaluated. The resulting harmonic frequencies are reported in Table 4. Ruden et al. also computed relativistic corrections, at the fc-CCSD/aug-cc-pVQZ level, and their computed shifts differ at most by 0.2 cm^{-1} from our slightly more accurate values. For reference, we have listed individual components of the computed relativistic corrections to the ground-state energies at the reference geometries in the Supporting Information (Table S7).

In Table 5, we have added our scalar relativistic corrections and the corrections of Ruden et al. due to core-valence and higher-order excitations to our CCSD(T)-R12 harmonic frequencies. In contrast to ref 24, we do not include diagonal Born−Oppenheimer corrections (DBOC). We observe that there appears to be a sign error in the reported DBOC value for HF in Table 5 of ref 24. The values labeled (d) and (f) in Table 1 of the original work of Handy and Lee[52] indicate a *decrease* of −0.35 cm^{-1} rather than an increase of 0.4 cm^{-1}. However, Müller et al. report in ref 53 that the (f) value in ref 52 was in fact erroneous. According to ref 53, the correct SCF/6-31G* DBOC value is 0.03 cm^{-1} and can be neglected. The DBOC values reported by Handy and Lee for N_2 and F_2 are similarly negligible, being 0.03 and 0.02 cm^{-1}, respectively.[52]

TABLE 5: Best Estimates of the Harmonic Vibrational Frequencies (in cm^{-1}) of the Diatomic Closed-Shell Molecules HF, N_2, F_2, and CO

contribution	HF	N_2	F_2	CO
CCSD(T)-R12[a]	4142.5	2363.4	931.9	2167.3
CCSDTQ-CCSD(T)[b]	−4.5	−9.1	−12.2	−6.5
CCSDTQ5-CCSDTQ[c]	−0.1	−3.9	−0.8	0.0
core-correlation correction[d]	4.0	9.8	1.6	9.9
relativistic DPT correction[e]	−2.8	−0.8	−0.4	−0.9
Breit correction[e]	−0.6	−0.5	−0.3	−0.4
best estimate	4138.5	2358.9	919.8	2169.4
experiment[f]	4138.4	2358.6	916.6	2169.8

[a] This work, cf. Table 1. [b] Frozen-core cc-pVTZ level, taken from ref 24. [c] Frozen-core cc-pVDZ level, taken from ref 24. [d] From ae- and fc-CCSD(T)/aug-cc-pCV5Z calculations, taken from ref 24. [e] This work, cf. Table 4. [f] Ref 44. See ref 53 for HF.

The final values are in exceedingly good agreement with the harmonic frequencies extracted from experimental spectra,[44] which underlines the accuracy of our fc-CCSD(T)-R12 harmonic frequencies for these four molecules. The deviation from the experimental values are 0.1, 0.3, 3.2, and 0.4 cm^{-1} for HF, N_2, F_2, and CO, respectively. Ruden et al. also performed a basis set convergence study of the post-CCSD(T) corrections and concluded that the most likely source of error for F_2 is the large basis set dependence of the quadruples contributions.

A further test of our basis set limit fc-CCSD(T) predictions is the comparison with those presented by Ruden et al., who combine aug-cc-pV6Z CCSD(T) corrections to CCSD-R12 values computed by Pawłowski et al.[43] The basis set used for the CCSD-R12 values in that work was 19s14p10d8f5g3h (9s6p4d3f for H), which has more d, f, and g functions than that used in this work but does not contain any i functions (or g functions for H). The deviations of their estimates of the basis set limit fc-CCSD(T) values from ours are 0.1, −0.8, and −0.3 cm^{-1} for HF, N_2, and CO, and −1.1 cm^{-1} for the challenging F_2 molecule. This is further confirmation of our estimated 1 cm^{-1} for the error bars of our near basis set limit fc-CCSD(T)-R12 harmonic frequencies.

As a final remark on the topic of comparison with experiment, we note that the Breit correction to the harmonic frequency is of the same order of magnitude as the DPT relativistic corrections even though the correction to the energies is an order of magnitude smaller (11−12% for the four molecules studied). We observe that it is important to include these very small contributions to the total energy when computing geometries and frequencies to spectroscopic accuracy. However, because the Breit term is independent of the nuclear charge, we expect that its relative importance with respect to the mass-velocity and one-electron Darwin terms will diminish quickly as we proceed to molecules containing second row elements.

5. Conclusions

We have presented benchmark, near basis set limit fc-CCSD(T) equilibrium harmonic frequencies for a set of 12 closed-shell and five open-shell molecules, computed numerically using the explicitly correlated CCSD(T)-R12 method with a careful elimination of the finite difference error. The subwavenumber agreement of our harmonic frequencies for the diatomics HF, N_2, F_2, and CO with values extrapolated from the cc-pV5Z and cc-pV6Z results indicates that our values are within 1 cm^{-1} of the basis set limit. Furthermore, combining our R12 values with scalar relativistic corrections and contributions from core-valence correlation and up to connected quintuple excitations in the cluster operator, we obtain an agreement with experimentally derived values for HF, N_2, and CO of 0.1, 0.3, and -0.4 cm^{-1}, respectively, which affirms our assessment of the accuracy of our basis set limit values. The agreement with experiment for F_2 is somewhat worse, with a deviation of 3.3 cm^{-1}, but this is considered to stem from the high basis set dependence of the quadruples rather than an error in the fc-CCSD(T) contribution.

We have used our benchmark data to perform a basis set convergence study of fc-CCSD(T) harmonic frequencies. We observe that equilibrium harmonic frequencies do not always converge monotonically to the basis set limit, primarily due to effects associated to the convergence of the equilibrium geometry. Direct extrapolation of the spectroscopic constant ω_e is therefore not recommended. The mean absolute errors reduce by a factor of 2 for each increment in the cardinal number, but basis sets larger than cc-pV6Z are required to reduce finite basis set errors to below 1 cm^{-1}. The fc-CCSD(T)/cc-pVTZ method has become a standard tool for computing potential energy surfaces to perform ro-vibrational studies. For the systems considered in this work, the mean and maximum absolute deviations of cc-pVTZ harmonic frequencies from the fc-CCSD(T) basis set limit are 13.8 and 17.5 cm^{-1}. For our simple diatomics, the basis set limit fc-CCSD(T) values typically differed by a further 5 cm^{-1} from the experimentally derived values. Coupled with the inadequate treatment of anharmonicity at the CCSD(T)/cc-pVTZ level of theory, it would be optimistic to expect an accuracy of 20 cm^{-1} in the fundamental frequencies computed using such a surface.

Having obtained high accuracy basis set limit fc-CCSD(T) equilibrium harmonic frequencies for a set of 12 closed-shell and five open-shell molecules, the next step is naturally to proceed to study post-CCSD(T) contributions for our test set. However, final comparison with experiment is only possible through a computation of the fundamental frequencies, which requires a knowledge of the potential energy surface beyond the harmonic approximation. The level to which electron correlation must be treated to obtain spectroscopic accuracy for general polyatomic molecules is largely undefined, and work is in progress to address this question.

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Supporting Information Available: Valence-shell energies of HF, H_2O, CH2 ($^1A_1$), F_2, N_2, CH_4, HCN, HNC, NH_3, CO, CO_2, C_2H_2, OH, CN, NO, CH_2 ($^3B_1$), and NH_2; relativistic energy corrections to the ground-state energies of HF, F_2, N_2, and CO. This material is available free of charge via the Internet at http://pubs.acs.org.

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