

Coupled-cluster connected quadruples and quintuples corrections to the harmonic vibrational frequencies and equilibrium bond distances of HF, N₂, F₂, and CO

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Using the coupled-cluster method, we have examined the contributions from the connected quadruple and quintuple virtual excitations to the harmonic vibrational frequencies and equilibrium bond distances of HF, N₂, F₂, and CO. Whereas the largest quadruples contributions are -18.8 cm^{-1} to the harmonic frequency of N₂ and 0.43 pm to the bond distance of F₂, the largest quintuples contributions are -3.9 cm^{-1} to the harmonic frequency of N₂ and 0.03 pm to the bond distances of N₂ and F₂. As we improve the description by going from the coupled-cluster singles-and-doubles model with a perturbative triples correction [CCSD(T)] to the coupled-cluster singles-doubles-triples-and-quadruples model, the mean and maximum absolute errors in the calculated frequencies relative to experiment are reduced from 11.3 and 15.8 cm^{-1} , respectively, to 3.2 and 4.7 cm^{-1} ; for the bond distances, the mean and maximum absolute errors are reduced from 0.16 and 0.47 pm , respectively, to 0.04 and 0.13 pm . The calculations presented here confirm previous observations that, to some extent, the relatively small errors in the CCSD(T) equilibrium bond distances and harmonic frequencies arise from a cancellation of errors in the approximate (perturbative) treatment of the connected triples and the neglect of higher-order connected excitations. Further inclusion of quintuples contributions, relativistic corrections, and adiabatic corrections reduces the mean and maximum absolute errors to 1.1 and 2.3 cm^{-1} , respectively, for the harmonic frequencies and to 0.02 and 0.05 pm , respectively, for the bond distances. © 2004 American Institute of Physics. [DOI: 10.1063/1.1780155]

I. INTRODUCTION

During the last 10–15 years, significant progress has been made with respect to the accurate calculation of vibrational frequencies (harmonic and fundamental) and equilibrium structures of molecular systems, following the development of codes capable of carrying out highly correlated calculations in large one-electron basis sets.¹ An important reason for this development has been the implementation of analytical molecular derivatives, which has significantly reduced the cost of the calculations and made them more straightforward—see Refs. 2–12 for coupled-cluster first- and second-order derivative theory. For the calculation of vibrational frequencies and equilibrium bond distances, the coupled-cluster singles-and-doubles model with a perturbative triples correction [CCSD(T)] has been particularly successful and high-quality calculations have been reported for a variety of molecules,^{13–27} yielding frequencies and bond distances within 10 cm^{-1} and 0.1 pm , respectively, of the experimental values. In some cases, a careful use of the correlation-consistent basis sets of Dunning and co-workers²⁸ has enabled the basis-set limit to be established for equilibrium bond distances^{14,15,18,29} and for vibrational frequencies.^{26,29–33} Indeed, in particular for harmonic fre-

quencies, such studies have recently indicated that the intrinsic error of the CCSD(T) method is significantly larger than previously thought.^{30,33}

Studies using wave-function models more elaborate than the CCSD(T) model are fewer. In a study of the spectroscopic constants of hydrides,²⁶ it was found that the full inclusion of connected triple excitations at the coupled-cluster single-doubles-and-triples (CCSDT) level of theory offers no improvement in the calculated harmonic frequencies relative to the CCSD(T) method; a similar conclusion was reached with respect to equilibrium bond distances.^{5,34} To obtain accurate harmonic frequencies, it is therefore important to include at least quadruple excitations in the calculations. However, relatively few studies of harmonic frequencies at the coupled-cluster singles-doubles-triples-and-quadruples (CCSDTQ) level of theory have appeared in the literature.^{6,32,35–39} In one of these studies, Kucharski, Watts, and Bartlett calculated the harmonic frequency of N₂ at the CCSDTQ level of theory in the correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set obtaining a surprisingly large quadruples contribution of -19 cm^{-1} .³⁵ Moreover, their CCSDTQ harmonic frequency of 2328 cm^{-1} is 5 cm^{-1} above the full configuration-interaction (FCI) value of 2323 cm^{-1} obtained in Ref. 40. By contrast, for the HF molecule, the CCSDTQ quadruples contribution is -5 cm^{-1} in the correlation-consistent polarized core-valence

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double-zeta (cc-pCBDZ) basis, leading to a harmonic frequency that is only 0.2 cm⁻¹ away from the FCI value.³² Finally, analytical second derivatives have recently been implemented for general coupled-cluster and configuration-interaction models by Kállay and Gauss,⁶ thereby making benchmarking of the coupled-cluster hierarchy more straightforward. In their study of water and ammonia using the cc-pVDZ basis, Kállay and Gauss found that the inclusion of connected quadruples is needed for agreement to within 1 cm⁻¹ of the FCI value.

As for frequencies, only a few studies of the quadruples contribution to equilibrium geometries have appeared in the literature.^{10,35-39} In a N₂ study, the quadruple contribution to the equilibrium bond distance was found to be 0.13 pm in the cc-pVDZ basis,³⁵ only 0.03 pm away from the FCI value in Ref. 36. Similar or smaller quadruples contributions have been found in several other diatomics and in some polyatomics.

In several studies, the quadruples contributions to harmonic frequencies have been estimated by perturbation theory. In this manner, Kucharski and Bartlett obtained a connected quadruples correction to the harmonic frequency of ozone of up to 30 cm⁻¹,⁴¹ whereas Martin obtained quadruples corrections between -6 and -9 cm⁻¹ to the harmonic frequency of OH⁻;⁴² the corresponding quadruples contributions to the bond distances of ozone and OH⁻ are 0.3 and 0.03 pm, respectively.^{41,42} There is therefore strong evidence of the importance of quadruple excitations for the accurate calculation of bond distances and, in particular, of harmonic frequencies.

In this paper, we investigate the importance of higher-order connected excitation contributions to the equilibrium bond distances and harmonic frequencies of the diatoms HF, N₂, F₂, and CO, calculating the full connected triples and connected quadruples contributions to these constants using the CCSDT and CCSDTQ models in the correlation-consistent polarized triple-zeta (cc-pVTZ) basis set and the connected quintuples contributions in the cc-pVDZ basis set using the coupled-cluster singles-doubles-triples-quadruples-and-quintuples (CCSDTQ5) model. In particular, we investigate whether higher-order connected contributions calculated in a small basis set may be combined with the CCSD(T) contribution calculated in a large basis to obtain accurate harmonic frequencies and bond distances. The accuracy of the calculated frequencies and bond distances is established by comparison with experiment, taking into account relativistic and adiabatic corrections. The approach taken in this paper follows closely that of a previous investigation of the CCSDTQ atomization energies of a series of small molecules, including those studied in the present investigation.⁴³

II. COMPUTATIONAL DETAILS

The CCSD, CCSDT, CCSDTQ, and CCSDTQ5 calculations presented in this paper were carried out using a recently developed general coupled-cluster approach⁴⁴ as implemented in the LUCIA program,⁴⁵ with integrals from DALTON.⁴⁶ Unlike its predecessor,⁴⁷ the present code exhibits, to leading order, the proper scaling with respect to the number of occupied and virtual orbitals. In particular, it ex-

hibits the same scaling as codes where the contractions have been explicitly coded in the spin-orbital formalism. The code does not use spin adaptation, but time-reversal symmetry is used to reduce the operation count for wave functions with an even number of electrons by a factor of 2.

The CCSD, CCSDT, CCSDTQ, and CCSDTQ5 potential energy curves were constructed around the equilibrium bond distances, with all points carefully selected to ensure full accuracy of the quoted results. The harmonic frequencies and equilibrium bond distances were obtained from quartic fits to the calculated energies. The connected triples contributions to the spectroscopic constants were then obtained as differences between the calculated CCSDT and CCSD constants, and similarly for the connected quadruples and quintuples. The full triples and quadruples corrections were determined using the correlation-consistent double- and triple-zeta cc-pVDZ and cc-pVTZ basis sets²⁸ in the frozen-core approximation; for the connected quintuple excitations, only the cc-pVDZ basis was used.

The CCSD(T) bond distances and harmonic frequencies were calculated with DALTON,⁴⁶ using a recently implemented numerical differentiation technique.²⁷ In these calculations, we used Dunning's correlation-consistent basis sets augmented with diffuse functions (aug-cc-pVXZ, X = T, Q, 5, 6) (Refs. 31 and 48) and the frozen-core approximation. The core contributions to the spectroscopic constants were estimated at the CCSD(T) level of theory, using the core-valence correlation-consistent basis sets (aug-cc-pCVXZ, X = T, Q, 5) (Ref. 49) in the usual manner.

III. RESULTS AND DISCUSSION

This section is divided into two parts, where we describe first the calculation of harmonic frequencies in Sec. III A and then the calculation of equilibrium bond distances in Sec. III B. Each subsection begins with a basis-set convergence discussion for the CCSD(T) method in the frozen-core approximation. After a brief discussion of core correlation, the effects of higher-order connected excitations are considered. Finally, our results are compared with experimental results.

A. Harmonic frequencies

1. Basis-set convergence of the CCSD(T) harmonic frequencies

Several CCSD(T) basis-set investigations have previously been performed on diatomic molecules. Among these, the most recent involves the four diatomic molecules of this study, focusing on the use of the valence correlation-consistent basis sets.³⁰ As diffuse functions are important for molecules containing fluorine, the harmonic frequencies of HF and F₂ were found to be somewhat too high in the cc-pV6Z basis. To correct for this while keeping the treatment consistent, we have here carried out an aug-cc-pVXZ basis-set investigation for all four molecules in the frozen-core CCSD(T) approximation. The results from this investigation are shown in Table I and Fig. 1. As expected, the convergence of the harmonic frequencies with the cardinal number is slow. Except in HF, the harmonic frequency changes by

TABLE I. Basis-set convergence of the CCSD and CCSD(T) harmonic frequencies and the perturbative triples contribution to the harmonic frequencies in the aug-cc-pVXZ series of basis sets. All calculations are within the frozen-core approximation (cm^{-1}).

	HF			N_2			F_2			CO		
	CCSD	(T)	CCSD(T)	CCSD	(T)	CCSD(T)	CCSD	(T)	CCSD(T)	CCSD	(T)	CCSD(T)
TZ	4169.8	-45.1	4124.8	2418.8	-79.3	2339.6	1010.8	-94.7	916.1	2215.1	-71.0	2144.1
QZ-TZ	19.3	-2.3	17.1	15.5	-0.6	14.9	5.9	-0.8	5.1	16.2	-0.2	16.0
5Z-QZ	1.6	-1.0	0.6	5.3	-0.4	4.9	5.8	-0.1	5.8	3.9	-0.2	3.7
6Z-5Z	0.3	-0.1	0.1	1.7	-0.3	1.3	2.0	-0.1	1.9	1.4	-0.1	1.2
Total	4191.0	-48.4	4142.6	2441.3	-80.6	2360.7	1024.4	-95.7	928.7	2236.8	-71.5	2165.3

more than 1 cm^{-1} as we increase the cardinal number from five to six. Also, as illustrated by F_2 , convergence is not always smooth.

It is important to realize, however, that the slow convergence of the harmonic constants arises mainly from the connected double excitations. As seen from Table I, where we have listed separately the CCSD and CCSD(T) contributions to the harmonic frequencies in the aug-cc-pVXZ basis sets, the perturbative triples contribution converges separately much faster than the total CCSD(T) harmonic frequency. Except for HF, where the frequency changes by -2.3 cm^{-1} , the absolute change in the perturbative triples contribution is less than 1 cm^{-1} as we increase the cardinal number from three to four. As the cardinal number is further incremented from five to six, the largest change in the CCSD(T) frequency is 1.9 cm^{-1} (for F_2), while the largest change in the triples contribution is only -0.3 cm^{-1} (for N_2). Indeed, except for the HF molecule, the change in the triples contribution is

usually an order of magnitude smaller than the change in the total CCSD(T) frequency. Note that, because of the opposite signs of the CCSD and triples contributions to the calculated frequencies, the CCSD(T) frequencies converge slightly faster than the CCSD frequencies.

Harmonic frequencies close to the basis-set limit may be obtained using the explicitly correlated R12 method.⁵⁰⁻⁵⁴ Because of the rapid triples convergence, the basis-set limit can be accurately estimated by adding to the CCSD(T)/aug-cc-pV6Z frequencies in Table I the differences between the CCSD-R12 results of Ref. 30 and the CCSD/aug-cc-pV6Z results calculated here. This approach gives our best estimates of the frozen-core CCSD(T) harmonic frequencies, listed in Table II. The remaining basis-set error is conservatively estimated to be less than 0.5 cm^{-1} . A comparison with the experimental values in Table II reveals that the mean absolute and maximum errors at this level of theory are 6.4 and 14.4 cm^{-1} , respectively.

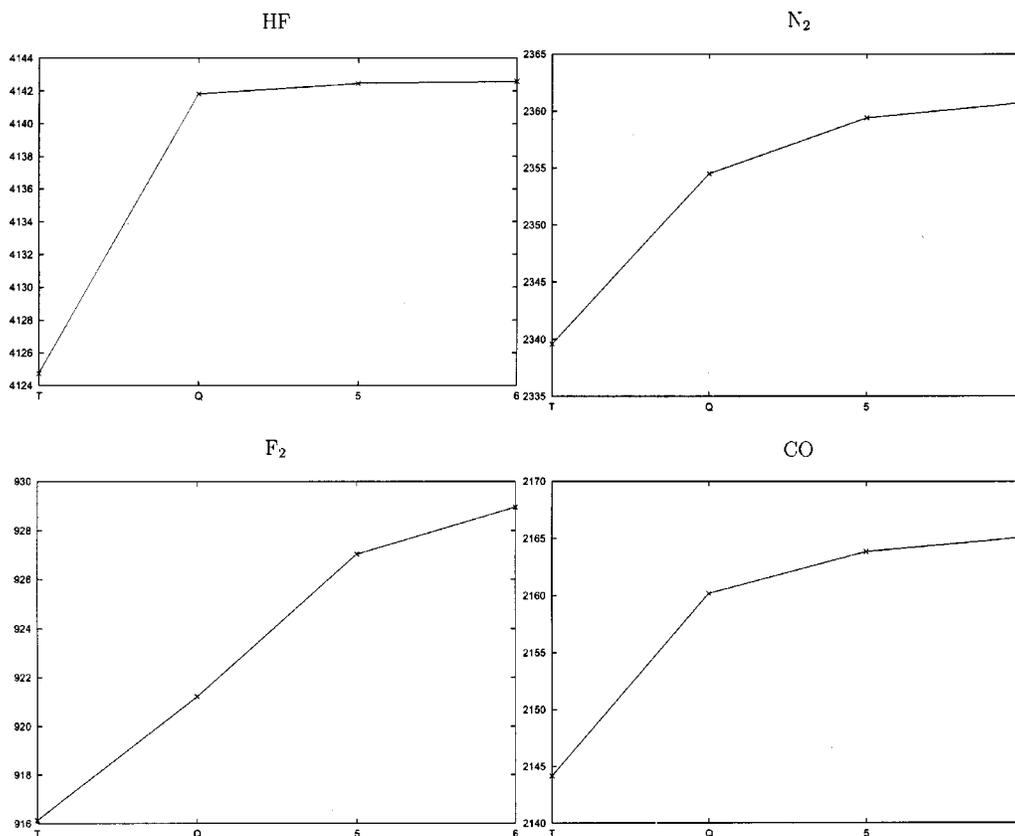
FIG. 1. The basis-set convergence using aug-cc-pVXZ, $X = T, Q, 5, 6$ of CCSD(T) harmonic frequencies.

TABLE II. Frozen-core (fc) and all-electron (ae) CCSD(T) harmonic frequencies compared with experimental values (cm⁻¹).

	HF	N ₂	F ₂	CO
CCSD(T)/aug-cc-pV6Z (fc)	4142.6	2360.7	928.7	2165.3
R12 correction ^a	0.0	1.9	2.1	1.7
CCSD(T)/basis-set limit (fc)	4142.6	2362.6	930.8	2167.0
Core-correlation correction ^b	4.0	9.8	1.6	9.9
CCSD(T)/basis-set limit (ae)	4146.6	2372.4	932.4	2176.9
Experiment	4138.3	2358.6	916.6	2169.8

^aReference 30.^bCalculated as the difference between all-electron and frozen-core CCSD(T)/aug-cc-pCV5Z frequencies.

2. Contributions from core correlation

The calculations discussed above have been performed in the frozen-core approximation. Several authors have pointed out the importance of core correlation for harmonic frequencies^{55–58} and systematic studies have been carried out to examine the dependence of core correlation on the correlation treatment and basis set.^{29,30} Such studies have shown that the core-correlation contribution to harmonic frequencies is not particularly sensitive to the basis-set size (provided that a basis set of at least triple-zeta quality is used). We here examine the core contribution at the CCSD(T) level of theory, using the augmented core-valence basis sets aug-cc-pCVXZ.

The plots in Fig. 2 confirm the expected relative insensitivity of the core contribution to the size of the basis set. As we increase the cardinal number from four to five, the largest change in the core contribution is 0.5 cm⁻¹. Good core-correlation estimates (to within 0.5 cm⁻¹) can therefore be obtained at the CCSD(T)/aug-cc-pCV5Z level of theory. We note that the core contributions found here are similar to those obtained in previous studies.^{29,30,33,55–58}

By adding the calculated core contribution to our best estimated valence harmonic frequencies, we arrive at our best estimates of the all-electron CCSD(T) harmonic frequency in Table II. With the inclusion of core correlation, the mean absolute and maximum absolute intrinsic errors increase from 6.4 and 14.4 cm⁻¹, respectively, to 11.3 and 15.8 cm⁻¹. Note that the CCSD(T) model consistently and significantly overestimates the harmonic frequency, substantiating the notion that higher-order correlation contributions are important.

3. Contributions from full triple, quadruple, and quintuple excitations

To investigate the importance of higher-order connected virtual excitations for harmonic frequencies, a systematic series of calculations were performed at the Hartree-Fock, CCSD, CCSDT, CCSDTQ, and CCSDTQ5 levels of theory in the cc-pVDZ and cc-pVTZ basis sets. As seen from Table III, none of the calculated high-order contributions can be neglected in high-accuracy work. Moreover, the large cc-pVDZ quadruples contribution of -18.5 cm⁻¹ to the har-

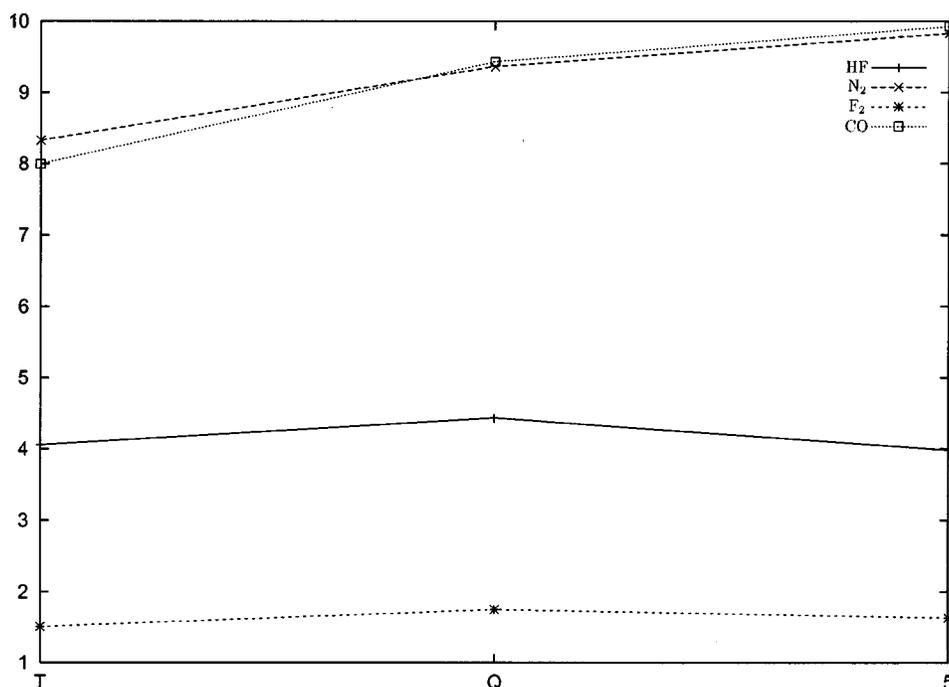


FIG. 2. The basis-set convergence of CCSD(T) core contributions to the harmonic frequencies using aug-cc-pCVXZ, X = T, Q, 5, 6.

TABLE III. Connected-excitation contributions to the harmonic frequencies in the cc-pVDZ and cc-pVTZ basis sets (cm^{-1}).

	HF		N_2		F_2		CO	
	D	T	D	T	D	T	D	T
RHF	4440.8 ^a	4481.8	2758.3	2731.7	1180.1	1266.8	2431.6	2425.0
CCSD-RHF	-271.8 ^a	-269.8	-349.5	-307.8	-294.3	-254.3	-222.5	-202.1
CCSDT-CCSD	-20.5 ^a	-35.1	-62.2	-68.3	-98.9	-89.4	-67.3	-69.9
CCSDTQ-CCSDT	-4.8 ^a	-4.0	-18.5	-18.8	-13.1	-15.3	-5.9	-5.7
CCSDTQ5-CCSDTQ	-0.1	-0.4	-3.9		-0.8		0.0	

^aReference 32.

monic frequency of N_2 is in perfect agreement with previous work.³⁵ Since this value is almost identical to the value of -18.8 cm^{-1} obtained in the larger cc-pVTZ basis, we conclude that the previously observed large quadruples contributions are not merely artifacts arising from the use of small basis sets. It is also interesting to note that the calculated quadruples contributions to the harmonic frequencies of N_2 and F_2 are larger than the previously stated intrinsic errors of the CCSD(T) method.^{13,33}

As expected, all high-order connected contributions to the harmonic frequencies are negative, converging monotonically towards the FCI limit. With each new excitation level in Table III, the contribution from the added excitations typically decreases by an order of magnitude, indicating that the remaining N -electron error is less than 0.5 cm^{-1} at the CCSDTQ5 level of theory. The results in Table III also show that, as we increase the basis from cc-pVDZ to cc-pVTZ, the mean absolute change in the quadruples contribution is 0.9 cm^{-1} , while the maximum absolute change is 2.2 cm^{-1} . This is significantly less than for the triples contribution, which has a mean absolute change of 8.2 cm^{-1} and a maximum change of 14.6 cm^{-1} . Extrapolating this trend, an even weaker basis-set dependence is expected for the quintuples contribution, suggesting that a good estimate of this contribution is obtained in the small cc-pVDZ basis. Indeed, this result is confirmed for HF, where the connected quintuples contribution has been determined in both basis sets: as the basis increases from cc-pVDZ to cc-pVTZ, the quintuples contribution changes by only -0.3 cm^{-1} .

Concerning the accuracy of the perturbative triples treatment in the CCSD(T) model, we compare in Table IV the CCSD(T)/cc-pVTZ harmonic frequencies with those calculated at the CCSDT and CCSDTQ levels of theory in the same basis. The CCSDT frequencies are no improvement on the CCSD(T) results, supporting the conclusions of Feller and Sordo, who found little to distinguish the two methods in calculations on 13 diatomic hydrides.²⁶ In fact, at the CCSDT level of theory, the N_2 and F_2 harmonic frequencies

TABLE IV. CCSD(T), CCSDT, and CCSDTQ harmonic frequencies calculated in the cc-pVTZ basis (cm^{-1}).

	CCSD(T)	CCSDT	CCSDTQ
HF	4177.4	4177.0	4172.9
N_2	2346.0	2355.7	2336.9
F_2	920.0	923.1	907.8
CO	2153.7	2153.0	2147.3

are further away from the CCSDTQ results than are the CCSD(T) frequencies; for HF and CO, there are only minor differences between the CCSD(T) and CCSDT frequencies.

4. Remaining electronic contributions to harmonic frequencies

In the above calculations, there may still be errors arising from the neglect of higher-order connected excitations and from basis-set incompleteness in the calculated full triples, quadruples, and quintuples contributions. FCI investigations in the cc-pVDZ basis are found in the literature for N_2 and HF.^{32,36} In view of the relatively weak basis-set dependence of the higher-order contributions, the cc-pVDZ results should give good estimates of the remaining N -electron error. For HF, the difference between our CCSDTQ5 value and the FCI value is only about -0.1 cm^{-1} ; for N_2 , the difference is less than 0.5 cm^{-1} . These small differences indicate that the error arising from the neglect of higher-order excitations is small indeed. Note that these comparisons with FCI calculations agree well with our previous estimate of the remaining N -electron error.

To estimate the remaining basis-set error, CCSDT and CCSDTQ calculations were carried out on the HF molecule in the cc-pVQZ basis. Comparing with the CCSD(T) model, we find that the remaining triples and quadruples contributions in the cc-pVQZ basis are 0.5 and -4.1 cm^{-1} , respectively. These results are in excellent agreement with the cc-pVTZ calculations, where the corresponding remaining contributions are 0.4 and -4.0 cm^{-1} . Note, however, that the quadruples contribution in F_2 changes by more than 2 cm^{-1} when the basis set is increased from cc-pVDZ to cc-pVTZ, indicating that a further basis-set extension might be important for this molecule.

Unlike for the quadruples contribution to the harmonic frequency, we have no cc-pVQZ results for the quintuples contribution. As previously discussed, the basis-set dependence of this contribution is weak, indicating that the effect of further basis-set extensions is small. Except for F_2 , the total remaining basis-set error is conservatively estimated to be less than 0.5 cm^{-1} .

5. Total calculated harmonic frequencies

Our best estimates of the harmonic frequencies of HF, N_2 , F_2 , and CO are obtained from the CCSD-R12 results of Ref. 30 by adding the aug-cc-pV6Z perturbative-triples contributions, the cc-pVTZ remaining triples contributions, the cc-pVTZ quadruples contributions, the cc-pVDZ quintuples

TABLE V. Contributions to the best estimates of harmonic frequencies (cm⁻¹).

	HF	N ₂	F ₂	CO
CCSD-R12 ^a	4191.0	2443.2	1026.5	2238.5
CCSD(T)-CCSD ^b	-48.4	-80.6	-95.7	-71.5
CCSDTQ-CCSD(T) ^c	-4.5	-9.1	-12.2	-6.5
CCSDTQ5-CCSDTQ ^d	-0.1	-3.9	-0.8	0.0
Core-correlation correction ^e	4.0	9.8	1.6	9.9
Total	4142.0	2359.4	919.4	2170.4
Adiabatic correction	0.4 ^g	0.0 ^f	0.0 ^f	
Relativistic correction	-3.5	-1.4	-0.5	-1.3
Best estimate	4138.9 ^f	2358.0 ^g	918.9 ^g	2169.1 ^g
Experiment	4138.3 ^g	2358.6 ^g	916.6 ^g	2169.8 ^g

^aReference 30.^bFrozen-core aug-cc-pV6Z.^cFrozen-core cc-pVTZ.^dFrozen-core cc-pVDZ.^eFrom all-electron and frozen-core CCSD(T)/aug-cc-pCV5Z calculations.^fReference 59.^gReference 62. A more recent value for HF is 4138.4 cm⁻¹ (Ref. 63).

contributions, and the CCSD(T)/aug-cc-pCV5Z core contributions—see Table V, where we have also listed the experimental harmonic frequencies. Comparing with experiment, it is clear that high accuracy has been attained in the calculations, with mean and maximum absolute errors of only 2.0 and 3.7 cm⁻¹, respectively. Still, some discrepancies remain—in particular, for HF and F₂, the calculated frequencies deviate from experiment by more than our estimated uncertainty of 2.0 cm⁻¹.

The main source of error in our calculations is the neglect of non-Born–Oppenheimer and relativistic corrections. In Table V, the adiabatic corrections are found using the Hartree-Fock diagonal Born–Oppenheimer corrections from Ref. 59. Parts of the nonadiabatic contributions are accounted for by using atomic rather than nuclear masses in the frequency calculations.⁶⁰ The first-order relativistic corrections (calculated at the CCSD/aug-cc-pVQZ level of theory with all one- and two-electron Breit–Pauli operators included) have been collected from Ref. 61. These corrections have been calculated at the CCSD level of theory using the aug-cc-pVQZ basis. With these corrections included where available, the mean and maximum absolute errors are reduced from 2.0 and 3.7 cm⁻¹, respectively, to 1.1 and 2.3 cm⁻¹. Except for F₂, all frequencies are now within spectroscopic accuracy (1 cm⁻¹). For F₂, the slow basis-set convergence of the quadruples contribution may be responsible for the remaining observed discrepancy.

Finally, it is perhaps worth pointing out that, even though the accuracy obtained in our calculations is high compared with previous electronic-structure calculations, our estimated total uncertainty is still twice what is considered spectroscopic accuracy, illustrating the difficulties associated with calculating harmonic frequencies to within this accuracy.

B. Equilibrium bond distances

1. Basis-set convergence of the CCSD(T) equilibrium bond distances

As for harmonic frequencies, a number of CCSD(T) basis-set investigations of equilibrium bond distances have appeared in the literature.^{14,16,26,29–31,33} For consistency, our treatment of the bond distances of HF, N₂, F₂, and CO follows closely that of the harmonic frequencies in Sec. III A. In Table VI and Fig. 3, the results of our CCSD(T)/aug-cc-pVXZ calculations in the frozen-core approximation are presented. As expected, the convergence of the equilibrium bond distances with the cardinal number *X* is smooth and faster than for the frequencies. In particular, when the basis set is increased from aug-cc-pV5Z to aug-cc-pV6Z, all four bond distances change by less than 0.1 pm.

From Table VI, we note that the triples contribution to the bond distance separately converges faster than does the total CCSD(T) bond distance. Indeed, in the relatively small

TABLE VI. Basis-set convergence of the CCSD and CCSD(T) equilibrium bond distances and the perturbative triples contribution to the bond distances in the aug-cc-pVXZ series of basis sets. All calculations are within the frozen-core approximation (pm).

	HF			N ₂			F ₂			CO		
	CCSD	(T)	CCSD(T)	CCSD	(T)	CCSD(T)	CCSD	(T)	CCSD(T)	CCSD	(T)	CCSD(T)
TZ	91.82	0.27	92.10	109.67	0.72	110.40	139.57	2.25	141.81	112.88	0.72	113.60
QZ-TZ	-0.33	0.01	-0.33	-0.35	0.00	-0.35	-0.53	0.03	-0.51	-0.41	0.01	-0.42
5Z-QZ	-0.04	0.01	-0.04	-0.10	0.00	-0.10	-0.19	-0.02	-0.21	-0.09	0.00	-0.09
6Z-5Z	-0.01	0.00	0.00	-0.03	0.00	-0.03	-0.08	0.00	-0.08	-0.03	0.00	-0.03
Total	91.44	0.29	91.73	109.20	0.72	109.92	138.76	2.26	141.02	112.34	0.72	113.06

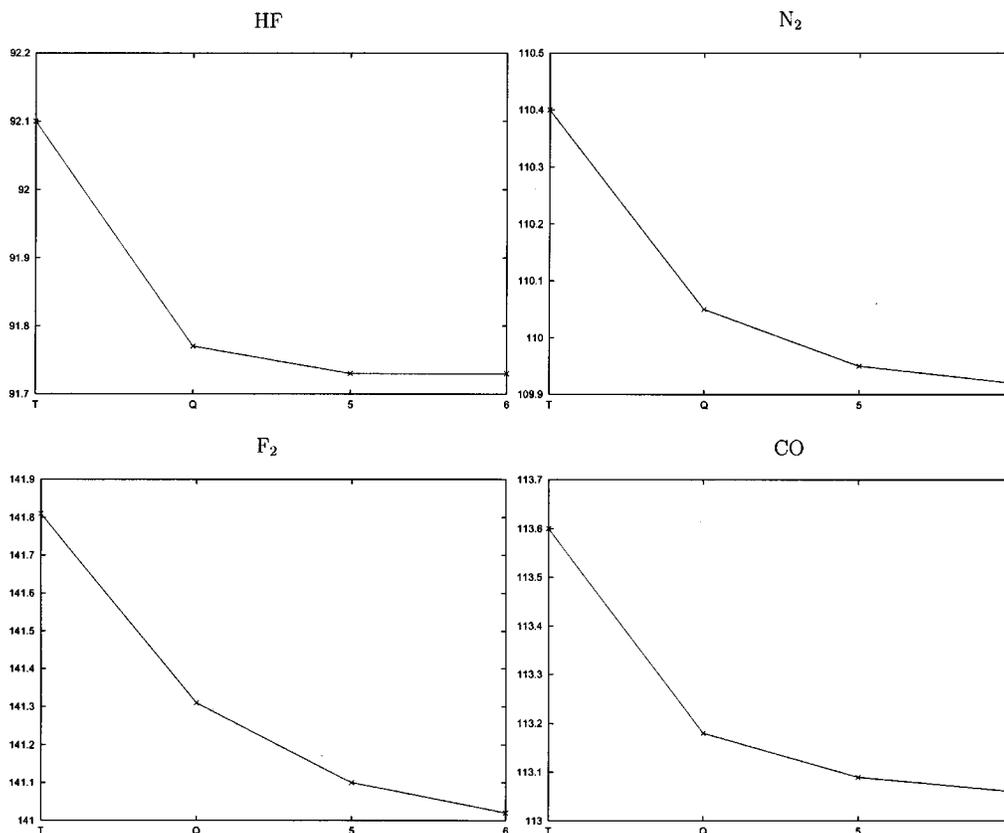


FIG. 3. The basis-set convergence using aug-cc-pVXZ, $X = T, Q, 5, 6$ of CCSD(T) equilibrium bond distances.

aug-cc-pVTZ basis, the triples contribution is in all cases within 0.02 pm of the basis-set limit, suggesting that the CCSD(T) basis-set limit can be obtained by adding a CCSD-R12 correction (obtained in the same way as for the frequencies) to the CCSD(T)/aug-cc-pV6Z results—see Table VII. Because of the fast triples convergence, the remaining basis-set error is not expected to affect the bond distances to the number of quoted digits. Comparing the calculated and experimental results in Table VII, we find that the mean absolute and maximum absolute intrinsic errors of the frozen-core CCSD(T) model are 0.17 and 0.33 pm, respectively, for these molecules.

2. Contributions from core correlation

As for harmonic frequencies, the core-correlation contribution to equilibrium bond distances can be important^{15,29,56} and systematic studies have recently been performed to examine its dependence on the correlation treatment and basis set.^{29,30} In some cases, core correlation has been found to affect bond distances by as much as 0.2 pm.

As for the harmonic frequencies in Sec. III A, the core-correlation correction to the bond distances has been calculated in the aug-cc-pCVXZ basis sets with $X \leq 5$. The plots in Fig. 4 demonstrate the expected insensitivity of the core cor-

TABLE VII. Frozen-core (fc) and all-electron (ae) CCSD(T) equilibrium bond distances compared with experimental values (pm).

	HF	N ₂	F ₂	CO
CCSD(T)/aug-cc-pV6Z (fc)	91.73	109.92	141.02	113.06
R12 correction ^a	-0.01	-0.04	-0.08	-0.04
CCSD(T)/basis-set limit (fc)	91.72	109.88	140.94	113.02
Core correction ^b	-0.06	-0.21	-0.14	-0.24
CCSD(T)/basis-set limit (ae)	91.66	109.68	140.80	112.78
Experiment ^c	91.69 ^d	109.77	141.27	112.84 ^e

^aReference 30.

^bCalculated as the difference between all-electron and frozen-core CCSD(T)/aug-cc-pCV5Z bond distances.

^cReference 16.

^dError in the experimental values is ± 0.01 pm.

^eError suggests the experimental equilibrium bond distances to be 112.83–112.84 pm.

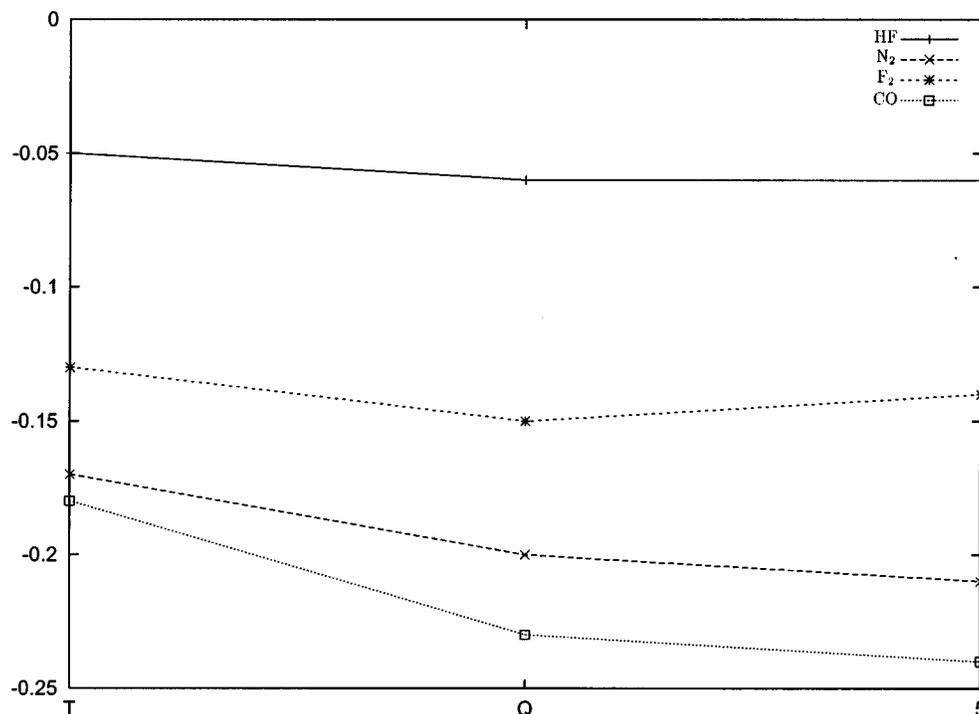


FIG. 4. The basis-set convergence of CCSD(T) core contributions to the equilibrium bond distances using aug-cc-pCVXZ, $X=T,Q,5,6$.

rection to basis-set expansion. Indeed, the largest change in the core correction from aug-cc-pCVQZ to aug-cc-pCV5Z is only 0.02 pm, indicating that the CCSD(T)/aug-cc-pCV5Z model provides a good estimate of this contribution. The remaining basis-set error in the core correction is estimated to be 0.03 pm. Note that the core contributions obtained here are similar to those found in previous studies.^{29,30,56}

Adding the core contributions to the best estimated frozen-core bond distances, we obtain the best estimates of the all-electron CCSD(T) equilibrium bond distances listed in Table VII. Comparing with experiment, we find that the inclusion of core correlation does not affect the mean absolute error of 0.17 pm, while the maximum absolute error increases from 0.33 to 0.47 pm. It is noteworthy that, upon the inclusion of core correlation, the CCSD(T) model consistently underestimates the experimental bond distances, indicating that the remaining error may be eliminated by including higher-order connected excitations in the description.

3. Contributions from full triple, quadruple, and quintuple excitations

As for the harmonic vibrational constants, the importance of higher-order connected excitations was examined by performing calculations at the Hartree-Fock, CCSD, CCSDT, CCSDTQ, and CCSDTQ5 levels of theory in the cc-pVDZ and cc-pVTZ basis sets. From Table VIII, it follows that the inclusion of quadruples is important for F₂, increasing the bond distance by 0.4 pm; for N₂ and CO, the correction is 0.1 pm; for HF, it is negligible. The quintuples correction is largest for N₂ and F₂ (0.03 pm), yielding total quadruples and quintuples corrections of 0.16 and 0.42 pm, respectively; for HF and CO, smaller corrections are observed.

As expected, all higher-order connected correlation contributions are positive, converging monotonically towards the FCI values. As for the frequencies, the corrections decrease by about an order of magnitude with each increment

TABLE VIII. Connected-excitation contributions to the equilibrium bond distances in the cc-pVDZ and cc-pVTZ basis sets (pm).

	HF		N ₂		F ₂		CO	
	D	T	D	T	D	T	D	T
RHF	90.15	89.79	107.73	106.71	134.76	132.91	110.45	111.01
CCSD-RHF	1.74	1.73	3.55	2.96	8.44	6.55	3.39	1.86
CCSDT-CCSD	0.10	0.20	0.57	0.64	2.57	2.07	0.64	0.71
CCSDTQ-CCSDT	0.03	0.02	0.13	0.14	0.43	0.39	0.06	0.04
CCSDTQ5-CCSDTQ	0.00	0.00	0.03		0.03		0.00	

TABLE IX. CCSD(T), CCSDT, and CCSDTQ equilibrium bond distances calculated in the cc-pVTZ basis (pm).

	CCSD(T)	CCSDT	CCSDTQ
HF	91.72	91.72	91.74
N ₂	110.38	110.31	110.45
F ₂	141.58	141.54	141.92
CO	113.57	113.59	113.63

in the excitation level, indicating that the remaining N -electron error is negligible to the number of digits quoted. When the basis set in Table VIII is increased from cc-pVDZ to cc-pVTZ, the quadruples correction changes by 0.02 pm on average and by 0.04 pm maximum—that is, by significantly less than the triples correction, which changes by 0.19 pm on average and by 0.50 pm maximum. Extrapolating to higher excitation levels, we expect an even weaker basis-set dependence in the quintuples contribution, suggesting that a good estimate of this contribution is obtained in the cc-pVDZ basis.

In Table IX, the CCSD(T)/cc-pVTZ equilibrium bond distances are compared with the CCSDT and CCSDTQ results in the same basis set. As observed by Halkier *et al.*,³⁴ the CCSD(T) model tends to overestimate the triples contribution, giving longer bond distances than does the CCSDT model.

4. Remaining electronic contributions to equilibrium bond distances

In the bond distances obtained above, small errors still remain because of the neglect of sextuple and higher connected excitations and because of the use of incomplete basis sets in the calculation of the full triples, quadruples, and quintuples corrections. For N₂, a FCI/cc-pVDZ study has been published.³⁶ In view of the observed weak basis-set dependence of the higher-order connected excitations, these

FCI results should give us good estimates of the contributions from the neglected excitations. For N₂, the difference between the FCI and CCSDTQ bond distances is 0.03 pm, which is the same as the quintuples correction obtained here, suggesting that the N -electron error is negligible to the quoted number of digits. Note that this result agrees with our previous estimate of the remaining N -electron error.

To estimate the basis-set error in the higher-order correlation corrections, we have carried out additional CCSDT and CCSDTQ calculations on the HF molecule in the cc-pVQZ basis. Comparing with the CCSD(T) model, we find that the full triples and quadruples corrections are identical in the cc-pVTZ and cc-pVQZ basis sets (0.02 and 0.00 pm, respectively), suggesting that, for HF at least, the basis-set errors are negligible. From the somewhat larger differences between the cc-pVDZ and cc-pVTZ results for F₂ and CO, we expect the basis-set errors for these molecules to be larger than for HF but smaller than 0.02 pm.

5. Total calculated equilibrium bond distances

As for the harmonic frequencies, our best estimates of the equilibrium bond distances of HF, N₂, F₂, and CO are obtained by adding to the CCSD-R12 values of Ref. 30 the following corrections determined in this paper: aug-cc-pV6Z perturbative triples corrections, cc-pVTZ remaining triples corrections, cc-pVTZ quadruples corrections, cc-pVDZ quintuples corrections, and CCSD(T)/aug-cc-pCV5Z core-correlation corrections. These best estimates are listed in Table X, together with the corresponding experimental values. The mean and maximum absolute deviations from experiment are only 0.03 and 0.10 pm, respectively. We note that three of the four experimental values fall within the estimated uncertainty of about 0.05 pm in the calculated bond distances.

In Table X, we have also listed the adiabatic and first-order relativistic corrections to the bond distances, obtained from the same source as for harmonic frequencies. The adia-

TABLE X. Contributions to the best estimates of equilibrium bond distances (pm).

	HF	N ₂	F ₂	CO
CCSD/R12 ^a	91.43	109.16	138.68	112.30
CCSD(T)-CCSD ^b	0.29	0.73	2.26	0.72
CCSDTQ-CCSD(T) ^c	0.02	0.07	0.34	0.06
CCSDTQ5-CCSDTQ ^d	0.00	0.03	0.03	0.00
Core-correlation correction ^e	-0.06	-0.21	-0.14	-0.24
Total	91.68	109.78	141.17	112.84
Adiabatic correction ^f	0.00	0.00	0.00	
Relativistic correction	0.01	0.00	0.05	0.00
Best estimate	91.69	109.78	141.22	112.84
Experiment ^g	91.69 ^h	109.77	141.27	112.84 ⁱ

^aReference 30.

^bFrozen-core aug-cc-pV6Z.

^cFrozen-core cc-pVTZ.

^dFrozen-core cc-pVDZ.

^eFrom all-electron and frozen-core CCSD(T)/aug-cc-pCV5Z calculations.

^fReference 59.

^gReference 16.

^hError in the experimental values is ± 0.01 pm.

ⁱError suggests the experimental equilibrium bond distance to be 112.83–112.84 pm.

batic corrections (where available) are negligible. The relativistic correction is 0.01 pm for HF and 0.05 pm for F₂ but otherwise negligible. With these corrections included, the mean and maximum absolute deviations relative to experiment are reduced from 0.03 and 0.10 pm, respectively, to 0.02 and 0.05 pm. Note that these deviations are significantly larger than the experimental uncertainties of about 0.01 pm.¹⁶

IV. CONCLUSION

We have calculated accurate harmonic vibrational frequencies and equilibrium bond distances of HF, N₂, F₂, and CO using coupled-cluster wave functions containing up to connected quintuple excitations. Employing larger one-electron basis sets than before, these investigations have confirmed the previous observations made by Kucharski, Watts, and Bartlett³⁵ and by Kállay and Gauss⁶ that connected quadruple excitations are needed to calculate frequencies rigorously to within ten wave numbers of the experimental measurements. In an effort to improve the accuracy further, the quintuples contributions to the harmonic frequencies and bond distances have been calculated and found to contribute up to 4 cm⁻¹ and 0.03 pm, respectively, to these spectroscopic constants.

The good agreement that is often observed between CCSD(T) and experimental harmonic frequencies and bond distances arises from a cancellation of the errors incurred by truncation of the coupled-cluster hierarchy and by truncation of the one-electron basis set. Indeed, for the four diatomic molecules studied here, the estimated intrinsic error of the CCSD(T) model is up to 16 cm⁻¹ for the harmonic frequency and up to 0.5 pm for the equilibrium bond distance. Relaxation of the triples at the CCSDT level does not improve the agreement with experiment, illustrating the need to include higher than connected triple excitations to calculate these constants to experimental accuracy.

Our best estimates of the harmonic frequencies and bond distances have been obtained by combining the CCSD-R12 results of Ref. 30 with aug-cc-pV6Z perturbative triples contributions, cc-pVTZ full triples and quadruples contributions, cc-pVDZ quintuples contributions, and CCSD(T)/aug-cc-pCV5Z core-correlation contributions. With adiabatic and relativistic corrections added, this approach yields harmonic frequencies of 4138.9, 2358.0, 918.9, and 2169.1 cm⁻¹, respectively, for HF, N₂, F₂, and CO, to be compared with the experimentally determined values of 4138.3, 2358.6, 916.6, and 2169.8 cm⁻¹, respectively. The similarly obtained equilibrium bond distances of HF, N₂, F₂, and CO are 91.69, 109.78, 141.22, and 112.84 pm, respectively, close to the corresponding experimental values of 91.69, 109.77, 141.27, and 112.84 pm. The mean and maximum absolute deviations from the experimental values are 1.1 and 2.3 cm⁻¹, respectively, for the harmonic frequencies and 0.02 and 0.05 pm, respectively, for the equilibrium bond distances. Our estimated uncertainties of 2 cm⁻¹ and 0.05 pm in the calculated frequencies and bond lengths, respectively, are larger than the experimental error bars.

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