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Anharmonic vibrational analysis of water with traditional and explicitly correlated coupled cluster methods

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It is well known that the convergence of harmonic frequencies with respect to the basis set size in traditional correlated calculations is slow. We now report that the convergence of cubic and quartic force constants in traditional CCSD(T) calculations on H₂O with Dunning's cc-pVXZ family of basis sets is also frustratingly slow. As an alternative, we explore the performance of R12-based explicitly correlated methods at the CCSD(T) level. Excellent convergence of harmonic frequencies and cubic force constants is provided by these explicitly correlated methods with R12-suited basis irrespective of the used standard approximation and/or the correlation factor. The Slater type geminal, however, outperforms the linear r_{12} for quartic force constants and vibrational anharmonicity constants. The converged force constants from explicitly correlated CCSD(T) calculations succeed in reproducing the fundamental frequencies of water molecule with spectroscopic accuracy after corrections for post-CCSD(T) effects are made. © 2010 American Institute of Physics. [doi:10.1063/1.3464837]

I. INTRODUCTION

Spectroscopic properties such as harmonic vibrational frequencies, rotational constants, centrifugal distortion constants, rovibrational coupling constants, and vibrational anharmonicities can be experimentally determined to a very high accuracy for many small molecules. The calculation of such properties *ab initio* at “spectroscopic accuracy,” usually understood to mean vibrational frequencies are accurate to about 1 cm⁻¹ (12 J/mol), has been proven challenging for even the most advanced computational approaches. For example, the prediction of fundamental frequencies with average errors below 1 cm⁻¹ for water molecule required multi-reference configuration interaction (MRCI) calculations with a large active valence orbital space, followed by corrections due to core correlation, relativistic effects, quantum electrodynamics, and the Born–Oppenheimer approximation. While MRCI offers an extremely accurate representation of a full configuration interaction potential energy surface, this approach is limited to molecules with a small number of valence electrons that can be well described by a limited number of orbitals in the active space.

Single reference coupled cluster methods promise to yield accurate representations of the potential energy surfaces of molecules at a lower cost than MRCI.¹ However, the fully iterative singles and doubles coupled cluster method (CCSD) falls well short of spectroscopic accuracy.^{2,3} The popular CCSD(T) approach offers an improvement, with

typical errors in harmonic frequencies in the range of 10–20 cm⁻¹.^{2–9} There are two major limitations to higher accuracy with the coupled cluster approach. First, the meaningful estimation of double excitation contributions requires large basis sets that include functions with high angular momentum.³ Second, the correlation contributions beyond triple excitations are not negligible.^{5,6,9} Due to the steep scaling of computational cost, both with the size of the basis set and the inclusion of higher excitations, calculations of near-spectroscopic accuracy, such as CCSDTQ/aug-cc-pV5Z, are not routinely possible for polyatomic molecules at the present time.

It has been shown that for many diatomic systems, spectroscopic accuracy can be obtained by combining the valence-only CCSD(T) results at the basis set limit with various correction terms that are evaluated with a smaller basis.^{3,6,7} Two approaches to obtain the correlation energy at the basis set limit have emerged in recent years. First, noting that the correlation energy converges systematically in correlation-consistent basis sets, one can extrapolate from results with finite basis sets.^{10–14} Second, one can use wave functions that explicitly depend on the interelectronic distance (r_{12}) when evaluating contributions from single and double excitations.^{3,4,8,15–21} The latter approach defines a family of explicitly correlated CCSD-R12 methods that promise near-basis-set-limit correlation energies using moderate size basis sets.

Almost 2 decades ago, CCSD(T)-R12 (Ref. 22) was implemented within the “standard approximation.”²³ More recently a full treatment has been described using one-particle relaxation, and a complementary auxiliary basis, to

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evaluate many-particle integrals.^{24,25} In addition, the implementation within the standard approximation (SA) has been extended to include a genuine Slater type germinal (STG) (*vide infra*) correlation factor [CCSD(T)-F12] with analytic evaluation of the resulting integrals.^{25,26} A first full implementation, based on a computer generated parallel code, has been reported.²⁷ However, it does not account for the one-particle basis set relaxation effects nor does it use analytic STG integrals.

The standard approximation uses a one-particle resolution of the identity approximated by a projector over the actual computational basis.²³ This significantly simplifies the coding but necessitates basis sets in which low angular momentum functions (e.g., *s*, *p*, *d*, and *f* for atoms with the highest occupied orbital being *p*) must be almost fully saturated in the radial dimension.²⁸ Such “Universal R12-optimized basis sets” have been developed recently.^{29,30} Different methods for evaluation of matrix elements involving the commutator of the kinetic operator and the correlation factor define approximations A, B, and C.²⁴ As an alternative to the SA, one can use large auxiliary basis sets for the resolution of the identity.³¹ The simplest formulation, and the best performance, is achieved when the auxiliary bases form orthogonal complement of the main orbital basis.³² Then, one can work with a much smaller orbital basis. Nevertheless, to achieve spectroscopic accuracy which is our target, one has to use fairly extensive basis sets even with explicitly correlated methods. In that case the SA is fully justified and leads to simpler algorithms.

In earlier versions of explicitly correlated codes the correlation factor was a linear function of interelectronic distance, but in 2004 one of us (Ten-no) showed that a very good accuracy can be obtained with an even smaller orbital basis if a nonlinear correlation factor—namely, a STG—is used.³³ Coupled cluster methods that use a linear r_{12} correlation factor are usually designated as CC-R12 while methods with a nonlinear correlation factor are labeled as CC-F12. It is important to realize that introducing the interelectronic distance explicitly into the wave function does not take care of all correlation effects. For example, CC-R12 and CC-F12 approaches cannot fully recover static electron correlation effects resulting from the multideterminantal nature of the wave function.

The good convergence of correlation energy in CCSD-R12 and CCSD-F12 methods has inspired several authors to apply these approaches to the calculation of molecular geometries, harmonic frequencies, and vibrational anharmonicities of diatomic molecules.^{3,4,8,34} Applications to the vibrational spectrum of polyatomic systems (including water) have also been reported recently.^{8,20,21,35} It should be noted that analytic gradients and Hessians are not available at this time for R12 methods so numerical techniques must be used. These studies have demonstrated that explicitly correlated calculations give good results with modest orbital basis sets, but true spectroscopic accuracy has remained elusive even for a relatively simple system such as the water molecule.

Relatively few studies have considered the basis set and correlation treatment needed to accurately calculate cubic and quartic force constants for anharmonic corrections to vi-

brational spectra. This is understandable since analytic third and fourth derivatives are not available at the CCSD and CCSD(T) levels, although first and second derivatives can be obtained.^{36–40} In the case of R12 methods, the lack of any analytical derivatives implies that a large number of well-converged single point calculations must be performed to evaluate the anharmonic force constants. Based on such calculations, we report here on the basis set convergence of cubic and quartic force constants for water. Our results illustrate the benefits of explicitly correlated CCSD(T) methods for anharmonic vibrational analysis.

II. METHODS

A. Geometry optimization and energy derivatives

The geometry of the water molecule was optimized in internal coordinates at each level of theory using a Newton–Raphson algorithm with numerically evaluated first and second derivatives. These optimizations, and the vibrational analysis, were performed using our custom code that interfaces to different *ab initio* packages, which provide energy values at each geometry. Our code evaluates derivatives with respect to displacements in curvilinear internal coordinates. For a given displacement the geometry is transformed from internal to Cartesian coordinates prior to energy evaluation by the external program. The derivatives were evaluated via central finite difference formulas, some of which were derived with the help of the computer algebra package MATHEMATICA.⁴¹ Due to numerical noise, ordinary $O(h^2)$ displacement formulas were not sufficiently accurate, and higher-order finite difference formulas were used for all derivatives (*vide infra*). This approach is analogous to one that was used to evaluate the full internal coordinate sextic force field of water,⁴² except that in our work, the structures were fully optimized prior to evaluation of derivatives.

We found that obtaining reliable third and fourth-order derivatives requires a careful choice of convergence criteria during energy evaluation and minimization. The often-used step sizes of $0.01a_0$ and 0.01 rad were good choices for geometry optimization and harmonic vibrational analysis, but larger step sizes (0.02 – 0.03) were needed for accurate calculation of third and fourth derivatives. Sufficient accuracy for all derivatives required tightening the energy convergence criteria to at least 5×10^{-10} a.u. for the Hartree–Fock energy and 1×10^{-11} a.u. for CCSD iterations. The accuracy of integral evaluations and molecular orbital transformations was increased to at least 1×10^{-14} and 1×10^{-13} a.u., respectively. Geometries were considered converged when the root mean square force was below 1×10^{-8} hartree/bohr and displacements did not exceed $0.1 \mu\text{\AA}$ for the bond length, and $0.1 \mu\text{rad}$ for the bond angle. With these settings we succeeded in reproducing the geometry and analytical internal coordinate quadratic, cubic, and quartic force constants for water reported by Gaw and Handy⁴³ at the SCF/6-31G-ext level. When coupled to NWCHEM, our code reproduced the previously reported geometries⁴⁴ and analytical harmonic frequencies (Table II in Ref. 9) for water at the CCSD, CCSD(T), and CCSDT levels. As a further check on the accuracy of our CCSD(T) numerical derivatives, we repro-

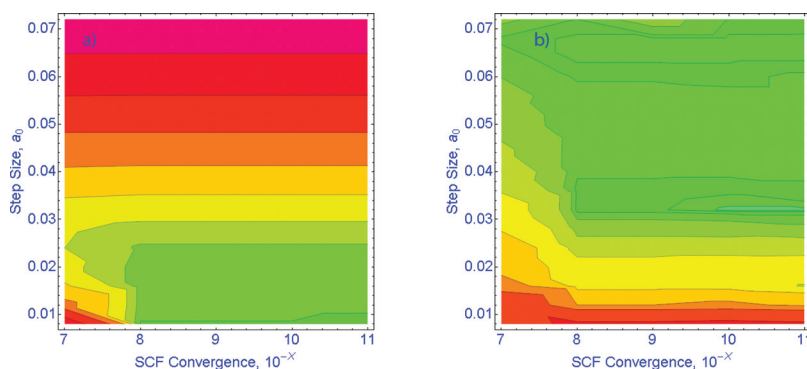


FIG. 1. Two dimensional error surfaces for f_{aaa} (panel a) and for $f_{rrr'r'}$ (panel b). Absolute errors relative to analytical SCF results (Ref. 43) are shown as contour plots. For f_{aaa} , the error range is from 0.000 27 to -0.000 14 (SCF value is -0.774 02 mdyn cm). For $f_{rrr'r'}$, the error range is from -0.128 to 0.010 (SCF value is 0.218 78 mdyn cm). Green corresponds to the lowest and red to the highest error.

duced the geometry, analytical harmonic frequencies, and fundamental frequencies of F_2O at the CCSD(T) level to within the number of digits reported in literature.⁴⁵

B. Accuracy of numerical force constants

At present, anharmonic vibrational analysis usually requires numerical evaluation of derivatives because implementations for cubic and quartic analytical derivatives are available only at the Hartree–Fock level.^{46–49} Analytical second derivatives are also available for some electron correlation methods such as MP2, CCSD, CCSD(T), CC3, and CCSDT.^{37,40,50–52} In those cases third and fourth derivatives can be obtained via numerical differentiation of the analytical second derivatives. While for SCF, MP2, and CCSD analytical evaluation of second derivatives is much faster than numerical differentiation, the speed advantage is diminished for CCSD(T) calculations.⁵³ So far, no analytical second derivatives have been reported for explicitly correlated coupled cluster methods.

Fully numerical derivatives are always possible as long as the energy can be evaluated,⁵⁴ although they are generally not considered as accurate as the analytical results. Improved accuracy over the usual three-point finite difference second derivatives, with an error of order $O(h^2)$, can be obtained for force constants involving a single coordinate (e.g., f_{rr} or f_{aa}) by using a five-, seven-, or nine-point stencil (errors on the order of h^4 , h^6 , and h^8 , respectively). Similarly, accurate third order derivatives along a single coordinate, such as f_{rrr} , can be evaluated using a six-, eight-, or ten-point stencil. Obviously, accurate evaluation of higher derivatives along multiple coordinates requires a large number of points; the evaluation of $f_{rr'aa}$ with $O(h^4)$ error, for example, requires an 80-point stencil. However, due to the molecular symmetry and reuse of many energy values, it is feasible to carry out an $O(h^4)$ numerical evaluation of the full quartic force field in an AX_2 -type system. This is done in our program by evaluating energies at 122 regularly spaced grid points. All second derivatives, five of the six third derivatives (all except $f_{rr'a}$) and four fourth-order derivatives (f_{rrrr} , $f_{rrr'r'}$, f_{rraa} , f_{aaaa}) are also evaluated with $O(h^6)$ error. Furthermore, all single-coordinate derivatives were evaluated with $O(h^8)$ error, allowing one to assess the error associated with smaller stencils.

Systematic analysis of the effects of the step size and SCF convergence (Fig. 1) revealed that small step sizes are appropriate for the second derivatives and some third deriva-

tives, but larger step sizes are needed for the quartic derivatives that depend on more than one coordinate. In this work, most calculations were repeated using step sizes 0.024, 0.028, and 0.032 (in units of a_0 for distances and radians for angles), and the consistency of results was checked.

C. Quantum chemical methodologies

The traditional and explicitly correlated single point CCSD(T) (Refs. 55 and 56) energy evaluations were performed with the program DIRCCR12-OS,⁵⁷ recently modified to include the STG correlation factor.²⁵ Even though the STG factor is always preferable with smaller basis sets, we have seen that with large basis sets there was no clear preference.²⁵ The differences between these variants are expected to reflect the inconsistency due to basis set unsaturation in SA evaluation of matrix elements. Dunning's cc-pVXZ, aug-cc-pVXZ, and aug-cc-pwCVXZ basis sets^{58–60} were employed in traditional valence-only calculations. The largest calculation involved harmonic vibrational analysis with the pV7Z basis.^{61,62} Contributions from core electron correlation were assessed with traditional correlated calculations using basis sets that contained appropriate tight functions.^{60,63} We have chosen to evaluate post-CCSD(T) corrections to geometries and force constants at the CCSDT(2)_Q level⁶⁴ because this method has been shown to yield results similar to the full CCSDTQ method for HF molecule.⁶⁵ CCSDT (Ref. 66) and CCSDT(2)_Q (Ref. 64) corrections were evaluated with NWCHEM (Ref. 67) using double and triple-zeta basis sets. R12-optimized basis sets were employed in explicitly correlated calculations.^{29,30} For hydrogen we always used the $9s6p4d3f$ set³⁰ because a preliminary investigation showed unsatisfactory results with basis sets lacking f -functions. For oxygen, we employed the $19s14p8d6f4g3h$ set and truncated $19s14p8d6f4g$ and $19s14p8d6f$ subsets of the former. These sets will be referred to as $spdfgh$, $spdfg$, and $spdf$. They are also suitable for description of core-valence correlation as these large sets are uncontracted and include functions with tight exponents. We also optimized two i -functions by minimizing the total energy of oxygen atom in its 3P ground state at the CCSD(T) level; the optimized i exponents in this $spdfghi$ basis were 2.025 and 0.900.

D. Evaluation of spectroscopic properties

The determination of normal coordinates and the evaluation of harmonic frequencies was performed via the familiar Wilson GF-matrix formalism⁶⁸ using the symmetrization procedure due to Miyazawa.⁶⁹ Transformation of force constants from curvilinear internal coordinates to normal coordinates was performed via the L-tensor transformations as described by Hoy *et al.*⁷⁰ Vibrational anharmonicity constants, including the corrections for the Coriolis coupling, were evaluated from cubic and quartic force constants in normal coordinates according to formulae provided by Mills.⁷¹ The force constant transformation code was implemented in the computer algebra package MATHEMATICA.⁴¹ Results from this code were checked against published analytical normal coordinate force constants and anharmonicity constants for water.^{43,70}

Composite methodology was used to evaluate the core correlation and quadruple excitation contributions to fundamental frequencies at the basis set limit. To obtain the corrections to geometry and internal coordinate force constants we, first, performed the optimization and anharmonic frequency analysis with a pair of modest-size basis sets. For example, the frozen-core quadruple correction to every force constant was calculated as the difference between CCSDT(2)_Q/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ results. Then, the fc-CCSD(T)-F12/*spdfghi* geometries and internal coordinate force constants were updated with these corrections which were followed by the transformation from internal to normal coordinates. This approach eliminates errors due to the use of small basis set geometries when determining normal modes and performing the L-tensor transformation. Fundamental frequencies at the ae-CCSDT(2)_Q complete basis set (essentially nonrelativistic Born–Oppenheimer limit) level were obtained in a similar manner by considering cumulative corrections to the geometry and force constants due to frozen-core quadruple excitations, core correlation corrections at the CCSD(T) level, and core correlation corrections to quadruple excitations.

The relativistic corrections, which are known to converge slowly with respect to basis set size and the level of electron correlation treatment,^{13,72} were not directly evaluated in this work. Their contribution to vibrational frequencies was estimated based on published results.^{9,13} We also included a small but non-negligible quantum electrodynamics Lamb-shift correction reported by Pyykkö,⁷³ as well as the somewhat larger Born–Oppenheimer diagonal and nonadiabatic corrections that were obtained by Schwenke.^{74,75}

III. RESULTS AND DISCUSSION

A. Basis set convergence of H₂O geometry and quadratic force constants

Prior to proceeding to our main goal it is appropriate to comment briefly on the convergence of the geometry and harmonic vibrational frequencies with respect to the basis set size. The convergence of the H₂O molecular geometry, especially of the angle, is known to be extremely slow in the cc-pVXZ series. There is a significant residual error even with the cc-pV6Z basis set.⁹ Convergence is somewhat better

when a set of diffuse functions is added, but a basis set of at least aug-cc-pV5Z quality (involves *h* functions) is needed to bring the bond angle within 0.1° of the apparent CCSD(T) limit of 104.46° (Table I). In contrast, explicitly correlated methods provide rapid convergence with increased basis set size. The apparent basis set limit is achieved with *spdfg* shells on oxygen and *spdf* shells on hydrogen (Fig. 2). Excellent agreement is observed between our R12/B, R12/C, and F12/C geometries using the *spdfg* or larger basis set on oxygen. Our geometries closely match a previously published numerically optimized R12/B structure obtained with a slightly different 19s14p8d6f4g3h2i/9s6p4d3f2g basis.⁸ As seen in Fig. 2, the frozen-core CCSD(T) structure differs from experiment only slightly. The main sources of this discrepancy are discussed in Secs. III C and III D.

Quadratic force constants in the traditional and explicitly correlated calculations are summarized in supplementary Table S1.⁷⁶ Figure 3 demonstrates that the main trends are the same as for geometry: (i) poor convergence in the cc-pVXZ hierarchy, (ii) improvement upon addition of diffuse functions, and (iii) rapid convergence in explicitly correlated calculations, especially when the Slater type correlation factor is employed. Slow convergence of harmonic frequencies in traditional coupled cluster calculations has been noted in the past.⁹ Here we see that there is still a difference of more than 1 cm⁻¹ between the aug-cc-pV6Z and pV7Z basis sets for the symmetric stretching and bending modes (Table I, and supplementary Figs. S1–S3).⁷⁶ Frozen core calculations with basis sets that incorporate additional tight functions on oxygen (i.e., aug-cc-pCVXZ and aug-cc-pwCVXZ) give results that are similar to the aug-cc-pVXZ values. We note, however, that f_{aa} is consistently lowered when tight functions are included at the fc-CCSD(T) level.

During the course of our work, a traditional coupled cluster based approach in which basis-set-limit harmonic and fundamental frequencies were obtained via basis set extrapolation was reported by Feller and Peterson.¹⁴ In their work, optimal geometries and frequencies were obtained by fitting a sixth-order polynomial to 84 grid energies. It is satisfying that despite different convergence criteria and grid spacing, our geometries and harmonic frequencies in the aug-cc-pVXZ series agree very nicely with their results. Although extrapolation from large correlation-consistent basis sets can be used to achieve spectroscopic accuracy,^{13,14} as Feller and Peterson observed, the extrapolated angle bending frequency depends strongly on details of extrapolation procedure. Moreover, the required aug-cc-pV6Z basis set calculations are eight times slower than our *spdfg* CCSD(T)-R12/F12 calculations (see supplementary Table S2 for timings),⁷⁶ which are essentially converged.

Recently, quite accurate results using the approximate variants CCSD(T)-F12a and CCSD(T)-F12b have been reported.^{20,21} Since both methods and the ultimate goal were different, a direct comparison would not be appropriate. We do note that significant (2–3 cm⁻¹) changes in harmonic frequencies took place when the orbital basis was enlarged from VTZ-F12 to VQZ-F12: The VQZ-F12 values are given for comparison in Table I. Our results with the *spdf* oxygen set still noticeably differ between the variants R12/C and

TABLE I. Geometries and harmonic vibrational frequencies of water at frozen-core (fc) and all-electron (ae) CCSD(T) levels in traditional and explicitly correlated calculations.

Method	Basis set	Distance (Å)	Angle (deg)	ω_1 (cm ⁻¹)	ω_2 (cm ⁻¹)	ω_3 (cm ⁻¹)
fc-CCSD(T)	cc-pVDZ	0.966 278	101.9127	3821.61	1690.30	3927.58
	cc-pVTZ	0.959 426	103.5822	3840.93	1668.88	3945.53
	cc-pVQZ	0.957 890	104.1159	3844.46	1659.30	3951.41
	cc-pV5Z	0.958 040	104.3724	3840.06	1653.37	3949.33
	cc-pV6Z	0.958 180	104.4221	3837.27	1651.28	3947.22
	pV7Z	0.958 210	104.4387	3836.54	1650.33	3946.84
fc-CCSD(T)	aug-cc-pVDZ	0.966 513	103.9366	3786.92	1638.21	3904.88
	aug-cc-pVTZ	0.961 580	104.1796	3810.82	1645.91	3919.92
	aug-cc-pVQZ	0.958 930	104.3643	3831.08	1650.12	3940.68
	aug-cc-pV5Z	0.958 414	104.4274	3834.64	1650.13	3945.03
	aug-cc-pV6Z	0.958 343	104.4473	3835.01	1649.27	3945.61
fc-CCSD(T)	aug-cc-pCVDZ	0.966 345	103.9175	3786.70	1638.78	3904.61
	aug-cc-pCVTZ	0.961 328	104.1912	3807.84	1646.03	3914.92
	aug-cc-pCVQZ	0.958 968	104.3670	3830.57	1649.19	3940.42
fc-CCSD(T)	aug-cc-pwCVDZ	0.966 404	103.9066	3786.12	1638.61	3903.44
	aug-cc-pwCVTZ	0.961 126	104.2091	3808.78	1646.24	3915.95
	aug-cc-pwCVQZ	0.958 945	104.3728	3830.63	1649.01	3940.57
	aug-cc-pwCV5Z	0.958 384	104.4328	3834.89	1649.83	3945.29
fc-R12/B	<i>spdf/spdf</i>	0.958 198	104.3926	3838.09	1653.03	3947.67
	<i>spdfg/spdf</i>	0.958 351	104.4591	3835.66	1648.64	3946.49
	<i>spdfgh/spdf</i>	0.958 312	104.4661	3835.31	1649.55	3946.09
	<i>spdfghi/spdf</i>	0.958 270	104.4627	3835.64	1649.24	3946.47
	<i>spdfghi/spdfg^a</i>	0.958 238	104.4627	3835.89	1649.39	3946.65
fc-R12/C	<i>spdf/spd</i>	0.958 252	104.4513	3833.89	1647.68	3944.50
	<i>spdf/spdf</i>	0.958 213	104.5076	3834.09	1647.14	3945.28
	<i>spdfg/spdf</i>	0.958 206	104.4648	3835.35	1650.14	3946.12
	<i>spdfgh/spdf</i>	0.958 245	104.4623	3836.36	1649.29	3947.25
fc-F12/C	<i>spdf/spd</i>	0.958 114	104.4169	3837.77	1649.96	3947.93
	<i>spdf/spdf</i>	0.958 137	104.4299	3838.47	1653.58	3947.76
	<i>spdfg/spdf</i>	0.958 253	104.4654	3836.04	1649.39	3946.76
	<i>spdfgh/spdf</i>	0.958 266	104.4634	3835.66	1649.55	3946.54
	<i>spdfghi/spdf</i>	0.958 270	104.4627	3835.64	1649.24	3946.47
fc-F12b	VQZ-F12 ^b			3835.02	1649.19	3945.66
	VQZ-F12 ^c	0.9583	104.45	3834.7	1649.8	3945.4
ae-CCSD(T)	cc-pCVTZ	0.958 430	103.6839	3841.66	1667.56	3944.68
	cc-pCVQZ	0.957 114	104.2253	3850.78	1658.01	3958.43
	aug-cc-pCVTZ	0.960 571	104.2891	3813.57	1645.52	3920.95
ae-CCSD(T)	aug-cc-pwCVDZ	0.965 924	103.9743	3790.03	1638.06	3907.60
	aug-cc-pwCVTZ	0.960 347	104.3149	3814.78	1645.60	3922.34
	aug-cc-pwCVQZ	0.958 064	104.4901	3837.28	1648.33	3947.66
	aug-cc-pwCV5Z	0.957 473	104.5536	3841.72	1649.14	3952.57
ae-F12/C	<i>spdfg/spdf</i>	0.957 316	104.5887	3843.02	1648.69	3954.21
	<i>spdfgh/spdf</i>	0.957 329	104.5869	3842.69	1648.89	3954.04
Expt. ^d		0.957 62	104.51	3832.17	1648.47	3942.53

^aFrom literature (Ref. 8).^bFrom literature (Ref. 20).^cFrom literature (Ref. 21).^dValues derived from observed spectra as reported by Benedict *et al.* (Ref. 81).

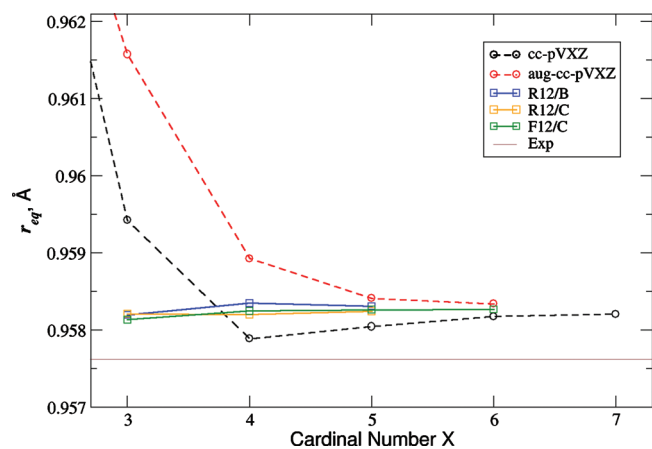


FIG. 2. Convergence of bond length in the traditional and explicitly correlated frozen-core CCSD(t) calculations of water. The cardinal number for “Universal R12” basis sets describes the highest angular momentum in the oxygen basis; the largest R12 basis used ($X=6$) was $19s14p8d6f4g3h2i$.

F12/C. However, all explicitly correlated variants provide values that differ within less than 1 cm^{-1} as soon as g -functions enter the oxygen basis, and it appears that F12/C slightly outperforms R12/B and R12/C as far as convergence is concerned.

B. Basis set convergence of cubic and quartic force constants

The basis set dependence of CCSD(T) cubic and quartic force constants has been less explored, and a primary goal of this work was to explore the basis set requirements for proper description of vibrational anharmonicities. Poor performance of the 6-311G family, and a comparison of the Dunning–Huzinaga type $5s4p2d$ and $5s4p2d1f$ oxygen basis sets in all-electron QCISD(T) calculations, suggest that f -type functions are important for obtaining accurate quartic force constants.⁷⁷ Our results for individual internal coordinate cubic and quartic force constants are shown in Figs. 4 and 5 and in supplementary Tables S3 and S4.⁷⁶ Convergence in conventional cc-pVXZ calculations is slow and of-

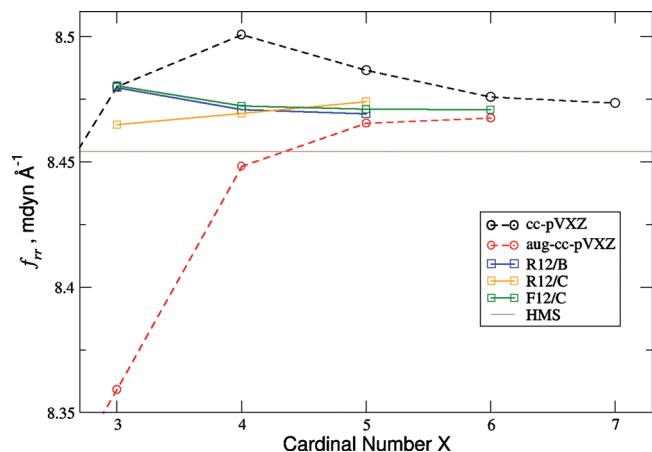


FIG. 3. Convergence of quadratic force constant f_{rr} in traditional and explicitly correlated frozen-core CCSD(t) calculations of water. The line labeled HMS corresponds to a value deduced from experimental data using a model quartic force field (Ref. 70).

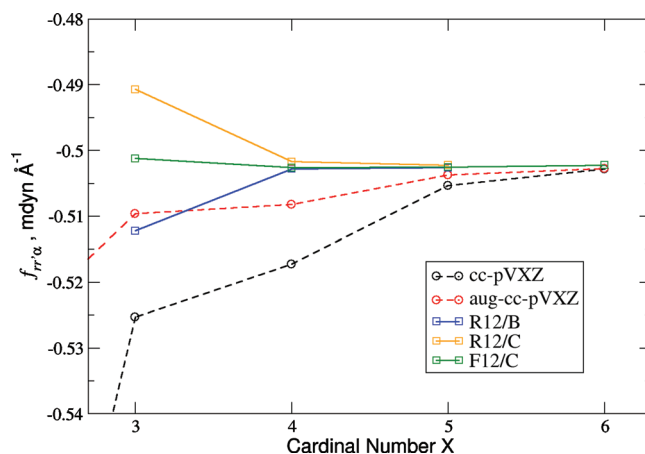


FIG. 4. Convergence of the internal coordinate cubic force constant $f_{rr'a}$ in traditional and explicitly correlated frozen-core CCSD(t) calculations of water.

ten nonmonotonic. Again, a significant improvement is observed when diffuse functions are added. It is noteworthy that aug-cc-pVQZ cubic and quartic force constants are rather close to the apparent basis set limit while double-zeta results are notably inaccurate.

Explicitly correlated methods consistently yield cubic force constants of near-basis-set-limit quality with the $spdfg$ or larger basis on oxygen, and results from the R12/B, R12/C, and F12/C methods agree with each other very well. Accurate calculation of the quartic force constants $f_{rrr'r'}$ and f_{aaaa} via finite difference formulas seem particularly challenging as we start seeing some step-size dependence of results despite tight convergence criteria. We also note larger than usual changes of some quartic force constants with respect to the basis set size in R12/B and R12/C calculations while F12/C quartic force constants varied very little as the basis was enlarged (Fig. 4). We believe that the origin of variations in the R12/B and R12/C quartic constants lies in the basis set incompleteness rather than with differentiation errors because very similar quartic derivatives were obtained with different step sizes. For example, the R12/C f_{aaaa} values in the $spdf$ basis were -0.510 and -0.515 for step sizes of

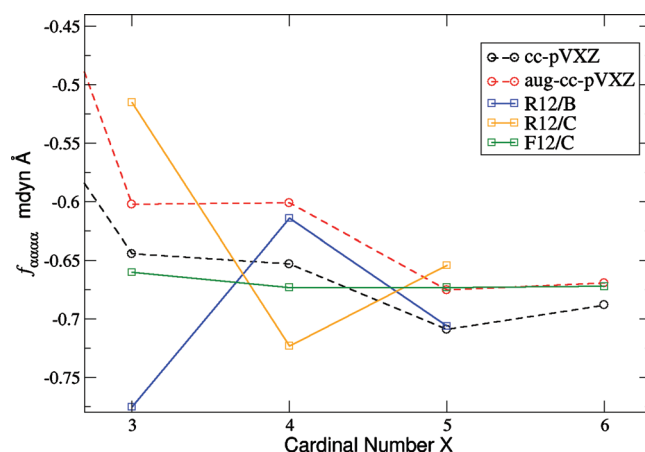


FIG. 5. Convergence of the internal coordinate quartic force constant f_{aaaa} in traditional and explicitly correlated frozen-core CCSD(t) calculations of water.

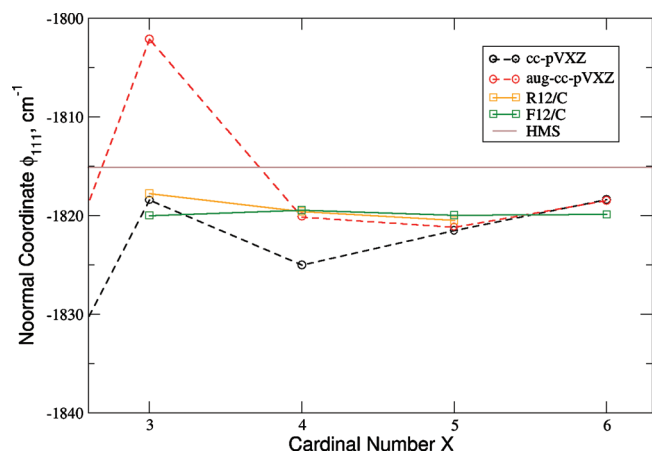


FIG. 6. Convergence of the normal coordinate force constant ϕ_{111} (third derivative along the symmetric stretching mode) in traditional and explicitly correlated F12/C frozen-core CCSD(t) calculations of water. The line labeled HMS corresponds to a value deduced from experimental data using a model quartic force field (Ref. 70).

0.02 and 0.28, respectively. With added g -functions, R12/C f_{aaaa} values were -0.724 and -0.723 for the same two step sizes. Most of the quartic constants from the R12/B, R12/C, and F12/C methods agree with each other within 5% but discrepancies up to 10% are observed for $f_{rrr'r'}$ and f_{aaaa} . With the exception of $f_{rrr'r'}$, coupled cluster cubic and quartic force constants at the apparent basis set limit are in good agreement with ic-MRCI results obtained via basis set extrapolation.¹³ We note, however, that even the converged cubic force constants differ significantly from experimental estimates. Moreover, experimentally deduced values of quartic constants have too large uncertainties for meaningful comparison with calculations.⁷⁰ This underscores the difficulty in deducing internal coordinate force fields from spectroscopic data.

The force constants discussed so far correspond to curvilinear internal displacements for bond stretching and bond bending vectors. Transformation of these force constants into normal mode force constants does not alter the convergence picture substantially. Several cubic and quartic normal coordinate force constants converge slowly or show oscillating patterns (Fig. 6) while explicitly correlated F12/C values are stable with respect to basis set size. Vibrational anharmonicity constants (elements of the diagonal x -matrix) are determined by combinations of normal coordinate force constants. Thus, vibrational anharmonicity constants depend on quadratic, cubic, and quartic internal coordinate force constants. Slow convergence of internal or normal coordinate force constants does not necessarily imply slow convergence of anharmonicity constants. Our anharmonicity constants are summarized in Table II. Although values calculated with a double-zeta basis still have large errors, with the exception of x_{22} (Fig. 7) and x_{13} , calculated vibrational anharmonicities do not vary significantly when basis sets of at least triple-zeta quality are used. The variation in anharmonicity constants with basis set size appears to be largely due to the variation in cubic and quartic internal coordinate force constants. Our results also tend to justify the use of multiple levels of methods for speeding up the evaluation of potential energy

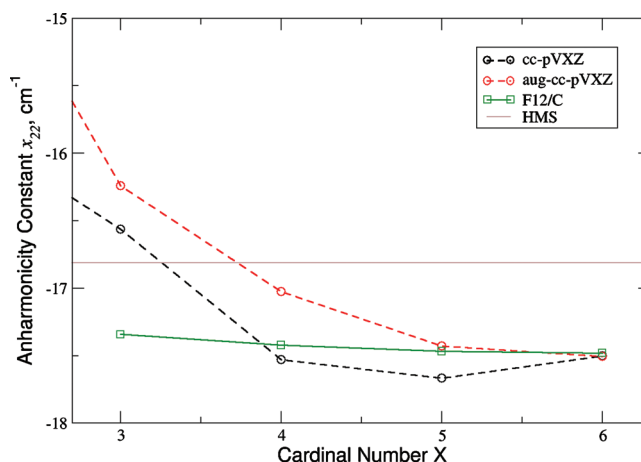


FIG. 7. Convergence of the anharmonicity constant x_{22} (angle bending term) in traditional and explicitly correlated F12/C frozen-core CCSD(t) calculations of water. The line labeled HMS corresponds to a value deduced from experimental data using a model quartic force field (Ref. 70).

surfaces.⁷⁸ The three explicitly correlated methods yield anharmonicity constants that are similar to the results of the largest conventional calculation. We are intrigued by the possibility that reliable anharmonicity constants could be obtained with an affordable $spdf$ basis using F12/C method. It is also noteworthy that CCSD(T)/cc-pVQZ anharmonicity constants are fairly close to the F12/C results. In this connection it is appropriate to note that accurate cubic and quartic force constants are not only important for deciphering experimental spectra of molecules but also contribute to atomization energies via their zero-point vibrational contributions. For example, CCSD(T)/cc-pVQZ anharmonic zero-point energies are part of the highly accurate *ab initio* thermochemistry model HEAT.^{79,80} Fundamental frequencies (Fig. 8) primarily reflect the convergence behavior of quadratic force constants. As expected, then, we find that fundamental frequencies were not converged with conventional CCSD(T) even using aug-cc-pV5Z basis. On the other hand, valence-only explicitly correlated CCSD(T) fundamental frequencies converge quickly and are within 2 cm⁻¹ of the experimental values.⁸¹

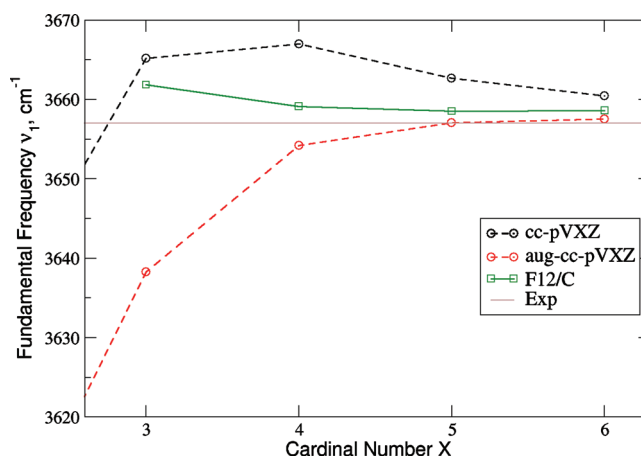


FIG. 8. Convergence of the symmetric bond stretching fundamental frequency in traditional and explicitly correlated F12/C frozen-core CCSD(t) calculations of water.

TABLE II. Anharmonicity constants at the CCSD(T) level in traditional and explicitly correlated calculations.

Method	Basis	x_{11} (cm^{-1})	x_{22} (cm^{-1})	x_{33} (cm^{-1})	x_{12} (cm^{-1})	x_{13} (cm^{-1})	x_{23} (cm^{-1})
fc-CCSD(T)	cc-pVDZ	-46.24	-15.78	-49.96	-22.24	-172.43	-21.16
	cc-pVTZ	-42.86	-16.56	-48.43	-14.88	-165.13	-19.77
	cc-pVQZ	-43.13	-17.53	-48.68	-16.01	-166.45	-19.89
	cc-pV5Z	-43.10	-17.67	-48.77	-15.77	-166.61	-19.81
	cc-pV6Z	-42.96	-17.50	-48.58	-15.69	-166.04	-19.80
fc-CCSD(T)	aug-cc-pVDZ	-45.55	-14.15	-50.97	-18.56	-174.84	-23.03
	aug-cc-pVTZ	-41.94	-16.24	-47.77	-15.27	-162.03	-19.99
	aug-cc-pVQZ	-42.98	-17.02	-48.61	-15.70	-166.13	-20.04
	aug-cc-pV5Z	-43.13	-17.43	-48.81	-15.91	-166.62	-20.02
	aug-cc-pV6Z	-43.12	-17.50	-48.78	-15.98	-166.48	-19.93
fc-CCSD(T)	aug-cc-pwCVDZ	-45.40	-14.13	-50.78	-18.50	-174.21	-23.03
	aug-cc-pwCVTZ	-42.32	-16.21	-47.59	-15.50	-162.60	-20.00
	aug-cc-pwCVQZ	-42.90	-16.90	-48.55	-15.66	-165.87	-19.96
	aug-cc-pwCV5Z	-43.12	-17.41	-48.77	-15.90	-166.64	-19.90
fc-R12/B	<i>spdf/spdf</i>	-43.25	-18.39	-48.86	-16.98	-167.04	-19.90
	<i>spdfg/spdf</i>	-43.04	-17.04	-48.73	-15.77	-166.38	-19.87
	<i>spdfgh/spdfg</i>	-43.21	-17.64	-48.84	-16.06	-167.05	-20.13
fc-R12/C	<i>spdf/spd</i>	-42.58	-18.55	-48.01	-16.78	-163.70	-19.77
	<i>spdf/spdf</i>	-42.54	-16.22	-48.06	-14.84	-164.24	-19.86
	<i>spdfg/spdf</i>	-42.87	-17.78	-48.50	-15.97	-165.63	-19.93
	<i>spdfgh/spdf</i>	-43.13	-17.36	-48.83	-15.84	-166.82	-19.83
fc-F12/C	<i>spdf/spd</i>	-42.84	-17.47	-48.33	-16.22	-165.31	-19.95
	<i>spdf/spdf</i>	-42.85	-17.34	-48.37	-16.00	-165.38	-20.02
	<i>spdfg/spdf</i>	-42.97	-17.42	-48.63	-15.89	-166.02	-19.94
	<i>spdfgh/spdf</i>	-43.02	-17.47	-48.69	-15.92	-166.25	-19.97
	<i>spdfghi/spdf</i>	-47.97	-17.48	-48.66	-15.85	-166.30	-19.95
ae-CCSD(T)	cc-pCVTZ	-42.78	-16.48	-48.01	-14.60	-164.15	-19.26
	cc-pVCQZ	-43.14	-17.57	-48.73	-15.82	-166.59	-19.64
ae-CCSD(T)	aug-cc-pwCVDZ	-45.44	-14.18	-50.83	-18.47	-174.38	-22.95
	aug-cc-pwCVTZ	-42.37	-16.32	-47.64	-15.45	-162.78	-19.85
	aug-cc-pwCVQZ	-42.97	-17.02	-48.62	-15.61	-166.10	-19.79
ae-F12/C	<i>spdfg/spdf</i>	-43.03	-17.52	-48.72	-15.78	-166.25	-19.75
	<i>spdfgh/spdf</i>	-43.08	-17.59	-48.75	-15.84	-166.49	-19.79
Expt. ^a		-42.576	-16.813	-47.566	-15.933	-165.824	-20.332

^aValues derived from observed spectra as reported by Benedict *et al.* (Ref. 81).

C. Correlation effects beyond CCSD(T)

It is well known that correlation effects beyond triple excitations lead to longer bonds and lower stretching frequencies.^{5,6,9,14} The effect is large (more than 10 cm^{-1} for harmonic frequencies) in the case of multiple bonds and crowded electron pairs. Previous observations suggest that quadruple excitations are responsible for the major part of this difference.⁹ The quintuples correction and the error due to approximate treatment of triple excitations are negligible.^{6,82-84} In agreement with previous findings,^{9,14} we observe that quadruple excitations increase the bond length and reduce the bond angle. The changes in quadratic force

constants (supplementary Table S1)⁷⁶ and harmonic frequencies correlate with the geometry changes. Specifically, with the aug-cc-pVTZ basis the harmonic stretching frequencies are reduced by 4.3 cm^{-1} and the bending frequency is lowered by 0.5 cm^{-1} in comparison with the CCSD(T) values. We note that our CCSDT(2)_Q contributions to harmonic frequencies are slightly smaller than the recently reported CCSDT(Q) correction.¹⁴ While it is reassuring that the harmonic frequencies in the cc-pVTZ, cc-pCVTZ, and aug-cc-pVTZ basis sets are similar, we believe that the bending frequency correction is not fully converged with respect to the basis set.

Very little is known about the effect of quadruple exci-

TABLE III. Internal coordinate cubic force constants obtained from traditional frozen-core calculations with and without connected quadruple excitations. The force constants are defined in Ref. 70. They are given in units consistent with energy measured in aJ, distances in Å, and angles in radians.

Basis	Method	f_{rrr}	$f_{rrr'}$	f_{rra}	$f_{rr'a}$	f_{raa}	f_{aaa}
cc-pVDZ	fc-CCSD(T)	-58.644	-0.2062	-0.1651	-0.6265	-0.3671	-0.7648
	fc-CCSDT	-58.613	-0.2049	-0.1658	-0.6276	-0.3674	-0.7642
	fc-CCSDT(2) _Q	-58.510	-0.2066	-0.1655	-0.6262	-0.3682	-0.7638
cc-pVTZ	fc-CCSD(T)	-58.761	-0.0491	-0.1178	-0.5253	-0.3047	-0.6907
	fc-CCSDT	-58.778	-0.0480	-0.1178	-0.5267	-0.3045	-0.6907
	fc-CCSDT(2) _Q	-58.695	-0.0520	-0.1172	-0.5258	-0.3054	-0.6902
aug-cc-pVDZ	fc-CCSD(T)	-58.234	-0.0806	-0.1772	-0.5324	-0.3607	-0.6954
	fc-CCSDT	-58.204	-0.0787	-0.1778	-0.5335	-0.3609	-0.6949
	fc-CCSDT(2) _Q	-58.086	-0.0808	-0.1769	-0.5323	-0.3613	-0.6943
aug-cc-pVTZ	fc-CCSD(T)	-57.601	-0.0432	-0.1289	-0.5096	-0.3033	-0.6720
	fc-CCSDT	-57.619	-0.0416	-0.1289	-0.5112	-0.3031	-0.6720
	fc-CCSDT(2) _Q	-57.532	-0.0457	-0.1289	-0.5104	-0.3036	-0.6714
cc-pCVTZ	fc-CCSD(T)	-58.487	-0.0771	-0.1107	-0.5132	-0.3022	-0.6938
	fc-CCSDT	-58.503	-0.0760	-0.1107	-0.513	-0.3020	-0.6938
	fc-CCSDT(2) _Q	-58.422	-0.0798	-0.1103	-0.5139	-0.3029	-0.6933
aug-cc-pCVTZ	fc-CCSD(T)	-57.506	-0.0633	-0.1165	-0.5032	-0.3034	-0.6719
	fc-CCSDT	-57.523	-0.0616	-0.1164	-0.5049	-0.3032	-0.6720

tations, or the iterative treatment of triples, on cubic and quartic force constants in water. Our results in Table III indicate that cubic constants are not significantly affected by quadruple excitations when double and triple-zeta basis sets are used. In relative terms, $f_{rrr'}$ is most significantly altered [up to 5% in comparison with CCSD(T)]. Quadruple corrections noticeably reduced the quartic force constants f_{rrrr} and $f_{rrr'r'}$ at the CCSDT(2)_Q/cc-pVTZ and CCSDT(2)_Q/aug-cc-pVTZ levels, but it is difficult to assess the significance of this observation as the values are far from converged with such small basis sets. The net effect of quadruple correction on anharmonicity constants ranges from 0.05 cm⁻¹ for x_{22} to 0.5 cm⁻¹ for x_{13} . The effect of iterative treatment of triples is small; the CCSDT-CCSD(T) difference is most noticeable for $f_{rr'}$, $f_{rrr'}$, and $f_{rrr'r'}$. These small differences translate to changes less than 0.15 cm⁻¹ in anharmonicity constants. The errors due to the perturbative treatment of triple excitations, and that due to the lack of quadruple excitations partially cancel.

Finally, to test the error due to approximate treatment of quadruples in the CCSDT(2)_Q method, we performed a full CCSDTQ anharmonic analysis using the cc-pVDZ basis set. These limited results hint that the error due to the approximate treatment of quadruple excitations may be of borderline significance for harmonic frequencies: stretching frequencies decreased by 0.57 cm⁻¹ in comparison with the CCSDT(2)_Q values. However, differences between CCSDTQ and CCSDT(2)_Q were negligible for cubic and quartic force constants.

We are not aware of any CCSDTQ5 frequency calculations for water, but a 0.4 cm⁻¹ reduction of the harmonic frequency in HF by quintuple excitations has been reported

for the cc-pVTZ basis set.⁶ Also, the contribution of connected quintuples to the atomization energy of water appears to be about 50 times smaller than the contribution of connected quadruples.¹² Considering the possible basis set truncation error, and errors due to neglect of higher-order excitations, we believe that our post-CCSD(T) corrections to stretching frequencies are accurate to about 1.5 cm⁻¹.

D. Core correlation effects

When we add the post-CCSD(T) corrections, evaluated at the frozen-core CCSDT(2)_Q/aug-cc-pVTZ level, to the best CCSD(T) values obtained with the explicitly correlated F12/C method, the overall agreement with experiment worsens. Thus, the seemingly good agreement at the fc-CCSD(T) level was fortuitous. It is well known that core correlation effects tend to shorten bonds and increase quadratic force constants for stretching modes.^{2,3,6,85} A previous systematic study of water molecule revealed that the contribution of core correlation to geometry and harmonic force constants is moderately basis set dependent when aug-cc-pCVXZ basis sets are used.⁹ We observed a similar basis set dependence with the newer aug-cc-pwCVXZ basis sets (Table I), resulting in slow convergence of the core correlation correction to geometry and harmonic frequencies. Based on CCSD(T)-F12/C results with the *spdfgh* basis, core correlation at the CCSD(T) level was found to shorten the bond by 0.000 94 Å and widen the angle by 0.123°. The core correlation corrections to the harmonic frequencies at the explicitly correlated CCSD(T) level were 7.03, -0.66, and 7.50 cm⁻¹ for ω_1 , ω_2 ,

TABLE IV. Estimation of water geometry and fundamental frequencies by correcting large basis CCSD(T) results with various post-CCSD(T) contributions.

Method/basis	r_{eq} (Å)	θ_{eq} (deg)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
fc-CCSD(T)/cc-pV5Z	0.958 41	104.427	3657.10	1597.31	3754.09
fc-CCSD(T)/cc-pV6Z	0.958 18	104.422	3660.47	1598.53	3757.12
fc-CCSD(T)/cc-pV7Z	0.958 21	104.438			
fc-CCSD(T)-aug-cc-pV5Z	0.958 41	104.427	3657.10	1597.31	3754.09
fc-CCSD(T)-aug-cc-pV6Z	0.958 34	104.447	3657.53	1596.30	3754.84
fc-CCSD(T)-R12/C/ <i>spdfgh</i>	0.958 24	104.462	3658.76	1596.73	3756.24
fc-CCSD(T)-F12/C/ <i>spdfgh</i>	0.958 27	104.463	3658.53	1596.67	3756.05
fc-CCSD(T)-F12/C/ <i>spdfghi</i>	0.958 27	104.463	3658.61	1596.38	3756.01
<i>Quadruples correction (fc)</i> ^a	0.000 21	-0.018	-4.95	-0.53	-5.04
<i>Core correction [CCSD(T)]</i> ^b	-0.000 93	0.123	6.82	-0.83	7.33
<i>Core correction (Q)</i> ^c	0.000 01	-0.001	-0.24	-0.01	-0.23
ae-CCSDT(2)_Q/CBS est. ^d	0.957 56	104.566	3660.28	1594.97	3757.97
<i>Relativistic correction</i> ^e	0.000 04	-0.070	-2.7	1.3	-2.6
<i>QED Lamb-shift correction</i> ^f			0.18	-0.06	0.18
<i>BODC correction</i> ^g	0.000 02	0.015	0.28	-0.45	0.47
<i>Nonadiabatic correction</i> ^h			-0.72	-0.07	-0.74
Corrected <i>ab initio</i>	0.957 62	104.51	3657.3	1595.7	3755.3
Expt. ⁱ	0.957 62	104.51	3657.05	1594.75	3755.93

^aGeometry and force constant corrections are calculated as a difference between fc-CCSDT(2)_Q/aug-cc-pVTZ and fc-CCSD(T)/aug-cc-pVTZ results.

^bGeometry and force constant corrections are calculated as a difference between all-electron and frozen-core CCSD(T)-F12/C results in the *spdfgh* basis.

^cCalculated as a difference between the core corrections in CCSDT(2)_Q/cc-pCVTZ and CCSD(T)/cc-pCVTZ calculations.

^dFundamental frequencies are estimated by starting with the fc-CCSD(T)-CBS estimate and adding incremental corrections to all geometric parameters, quadratic, cubic, and quartic force constants before performing the L-tensor transformation and evaluation of anharmonicity constants.

^eFrequency corrections are harmonic frequency corrections based on published Douglas-Kroll CCSD(T)/cc-pV6Z calculation (Ref. 9).

^fFrequency corrections are fundamental frequency corrections based on published CCSD(T)/cc-pVQZ data (Refs. 13 and 73).

^gGeometry corrections are based on published fc-icMRCI/aug-cc-pVTZ data; frequency corrections are based on published fc-icMRCI/cc-pVTZ data (Ref. 74).

^hFrequency corrections are based on published CASSCF/cc-pVTZ calculation (Ref. 75).

ⁱExperimental fundamental frequencies from literature (Ref. 94).

and ω_3 , respectively. These values are similar to those recently reported by Feller and Peterson¹⁴ based on basis set extrapolation.

Of the six cubic force constants, $f_{rrr'}$ and f_{rra} were most significantly affected (about 3%) by core correlation effects at the CCSD(T) level (supplementary Table S3).⁷⁶ Comparison of traditional aug-cc-pwCVXZ (X=D, T, Q, and 5) values with explicitly correlated results suggest that reliable core corrections to cubic force constants can be obtained with the aug-cc-pwCVQZ basis. Out of nine quartic constants, $f_{rrrr'}$ and $f_{rrr'r'}$ appear to be most strongly affected (about 5%) by core correlation. These small corrections translate into changes of 0.1–0.2 cm^{-1} in anharmonicity constants (Table II).

Core correlation corrections to geometry and force constants at the fully iterative CCSDT level are nearly identical to core corrections at the CCSD(T) level, when evaluated with the aug-cc-pCVTZ basis set. The core correlation correction due to quadruple excitations [evaluated as the difference between the core contribution in CCSDT(2)_Q and CCSD(T) calculations with the cc-pCVTZ basis set] was negligible for geometry. The sum of core correlation due to

quadruple excitations and fully iterative treatment of triple excitations is noticeable (-0.23 cm^{-1}) for the bond stretching frequencies, but is small in both absolute and relative terms for cubic and quartic force constants.

E. Comparison with experimental data

How well does the coupled cluster method predict the molecular geometry and fundamental frequencies after approximate corrections due to higher-order correlation effects and core contributions are made? What are the remaining sources of errors? We have compiled the results that will help to answer these questions in Table IV. The residual basis set incompleteness errors in frozen-core CCSD(T) explicitly correlated calculations with very large basis sets are about 0.0001 Å and 0.002° for the bond distance, and bond angle, respectively. The three explicitly correlated methods yield mutually consistent geometries but the possibility of small errors due to the “standard approximation” remains. This error, however, appears to be negligible because the observed geometry is reproduced within experimental accuracy after addition of all correction terms.

To estimate the fundamental frequencies at the all-electron-CCSDT(2)_Q complete basis set (CBS) limit, we have estimated the geometries and force constants by adding appropriate corrections to the fc-CCSD(T)-F12/C results for the *19s14p8d6f4g3h2i* oxygen basis. This enlarged basis was used because the angle bending force constant and bending frequencies were not fully converged in the *spdfgh* basis. Specifically, the addition of two *i*-functions reduced $f_{\alpha\alpha}$ from 0.703 50 to 0.703 24. This difference is small but not negligible when one seeks spectroscopic accuracy. As can be seen from Table IV, the estimated all-electron CCSDT(2)_Q/CBS fundamental frequencies are within 3–4 cm⁻¹ of experimental data. The discrepancy between the estimated ae-CCSDT(2)_Q/CBS and the experimental values arises from neglect of several small effects, which we take into account using previously published data. Of these, relativistic effects are the most significant and also most difficult to calculate due to slow convergence with respect to basis set size.^{9,72} The Born–Oppenheimer diagonal correction (BODC) is also significant. With a choice of correction terms specified in Table IV, the corrected coupled cluster fundamental frequencies agree with experiment⁸¹ to within 1 cm⁻¹.

Despite the above agreement, some uncertainties remain. First, many of the small correction factors do not correspond to the basis set limit, and have significant uncertainties. Second, it is worth noting that different relativistic treatments yield results that differ by as much as 0.3 cm⁻¹.^{9,13,86} The BODC from two groups using slightly different methodologies, basis sets and reference geometries differ by up to 0.2 cm⁻¹.^{14,74} Third, we have omitted the rather uncertain corrections due to Breit and Gaunt relativistic terms.⁸⁷ These corrections have been estimated only with a relatively small *11s6p3d* oxygen basis and are usually ignored in vibrational analysis.⁸⁸ Last, our analysis relies on a second-order perturbation treatment of the quartic potential energy surface.

IV. CONCLUSIONS AND FUTURE WORK

Quadratic, cubic, and quartic force constants converge slowly in traditional CCSD(T) calculations. However, basis-set-limit quality force constants can be readily obtained using explicitly correlated coupled cluster methods with modest basis sets. The F12/C approach, which incorporates a nonlinear correlation factor appears most suitable in conjunction with a universal R12 basis set consisting of *s*, *p*, *d*, *f*, and *g*-functions.

Universal R12 basis sets and explicitly correlated methods seem well suited for description of core correlation effects, which significantly increase stretching frequencies. CCSDT(2)_Q calculations with small basis sets confirm previously observed trends regarding geometries and harmonic frequencies. They also reveal that cubic and quartic force constants linked to bond stretching modes are affected the most by quadruple excitations. Quadruple excitations reduce harmonic stretching frequencies by about 4 cm⁻¹ and change anharmonicity constants by up to 0.5 cm⁻¹.

Our results suggest that near-spectroscopic accuracy for many small molecules can be economically achieved via ex-

PLICITLY CORRELATED COUPLED CLUSTER calculations using the F12/C ansatz. The results from F12/C calculations with modest basis sets appear to be competitive in accuracy and potentially more efficient than ic-MRCI or traditional coupled cluster results that require extrapolation from very large basis sets.^{13,14,89} The largest offender for water is the bending mode; the stiffness of this mode is overestimated even when large basis sets are used in CCSD(T)-F12/C calculations. However, reaching true spectroscopic accuracy requires inclusion of several corrections, such as the relativistic effects and Born–Oppenheimer diagonal corrections which are currently unavailable within the F12/C ansatz. Developments such as the recently reported CCSDTQ-R12 method⁹⁰ promise to make *ab initio* prediction of vibrational spectra of many small molecules with spectroscopic accuracy a reality in the near-future.

Rigorous treatment of relativistic effects via explicitly correlated wave functions appears challenging because the electron correlation and relativistic effects are strongly intertwined.⁹¹ We plan to explore the basis set convergence of quadruple excitation contributions and the importance of different relativistic terms in the future. Also, we hope to address the adequacy of the second-order perturbation treatment of anharmonic effects via a variational solution of the vibrational Schrödinger equation^{92,93} using an accurate explicitly correlated potential energy surface.

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