

XH-stretching overtone transitions calculated using explicitly correlated coupled cluster methods

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We have calculated XH-stretching (where X=O, C, F, Cl) fundamental and overtone transitions for three diatomics and a few small molecules using a local mode model. The potential energy curves and dipole moment functions are calculated using the recently developed explicitly correlated coupled cluster with single doubles and perturbative triples theory [CCSD(T)-F12] with the associated VXZ-F12 (where X=D, T, Q) basis sets. We find that the basis set convergence of calculated frequencies and oscillator strengths obtained with the explicitly correlated method is much more rapid than with conventional CCSD(T) and the Dunning type correlation consistent basis sets. Furthermore, CCSD(T)-F12 frequencies and oscillator strengths obtained with the VTZ-F12 and VQZ-F12 basis sets are found to be in excellent agreement with the CCSD(T) complete basis set limit. We find that comparison of CCSD(T)-F12 frequencies with experiment is less good. The inclusion of explicit correlation exposes the inherent error of the CCSD(T) method to overestimate vibrational frequencies, which is normally compensated by basis set incompleteness error. As a consequence, we suggest that conventional CCSD(T) in combination with the aug-cc-pVTZ or aug-cc-pVQZ basis sets is likely to yield calculated XH-stretching frequencies in closest agreement with experiment. © 2010 American Institute of Physics. [doi:10.1063/1.3408192]

I. INTRODUCTION

Coupled cluster theory including singles doubles and perturbative triples excitations [CCSD(T)] has emerged as the so-called “gold standard” method of modern computational chemistry that can be routinely applied to small systems of chemical interest.^{1–3} The computational demands of the CCSD(T) method are very high (scaling nominally n^7 , where n is the size of the system) and because extensive basis sets are necessary to reliably achieve accurate results, it is impracticable for larger systems. However, the painfully slow convergence of electron correlation energy with increasing basis set size can be significantly improved by including a small number of terms to the wave function that depend explicitly on the interelectronic distance r_{12} .⁴ The recently developed explicitly correlated CCSD(T)-F12 methods have shown to give results using a triple- ζ basis set that are better than conventional CCSD(T) with a quintuple- ζ basis set.^{5–7} Very recently, fundamental frequencies calculated using a vibrational configuration interaction (VCI) anharmonic vibrational model with CCSD(T)-F12 force constants were found to have an absolute mean deviation of just 4 cm⁻¹ when compared to experiment.⁸

Overtone vibrational spectra are very sensitive to bond properties and can be used to study subtle effects in molecular structure and conformation.⁹ As higher regions of the potential energy curve are probed, differences that might appear small in the fundamental region become much more apparent for overtone transitions. Vibrational spectra in the near-

infrared and visible regions are dominated by XH-stretching overtone transitions, where X is a heavy atom such as C, O, and N.^{9–11} The vibrations of XH-stretching oscillators are highly anharmonic and can be described both theoretically and experimentally using an anharmonic oscillator local mode model.⁹ Earlier theoretical predictions of XH-stretching transitions used input from low level *ab initio* and density functional calculations that were empirically scaled to improve agreement with experiment.¹² In more recent years, XH-stretching transitions of several small molecules including ethylene glycol, peroxyxynitrous acid, hydroxymethyl hydroperoxide, sulfuric acid, methanesulfonic acid, ethanol, ethanethiol, *tert*-butanol, and *tert*-butylthiol have been successfully calculated entirely *ab initio* with potential energy and dipole moment curves obtained with the CCSD(T) method.^{13–20} For many of these systems, a triple- ζ correlation consistent basis set was pragmatically used as larger basis sets were not considered practicable at the CCSD(T) level of theory.

In this work, we investigate the basis set convergence of XH-stretching fundamental and overtone transitions of hydroxyl radical (OH), hydrogen fluoride (HF), hydrogen chloride (HCl), formic acid (HCOOH), methanol (CH₃OH), nitric acid (HNO₃), and water dimer (H₂O–H₂O) calculated with a one-dimensional (1D) local mode model at the CCSD(T) level of theory. The potential energy and dipole moment curves are calculated using both conventional CCSD(T) theory and explicitly correlated CCSD(T)-F12 theory with appropriate correlation consistent basis sets. For the three diatomic systems, we compare the basis set conver-

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gence of the calculated XH-stretching frequencies and oscillator strengths to results obtained at the complete basis set (CBS) limit and to experiment. For the polyatomic systems, we consider the relative basis set convergence of the conventional and explicitly correlated XH-stretching transitions and compare both sets of calculated results to experiment.

II. THEORETICAL METHODS

We have optimized the geometries of OH, HF, HCl, HCOOH, CH₃OH, HNO₃, and H₂O–H₂O with conventional CCSD(T) *ab initio* theory using Dunning type correlation consistent basis sets. With a suitably large basis set, the CCSD(T) method has been shown to give accurate geometries of small systems that are in excellent agreement with experiment.^{1–3} We have used the aug-cc-pVXZ basis sets (where X=D, T, Q, 5, 6) for first row elements and the aug-cc-pV(X+d)Z basis sets (where X=D, T, Q, 5, 6) for all second row elements.^{21,22} For brevity, we refer to these basis sets as AVXZ (where X=D, T, Q, 5, 6) whereby it is assumed that second row elements have the additional tight d basis functions. For H₂O–H₂O, we have also constructed basis sets where only the oxygen atoms are augmented with diffuse basis functions and refer to these as A'VXZ (where X=D, T, Q, 5).²³

We have also optimized the geometries of OH, HF, HCl, HCOOH, CH₃OH, HNO₃, and H₂O–H₂O with the recently developed explicitly correlated CCSD(T)-F12 methods as implemented in MOLPRO 2008.1.^{7,24} We have used the VXZ-F12 orbital basis sets (where X=D, T, Q) of Peterson *et al.* that have been specifically optimized for use with explicitly correlated F12 methods.²⁵ For a given cardinal number, the VXZ-F12 basis sets have been designed to be of similar size to the equivalent aug-cc-pVXZ and aug-cc-pV(X+d)Z basis sets. Density fitting approximations^{26,27} were used in all explicitly correlated calculations using the VXZ/JKFIT (where X=D, T, Q) and the AVXZ/MP2FIT (where X=D, T, Q) auxiliary basis sets of Weigend *et al.*^{28,29} We have used the resolution of the identity (RI) auxiliary basis sets of Yousaf *et al.* for all RI approximations.³⁰ The default CCSD-F12 correlation factor $[(1/\beta)e^{-\beta r_{12}}$, where $\beta=1$] was used in all explicitly correlated calculations.

Two different approximations are available for solving the CCSD(T)-F12 energies in MOLPRO 2008.1, denoted CCSD(T)-F12a and CCSD(T)-F12b. Overall, we find that results obtained with the two approximations are in very good agreement with each other, with the CCSD(T)-F12b frequencies consistently slightly higher than the CCSD(T)-F12a frequencies. We limit discussion in the manuscript to CCSD(T)-F12b results, which appear to converge more smoothly to the CBS limit, in agreement with previous work.³¹ The equivalent CCSD(T)-F12a results are included in the supplementary deposit.³²

The dimensionless oscillator strength f of a transition from the vibrational ground state $|0\rangle$ to a vibrationally excited state $|\nu\rangle$ is given by^{33,34}

$$f_{\nu 0} = 4.702 \times 10^{-7} [\text{cm D}^{-2}] \bar{\nu}_{\nu 0} |\bar{\mu}_{\nu 0}|^2, \quad (1)$$

where $\bar{\nu}_{\nu 0}$ is the vibrational wavenumber of the transition in cm^{-1} and $\bar{\mu}_{\nu 0} = \langle \nu | \bar{\mu} | 0 \rangle$ is the transition dipole moment matrix element in Debye (D).

We calculate the XH-stretching frequencies and oscillator strengths for OH, HF, HCl, HCOOH, CH₃OH, HNO₃, and H₂O–H₂O with a 1D local mode vibrational model.^{9,10,14} The 1D Schrödinger equation is solved numerically using a finite element method to give both the vibrational energy levels and wave functions.³⁵ The potential energy curve used for this covers the range from -0.3 to 0.8 Å in 0.025 Å steps around equilibrium. This ensures converged energy levels, better than 0.1 cm^{-1} , and wave functions (f better than 0.1%) for $\nu \leq 5$ when tested for range and step size in the potential energy curve.

The transition dipole matrix element of Eq. (1) can be expanded as

$$\langle \nu | \bar{\mu} | 0 \rangle = \frac{\partial \bar{\mu}}{\partial q} \langle \nu | q | 0 \rangle + \frac{1}{2} \frac{\partial^2 \bar{\mu}}{\partial q^2} \langle \nu | q^2 | 0 \rangle + \frac{1}{6} \frac{\partial^3 \bar{\mu}}{\partial q^3} \langle \nu | q^3 | 0 \rangle + \dots, \quad (2)$$

where q is the internal vibrational displacement coordinate. The integrals $\langle \nu | q^n | 0 \rangle$ required for the transition dipole moment are evaluated by trapezoidal numeric integration. The dipole moment coefficients are found from a sixth order polynomial fit to a 15 point dipole moment curve calculated over values of q from -0.3 to 0.4 Å in 0.05 Å steps.^{36,37} These dipole moment coefficients provide oscillator strengths that are converged to better than 1% when compared to larger dipole moment curves.¹³

For the diatomics, we have also constructed conventional CCSD(T)/CBS limit potential energy curves. We have extrapolated the CCSD(T) energies at each point with the following two parameter extrapolation for the correlation energy:

$$E_{XY}^{\text{corr}} = \frac{X^3 E_X^{\text{corr}} - Y^3 E_Y^{\text{corr}}}{X^3 - Y^3}, \quad (3)$$

where X and Y are the cardinal numbers of the two basis sets and E_X^{corr} and E_Y^{corr} are the corresponding correlation energies.^{38,39} The extrapolated correlation energy, E_{56}^{corr} is added to the HF/AV6Z energy to give an estimate of the CCSD(T)/CBS energy. All energies are obtained at displacements from the CCSD(T)/AV6Z optimized bond length. The CCSD(T) and CCSD(T)-F12 dipole moment at each geometry is calculated using a finite field approach with a field strength of ± 0.0005 a.u. We construct CCSD(T)/CBS dipole moment curves by extrapolating the correlation energy using Eq. (3) under the influence of both positive and negative electric fields and then evaluate the dipole moment.⁴⁰

To investigate the appropriateness of our 1D local mode vibrational model for the polyatomic systems, we have also calculated the fundamental and overtone vibrational frequencies of HCOOH, CH₃OH, HNO₃, and H₂O–H₂O using second order vibrational perturbation theory (VPT2). The VPT2 vibrational model has been shown to give accurate fundamental, overtone, and combination vibrational frequencies for

TABLE I. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental frequencies (in cm^{-1}) for hydroxyl radical.

Basis set	$\Delta v=1$	$\Delta v=2$	$\Delta v=3$	$\Delta v=4$	$\Delta v=5$
AVDZ	3510	6849	10 022	13 030	15 871
AVTZ	3554	6947	10 177	13 245	16 151
AVQZ	3572	6979	10 223	13 306	16 227
AV5Z	3575	6985	10 233	13 320	16 245
AV6Z	3575	6986	10 235	13 322	16 249
CBS ^a	3576	6987	10 236	13 325	16 253
VDZ-F12	3576	6987	10 235	13 321	16 244
VTZ-F12	3574	6983	10 230	13 315	16 240
VQZ-F12	3576	6989	10 239	13 328	16 256
Expt. ^b	3569.61	6973.68	10 214.05	13 291.82	16 207.12

^aExtrapolation to the CBS limit utilizes AV5Z and AV6Z results.

^bExperimental frequencies from HITRAN (Ref. 62).

several small molecules at the CCSD(T) level of theory with ANO and correlation consistent basis sets.^{41,42} Anharmonic VPT2 frequencies were performed using CFOUR⁴³ with the following convergence threshold criteria: SCF_CONV= 1×10^{-9} a.u., CC_CONV= 1×10^{-10} a.u., LINEQ_CONV= 1×10^{-10} a.u., and GEO_CONV= 1×10^{-10} a.u.

All coupled cluster calculations assume a frozen core (C:1s; N:1s; O:1s; S:1s,2s,2p; Cl:1s,2s,2p) and unless otherwise specified were performed using MOLPRO 2008.1.²⁴ The optimization threshold criteria in MOLPRO was set to gradient= 1×10^{-6} a.u., stepsize= 1×10^{-6} a.u., energy= 1×10^{-8} a.u. The single point threshold criterion was set to: energy= 1×10^{-9} a.u., orbital= 1×10^{-8} a.u., coefficient= 1×10^{-8} a.u.

III. RESULTS AND DISCUSSION

A. Diatomics

In Tables I–III we present fundamental and overtone vibrational frequencies for OH, HF, and HCl obtained with both conventional and explicitly correlated CCSD(T) potential energy curves. If we first consider the conventional CCSD(T) results, we find that in general the vibrational frequencies of the three diatomics converge upwards to the CCSD(T)/CBS limit as we increase the cardinal number of the basis set from AVDZ to AV6Z. This result is consistent

with previous basis set investigations of the harmonic frequencies of diatomic molecules obtained with the CCSD(T) method.^{44,45} For OH and HF, convergence of the fundamental and overtone frequencies is slow but proceeds monotonically from AVDZ to AV6Z. For HCl, the calculated frequencies appear to converge a little more rapidly although there is some small oscillation between the AVQZ-AV6Z results. This oscillation in the HCl vibrational frequencies is due to a small oscillation in the optimized CCSD(T) HCl bond length with the AVQZ-AV6Z basis sets.

Not surprisingly, the absolute error between frequencies obtained with a given basis set and the CBS limit is smallest for the fundamental transitions and becomes increasingly large for the higher overtones. For example, the AVDZ OH fundamental frequency is underestimated by 66 cm^{-1} , whereas the AVDZ OH fourth overtone is underestimated by 382 cm^{-1} . However, in relative terms, the percentage error also generally increases slightly as the quanta of excitation increases. For example, the AVDZ OH fundamental frequency is underestimated by 1.9% and the AVDZ OH fourth overtone is underestimated by 2.5%. This suggests that the higher parts of the potential energy curve have greater basis set requirements than points closer to equilibrium.

If we now consider the explicitly correlated results, we find that the calculated fundamental and overtone vibrational frequencies oscillate as the cardinal number of the basis set

TABLE II. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental frequencies (in cm^{-1}) for hydrogen fluoride.

Basis set	$\Delta v=1$	$\Delta v=2$	$\Delta v=3$	$\Delta v=4$	$\Delta v=5$
AVDZ	3891	7604	11 148	14 529	17 752
AVTZ	3952	7734	11 349	14 800	18 091
AVQZ	3965	7759	11 384	14 847	18 150
AV5Z	3966	7760	11 387	14 851	18 156
AV6Z	3966	7760	11 387	14 852	18 157
CBS ^a	3966	7759	11 387	14 851	18 157
VDZ-F12	3971	7771	11 405	14 877	18 190
VTZ-F12	3964	7757	11 384	14 847	18 151
VQZ-F12	3966	7760	11 388	14 853	18 159
Expt. ^b	3961.40	7750.80	11 372.81	14 831.68	18 131

^aExtrapolation to the CBS limit utilizes AV5Z and AV6Z results.

^bExperimental frequencies from HITRAN (Ref. 62).

TABLE III. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental frequencies (in cm^{-1}) for hydrogen chloride.

Basis set	$\Delta v=1$	$\Delta v=2$	$\Delta v=3$	$\Delta v=4$	$\Delta v=5$
AVDZ	2879	5651	8317	10 877	13 330
AVTZ	2890	5674	8353	10 927	13 398
AVQZ	2891	5678	8362	10 943	13 422
AV5Z	2892	5680	8365	10 948	13 428
AV6Z	2891	5679	8364	10 947	13 428
CBS ^a	2890	5676	8361	10 944	13 425
VDZ-F12	2906	5708	8407	11 003	13 496
VTZ-F12	2891	5679	8364	10 947	13 428
VQZ-F12	2892	5680	8366	10 949	13 431
Expt. ^b	2885.9	5668.0	8346.9	10 923.1	13 396.5

^aExtrapolation to the CBS limit utilizes AV5Z and AV6Z results.

^bExperimental frequencies from HITRAN (Ref. 62).

increases from VDZ-F12 to VQZ-F12. For all three diatomics, the VDZ-F12 vibrational frequencies are higher than the VTZ-F12 vibrational frequencies, which in turn are marginally lower than the VQZ-F12 vibrational frequencies. However, it should be noted that the oscillation from VDZ-F12 to VQZ-F12 is significantly smaller than the monotonic variation in the vibrational frequencies from AVDZ to AVQZ observed with conventional CCSD(T). Furthermore, fundamental and overtone frequencies obtained with a given cardinal number and the explicitly correlated CCSD(T)-F12b method are in much better agreement with the CCSD(T)/CBS limit than results obtained with conventional CCSD(T). Impressively for all three diatomics, CCSD(T)-F12b vibrational frequencies obtained with the VTZ-F12 basis set are of comparable accuracy [with respect to the CCSD(T)/CBS limit] to CCSD(T)/AV5Z results and are much less computationally demanding.

Now that we have established the basis set convergence of both the conventional and explicitly correlated CCSD(T) vibrational frequencies, it is pertinent to compare our calculated results to experiment. We find that the CCSD(T)/CBS fundamental frequencies are overestimated by 4–6 cm^{-1} (0.11%–0.18%) with respect to experiment. This result is comparable to the 3–14 cm^{-1} overestimate of CCSD(T) harmonic frequencies with respect to experiment that was previously observed for the diatomics HF, N₂, F₂, and CO.⁴⁵

The absolute and relative error of the CCSD(T)/CBS frequencies increases as the quanta of excitation increases. For the fourth overtone, the CCSD(T)/CBS frequencies are overestimated by 26–46 cm^{-1} (0.14%–0.28%)

For OH and HF, the conventional CCSD(T) vibrational frequencies obtained with the AVDZ and AVTZ basis sets are underestimated with respect to experiment while the AVQZ-AV6Z results are overestimated. For HCl, only the AVDZ vibrational frequencies are underestimated with the AVTZ-AV6Z results overestimated. As a consequence of the rapid basis set convergence of the explicitly correlated CCSD(T)-F12b method, even XH-stretching frequencies obtained with the VDZ-F12 basis set are overestimated when compared to the experimental values for OH, HF, and HCl. The inclusion of explicit correlation appears to expose the inherent error of the CCSD(T) method for calculating vibrational frequencies that is normally compensated to a certain extent by basis set incompleteness error. Fortunately, we find conventional CCSD(T)/AVQZ frequencies for OH and HF and conventional CCSD(T)/AVTZ frequencies of HCl are in closest agreement with experiment.

In Tables IV–VI we present fundamental and overtone vibrational oscillator strengths for OH, HF, and HCl obtained with both conventional and explicitly correlated CCSD(T) potential energy and dipole moment curves. In comparison with the vibrational frequencies, the convergence of calcu-

TABLE IV. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental oscillator strengths for hydroxyl radical.

Basis set	$\Delta v=1$	$\Delta v=2$	$\Delta v=3$	$\Delta v=4$	$\Delta v=5$
AVDZ	9.3×10^{-7}	2.2×10^{-7}	1.1×10^{-8}	8.4×10^{-10}	7.9×10^{-11}
AVTZ	1.4×10^{-6}	2.4×10^{-7}	1.1×10^{-8}	6.4×10^{-10}	5.4×10^{-11}
AVQZ	1.6×10^{-6}	2.5×10^{-7}	1.1×10^{-8}	6.4×10^{-10}	5.5×10^{-11}
AV5Z	1.7×10^{-6}	2.5×10^{-7}	1.0×10^{-8}	6.3×10^{-10}	5.4×10^{-11}
AV6Z	1.7×10^{-6}	2.5×10^{-7}	1.0×10^{-8}	6.2×10^{-10}	5.3×10^{-11}
CBS ^a	1.7×10^{-6}	2.5×10^{-7}	1.0×10^{-8}	6.3×10^{-10}	5.3×10^{-11}
VDZ-F12	1.7×10^{-6}	2.7×10^{-7}	1.1×10^{-8}	6.9×10^{-10}	6.1×10^{-11}
VTZ-F12	1.8×10^{-6}	2.6×10^{-7}	1.1×10^{-8}	6.2×10^{-10}	5.2×10^{-11}
VQZ-F12	1.8×10^{-6}	2.5×10^{-7}	1.0×10^{-8}	6.2×10^{-10}	5.3×10^{-11}
Expt. ^b	1.17×10^{-6}	2.07×10^{-7}	1.07×10^{-8}	7.54×10^{-10}	7.26×10^{-11}

^aExtrapolation to the CBS limit utilizes AV5Z and AV6Z results.

^bExperimental oscillator strengths from HITRAN (Ref. 62).

TABLE V. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental oscillator strengths for hydrogen fluoride.

Basis set	$\Delta v=1$	$\Delta v=2$	$\Delta v=3$	$\Delta v=4$	$\Delta v=5$
AVDZ	1.7×10^{-5}	5.7×10^{-7}	1.9×10^{-8}	1.1×10^{-10}	9.0×10^{-11}
AVTZ	1.8×10^{-5}	5.7×10^{-7}	1.6×10^{-8}	7.2×10^{-10}	4.6×10^{-11}
AVQZ	1.9×10^{-5}	5.7×10^{-7}	1.6×10^{-8}	8.2×10^{-10}	6.0×10^{-11}
AV5Z	1.9×10^{-5}	5.7×10^{-7}	1.6×10^{-8}	8.3×10^{-10}	6.1×10^{-11}
AV6Z	1.9×10^{-5}	5.7×10^{-7}	1.6×10^{-8}	8.3×10^{-10}	6.1×10^{-11}
CBS ^a	1.9×10^{-5}	5.7×10^{-7}	1.6×10^{-8}	8.2×10^{-10}	5.9×10^{-11}
VDZ-F12	1.9×10^{-5}	5.9×10^{-7}	1.7×10^{-8}	9.1×10^{-10}	7.3×10^{-11}
VTZ-F12	1.9×10^{-5}	5.8×10^{-7}	1.6×10^{-8}	8.2×10^{-10}	5.9×10^{-11}
VQZ-F12	1.9×10^{-5}	5.8×10^{-7}	1.6×10^{-8}	8.4×10^{-10}	6.2×10^{-11}
Expt. ^b	1.78×10^{-5}	5.61×10^{-7}	1.39×10^{-8}

^aExtrapolation to the CBS limit utilizes AV5Z and AV6Z results.

^bExperimental oscillator strengths from HITRAN (Ref. 62).

lated oscillator strengths is not consistent across the quanta of excitation. For example, the fundamental oscillator strengths generally converge upwards whereas the oscillator strengths of the higher overtones generally converge downwards with increasing basis set size. However, the calculated oscillator strengths do appear to converge more rapidly than the calculated frequencies as the cardinal number of the basis set is increased, which suggests that the dipole moment curve is less sensitive to basis set size than the potential energy curve. With conventional CCSD(T), oscillator strengths obtained with the AVQZ basis set are essentially converged to the CCSD(T)/CBS limit. The basis set convergence of the explicitly correlated CCSD(T)-F12b method is a little better, with oscillator strengths obtained using the VTZ-F12 basis found to be in excellent agreement with the CCSD(T)/CBS limit. Notably, the fundamental, first and second overtone oscillator strengths of the three diatomics are also essentially converged to the CCSD(T)/CBS limit with just the VDZ-F12 basis set.

In general, our calculated CCSD(T)/CBS limit oscillator strengths are in reasonably good agreement with experiment, particularly given that the oscillator strengths of the fundamental to fourth overtone transitions span several orders of magnitude. For OH, our calculated oscillator strengths of the fundamental and first overtone transitions are slightly overestimated whereas the higher overtones are slightly under-

estimated. For HF, our calculated fundamental, first and second overtone oscillator strengths are all slightly overestimated with respect to experiment. For HCl, all of our calculated oscillator strengths are larger than experiment with the fundamental and first overtone transition overestimated by 40%–50% and the higher overtones overestimated by a factor of 2.

B. Polyatomic frequencies

In Tables VII–XI we present experimental and calculated XH-stretching frequencies for CH₃OH, HNO₃, HCOOH, and H₂O–H₂O obtained with conventional and explicitly correlated CCSD(T) potential energy curves. It is important to note that our simple 1D local mode vibrational model assumes that the XH-stretching mode is isolated from all other vibrational modes. The appropriateness of this assumption complicates comparison of our calculated XH-stretching transitions for these polyatomic systems to experiment. Nonetheless, the four molecular systems (and five XH-stretching modes) chosen have been previously found to be at least reasonably described both theoretically and experimentally using a simple 1D vibrational model.^{12,46–49} We investigate this issue further by comparing our 1D XH-stretching frequencies to results obtained using a full 3N-6 (where N is the number of atoms) VPT2 anharmonic vibra-

TABLE VI. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental oscillator strengths for hydrogen chloride.

Basis set	$\Delta v=1$	$\Delta v=2$	$\Delta v=3$	$\Delta v=4$	$\Delta v=5$
AVDZ	5.3×10^{-6}	1.5×10^{-7}	1.6×10^{-9}	2.1×10^{-11}	3.4×10^{-13}
AVTZ	6.4×10^{-6}	1.7×10^{-7}	1.5×10^{-9}	1.9×10^{-12}	2.2×10^{-12}
AVQZ	7.1×10^{-6}	1.7×10^{-7}	1.6×10^{-9}	6.1×10^{-12}	6.0×10^{-13}
AV5Z	7.3×10^{-6}	1.7×10^{-7}	1.5×10^{-9}	5.9×10^{-12}	4.7×10^{-13}
AV6Z	7.4×10^{-6}	1.7×10^{-7}	1.6×10^{-9}	6.3×10^{-12}	5.0×10^{-13}
CBS ^a	7.6×10^{-6}	1.8×10^{-7}	1.6×10^{-9}	6.7×10^{-12}	5.0×10^{-13}
VDZ-F12	7.2×10^{-6}	1.9×10^{-7}	1.8×10^{-9}	8.7×10^{-12}	2.4×10^{-13}
VTZ-F12	7.5×10^{-6}	1.8×10^{-7}	1.7×10^{-9}	9.4×10^{-12}	3.1×10^{-13}
VQZ-F12	7.7×10^{-6}	1.8×10^{-7}	1.7×10^{-9}	9.7×10^{-12}	4.3×10^{-13}
Expt. ^b	5.37×10^{-6}	1.22×10^{-7}	8.11×10^{-10}	3.6×10^{-12}	...

^aExtrapolation to the CBS limit utilizes AV5Z and AV6Z results.

^bExperimental oscillator strengths from HITRAN (Ref. 62).

TABLE VII. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental OH-stretching frequencies (in cm^{-1}) for methanol.

Basis set	$\Delta v=1$	$\Delta v=2$	$\Delta v=3$	$\Delta v=4$	$\Delta v=5$
AVDZ	3642	7108	10 401	13 523	16 474
AVTZ	3676	7184	10 524	13 697	16 701
AVQZ	3693	7217	10 572	13 759	16 779
VDZ-F12	3694	7218	10 574	13 761	16 780
VTZ-F12	3695	7221	10 578	13 768	16 790
VQZ-F12	3697	7225	10 585	13 777	16 803
Expt. ^a	3683.91	7196.09	10 525.6	13 704.6	16 705.9

^aExperimental frequencies are from Ref. 63.

tional model. The VPT2 vibrational model assumes each vibrational mode can be described using a fourth order polynomial, which when treated by second order perturbation theory gives the same energy expression as the Morse oscillator potential.⁵⁰ To facilitate comparison with the VPT2 frequencies, we have also calculated the 1D local mode XH-stretching frequencies using a Morse oscillator approach.^{14,51} We include these 1D Morse oscillator XH-stretching frequencies, the equivalent VPT2 frequencies and the difference between the 1D Morse and VPT2 results (as an estimate of the magnitude of vibrational coupling) in the supplementary deposit.³² Finally, it should be noted that the primary purpose of this paper is not to calculate XH-stretching transitions to spectroscopic accuracy but to consider the basis set convergence of calculated frequencies and intensities of XH-stretching vibrational modes using conventional and explicitly correlated CCSD(T) theory. Given the excellent agreement observed for the diatomic systems in the previous section, we consider the present polyatomic CCSD(T)-F12b/VQZ-F12 frequencies and oscillator strengths as representative of the CCSD(T)/CBS limit.

The CH_3OH fundamental and overtone OH-stretching frequencies obtained with conventional CCSD(T) converge monotonically upwards from AVDZ to AVQZ. The explicitly correlated OH-stretching frequencies also systematically increase as the cardinal number of the basis set increases, although the variation in frequencies is much smaller than the conventional CCSD(T) results. The conventional CCSD(T) frequencies appear to converge toward the explicitly correlated results and we find that the conventional CCSD(T)/AVQZ frequencies are in good agreement with the CCSD(T)-F12b/VDZ-F12 frequencies. The OH-stretching frequencies obtained with conventional CCSD(T) and the

AVDZ and AVTZ basis are lower than the experimentally determined values whereas the CCSD(T)/AVQZ and explicitly correlated CCSD(T)-F12b frequencies are all higher than experiment. Furthermore, we find that the conventional CCSD(T)/AVTZ calculated OH-stretching frequencies are in closest agreement with experiment. The CCSD(T)-F12b/VQZ-F12 frequencies [as an estimate of the CCSD(T)/CBS limit] are overestimated by 13 cm^{-1} in the fundamental region and $\sim 100 \text{ cm}^{-1}$ in fourth overtone region. This discrepancy with experiment is larger than but still comparable to the diatomic results in the previous section and indicates that the OH-stretching mode of CH_3OH is reasonably well localized. We find that the effect of vibrational coupling within the VPT2 model is modest and lowers the OH-stretching frequency of CH_3OH by 11 cm^{-1} in the fundamental region and $\sim 70 \text{ cm}^{-1}$ in the fourth overtone region. Addition of this VPT2 vibrational coupling “correction” to the CCSD(T)-F12b/VQZ-F12 1D OH-stretching frequencies gives results for CH_3OH that are of comparable accuracy (with respect to experiment) to the diatomic frequencies in the previous section.

The fundamental and overtone OH-stretching frequencies of HNO_3 calculated with conventional CCSD(T) increase monotonically as the cardinal number of the basis set increases from AVDZ-AVQZ. In contrast, the explicitly correlated CCSD(T)-F12b OH-stretching frequencies obtained with the VDZ-F12, VTZ-F12 and VQZ-F12 basis sets oscillate to a small extent. Fundamental and overtone OH-stretching frequencies obtained with conventional CCSD(T) appear to converge toward the explicitly correlated frequencies as the basis set increases. With exception of the conventional CCSD(T)/AVDZ results, all of our other calculated OH-stretching frequencies are overestimated when compared

TABLE VIII. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental OH-stretching frequencies (in cm^{-1}) for nitric acid.

Basis set	$\Delta v=1$	$\Delta v=2$	$\Delta v=3$	$\Delta v=4$	$\Delta v=5$
AVDZ	3534	6905	10 118	13 178	16 088
AVTZ	3567	6980	10 239	13 348	16 310
AVQZ	3583	7008	10 280	13 402	16 376
VDZ-F12	3589	7021	10 300	13 429	16 410
VTZ-F12	3584	7011	10 285	13 409	16 385
VQZ-F12	3585	7014	10 289	13 415	16 394
Expt. ^a	3551	~ 6940	10 173	13 245	16 160

^aExperimental frequencies are from Refs. 64–66.

TABLE IX. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental OH-stretching frequencies (in cm^{-1}) for formic acid.

Basis set	$\Delta\nu=1$	$\Delta\nu=2$	$\Delta\nu=3$	$\Delta\nu=4$	$\Delta\nu=5$
AVDZ	3557	6948	10 179	13 253	16 174
AVTZ	3587	7016	10 289	13 409	16 378
AVQZ	3602	7043	10 328	13 460	16 442
VDZ-F12	3606	7052	10 342	13 479	16 466
VTZ-F12	3603	7046	10 332	13 466	16 449
VQZ-F12	3604	7049	10 337	13 473	16 459
Expt. ^a	3568.9	6968.26	10 200	13 284.1	...

^aExperimental frequencies are from Refs. 49, 52, and 57.

to the experimental values. Fortuitously, OH-stretching frequencies for HNO_3 obtained with conventional CCSD(T)/AVDZ are in best agreement with experiment. The CCSD(T)-F12b/VQZ-F12 frequencies are overestimated by 34 cm^{-1} in the fundamental region and $\sim 230 \text{ cm}^{-1}$ in fourth overtone region when compared to experiment. This discrepancy is much larger than the inherent overestimation error of the CCSD(T) method that was observed for the diatomic systems and suggests that the OH-stretching mode in HNO_3 is significantly coupled to the other vibrational modes.⁴¹ We find that the effect of vibrational coupling within the VPT2 model is significant, lowering the OH-stretching frequency of HNO_3 by 28 cm^{-1} in the fundamental region and $\sim 160 \text{ cm}^{-1}$ in the fourth overtone region. Thus inclusion of coupling to the other vibrational modes brings the calculated OH-stretching frequencies for HNO_3 in closer agreement with experiment.

The fundamental and overtone OH-stretching frequencies of HCOOH calculated with conventional CCSD(T) are found to monotonically converge upwards as the cardinal number of the basis set increases AVDZ-AVQZ. The explicitly correlated CCSD(T)-F12b OH-stretching frequencies do not exhibit any systematic convergence as the basis set increases, however, the oscillation from VDZ-F12 to VQZ-F12 is small. Similar to HNO_3 , the conventional CCSD(T) fundamental and overtone frequencies of HCOOH appear to converge toward the explicitly correlated results as the basis set increases. With exception of the conventional CCSD(T)/AVDZ frequencies, all other calculated frequencies are higher than the experimentally measured values. We find that the CCSD(T)-F12b/VQZ-F12 OH-stretching frequencies of HCOOH are overestimated by 35 cm^{-1} in the fundamental region and $\sim 190 \text{ cm}^{-1}$ in third overtone region when com-

pared to experiment. This discrepancy is much larger than the inherent overestimation error of the CCSD(T) method and suggests that like HNO_3 , the OH-stretching mode in HCOOH is significantly coupled to the other vibrational modes.⁵² We find that the effect of vibrational coupling within the VPT2 model is significant, lowering the OH-stretching frequency of HCOOH by 30 cm^{-1} in the fundamental region and $\sim 210 \text{ cm}^{-1}$ in the fourth overtone region. Addition of this VPT2 anharmonic coupling correction to the calculated 1D results improves the agreement with the experimental frequencies.

The fundamental CH-stretching frequency of HCOOH calculated with conventional CCSD(T) oscillates as the cardinal number of the basis set increases AVDZ-AVQZ whereas the CH-stretching overtone frequencies all monotonically converge upwards. It is worth noting that variation in both the fundamental and overtone CH-stretching frequencies of HCOOH obtained with conventional CCSD(T) is much smaller than the corresponding OH-stretching frequencies in CH_3OH , HNO_3 , and HCOOH. We find that the explicitly correlated CH-stretching frequencies of HCOOH do not exhibit any systematic convergence with increasing basis set, although again the variation is small. The conventional CCSD(T)/AVQZ fundamental and overtone frequencies are found to be in good agreement with all of the explicitly correlated results. The conventional and explicitly correlated CCSD(T) CH-stretching frequencies of HCOOH are all significantly overestimated with respect to experiment. We find that the CCSD(T)-F12b/VQZ-F12 CH-stretching frequencies of HCOOH are overestimated by 38 cm^{-1} in the fundamental region and $\sim 210 \text{ cm}^{-1}$ in third overtone region when compared to experiment. Again, this relatively large discrepancy is attributed to vibrational coupling, which within the

TABLE X. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated and experimental CH-stretching frequencies (in cm^{-1}) for formic acid.

Basis set	$\Delta\nu=1$	$\Delta\nu=2$	$\Delta\nu=3$	$\Delta\nu=4$	$\Delta\nu=5$
AVDZ	2979	5836	8571	11 186	13 681
AVTZ	2977	5837	8579	11 206	13 717
AVQZ	2980	5842	8587	11 216	13 731
VDZ-F12	2981	5844	8591	11 223	13 740
VTZ-F12	2979	5840	8585	11 215	13 730
VQZ-F12	2981	5844	8591	11 223	13 740
Expt. ^a	2943	5774	8446	11 012	...

^aExperimental frequencies are from Refs. 49, 52, and 57.

TABLE XI. Conventional CCSD(T) and explicitly correlated CCSD(T)-F12b calculated OH(b)-stretching frequencies (in cm^{-1}) for water dimer.

Basis set	$\Delta\nu=1$	$\Delta\nu=2$	$\Delta\nu=3$	$\Delta\nu=4$	$\Delta\nu=5$
AVDZ ^a	3546	6902	10 069	13 045	15 825
AVTZ ^a	3572	6961	10 162	13 169	15 974
AVQZ ^a	3585	6983	10 193	13 208	16 022
A'VDZ	3564	6940	10 129	13 128	15 933
A'VTZ	3579	6977	10 190	13 211	16 034
A'VQZ	3588	6991	10 204	13 224	16 043
A'V5Z	3591	6996	10 212	13 235	16 056
VDZ-F12	3597	7010	10 235	13 269	16 101
VTZ-F12	3589	6994	10 210	13 233	16 055
VQZ-F12	3591	6996	10 214	13 238	16 061
Expt. ^b	3601	7018

^aFrom Ref. 46.^bExperimental frequencies are from Refs. 55 and 56.

VPT2 model is found to lower the CH-stretching frequency of HCOOH by 60 cm^{-1} in the fundamental region and $\sim 340 \text{ cm}^{-1}$ in the fourth overtone region.

The final polyatomic system considered is the $\text{H}_2\text{O}-\text{H}_2\text{O}$ complex, where we consider only the vibrational frequencies of the hydrogen bonded OH(b)-stretching mode. The accurate calculation of vibrational frequencies in molecular complexes is further complicated by basis set superposition error, which artificially increases the interaction energy and hence overestimates the effects of complexation.^{53,54} Recently, we showed that basis set superposition error could be significantly reduced by including diffuse basis functions only on the heavy atoms (i.e., all atoms but hydrogen) in a series of hydrogen bonded complexes, including $\text{H}_2\text{O}-\text{H}_2\text{O}$.²³ The fundamental and overtone OH(b)-stretching frequencies of $\text{H}_2\text{O}-\text{H}_2\text{O}$ obtained with conventional CCSD(T) and both the fully (AVDZ-AVQZ) and partially (A'VDZ-A'V5Z) augmented basis sets converge upwards as the cardinal number of the basis set is increased. Consistent with the previous monomeric systems investigated, the OH(b)-stretching frequencies obtained with the explicitly correlated CCSD(T)-F12b method oscillate to a small extent from VDZ-F12 to VQZ-F12. For a given cardinal number, we find that fundamental and overtone OH(b)-stretching frequencies obtained with the partially augmented basis sets are in better agreement with the explicitly correlated results than frequencies obtained with the fully augmented basis sets. This indicates, as expected, that the effect of basis set superposition error on the OH(b)-stretching frequencies is reduced by restricting diffuse basis functions to the heavy atoms.

There are limited experimental results available for the OH(b)-stretching frequencies of $\text{H}_2\text{O}-\text{H}_2\text{O}$, with only the fundamental transition observed in gas phase and the first overtone transition observed in a Ne matrix.^{55,56} In contrast to the other polyatomic systems, all of our calculated frequencies for the $\text{H}_2\text{O}-\text{H}_2\text{O}$ complex are underestimated with respect to the experimental values. We find that the CCSD(T)-F12b/VQZ-F12 OH(b)-stretching frequencies of $\text{H}_2\text{O}-\text{H}_2\text{O}$ are underestimated by 10 cm^{-1} in the fundamental region and 22 cm^{-1} in the first overtone region when

compared to experiment. We have previously shown that the fundamental OH(b)-stretching frequency of $\text{H}_2\text{O}-\text{H}_2\text{O}$ calculated using a 1D vibrational model is lowered by 9 cm^{-1} by inclusion of intramolecular vibrational coupling calculated with a harmonically coupled anharmonic oscillator (HCAO) vibrational model.⁴⁶ However, vibrational coupling to the remaining intermolecular vibrational modes is also important and the VPT2 fundamental OH(b)-stretching frequency is found to be 17 cm^{-1} higher in energy than the 1D approach.^{42,46} It follows that for $\text{H}_2\text{O}-\text{H}_2\text{O}$, unlike the other polyatomic systems, the net effect of vibrational coupling is to increase the 1D OH(b)-stretching frequency.

In summary, we find that the basis set dependence of calculated frequencies obtained with the explicitly correlated CCSD(T)-F12b method is much smaller than with conventional CCSD(T) and even CCSD(T)-F12b/VDZ-F12 frequencies are in good agreement with results obtained with much larger basis sets. The computational demands of the CCSD(T)-F12b/VDZ-F12 method are not excessive and as such its use with full 3N-6 multidimensional anharmonic vibrational models such as VSCF, VCI, VCC, and VPT2 should be practicable for systems up to ten atoms. However, it is important to remember that the accuracy of any CCSD(T)-F12b multidimensional anharmonic frequencies will still be limited to the inherent accuracy of the CCSD(T) method, which we found to be $4-6 \text{ cm}^{-1}$ for fundamental frequencies and $26-46 \text{ cm}^{-1}$ for fourth overtone transitions in the previous section. When multidimensional anharmonic models are not practicable and instead a local mode vibrational model is used we suggest calculating the corresponding potential energy surfaces at the CCSD(T)/AVTZ level of theory. With conventional CCSD(T), meaningful results can only be expected with a triple- ζ or larger basis set³⁸ and the additional computational demands of a quadruple- ζ basis set are not warranted when using a vibrational model that neglects coupling to the other modes. We find that even for the well-localized vibrational modes considered here, the inclusion of vibrational coupling has a much greater effect on the calculated frequencies than increasing the basis set from AVTZ to AVQZ.

TABLE XII. Explicitly correlated CCSD(T)-F12b/VQZ-F12 calculated and experimental XH-stretching oscillator strengths (in cm^{-1}).

	$\Delta\nu=1$	$\Delta\nu=2$	$\Delta\nu=3$	$\Delta\nu=4$	$\Delta\nu=5$
CH ₃ OH ^a					
Calc.	3.6×10^{-6}	6.2×10^{-7}	2.9×10^{-8}	1.9×10^{-10}	2.0×10^{-10}
Expt.	$(2.9-3.7) \times 10^{-6}$	$(3.1-6.3) \times 10^{-7}$	$(2.7-4.7) \times 10^{-8}$	$(1.9-2.5) \times 10^{-10}$	4.0×10^{-10}
HNO ₃ ^b					
Calc.	1.6×10^{-5}	6.3×10^{-7}	2.8×10^{-8}	2.4×10^{-9}	2.9×10^{-10}
Expt.	$(1.1-1.6) \times 10^{-5}$	$(3.8-7.8) \times 10^{-7}$	$(3.0-3.3) \times 10^{-8}$	$(2.5-3.2) \times 10^{-9}$	2.9×10^{-10}
HCOOH OH-stretching ^c					
Calc.	1.0×10^{-5}				
Expt.	1.6×10^{-5}				
HCOOH CH-stretching ^c					
Calc.	2.6×10^{-6}				
Expt.	9.6×10^{-6}				
H ₂ O-H ₂ O ^d					
Calc.	6.9×10^{-5}	2.0×10^{-8}	2.6×10^{-9}	6.6×10^{-10}	1.1×10^{-10}
Expt.	2.5×10^{-5}				

^aExperimental oscillator strengths are from Refs. 67–70.^bExperimental oscillator strengths are from Refs. 41, 64–68, and 71.^cExperimental oscillator strengths are from Ref. 58.^dExperimental oscillator strengths are from Ref. 61.

C. Polyatomic intensities

In Table XII, we present CCSD(T)-F12b/VQZ-F12 calculated and experimental fundamental and overtone XH-stretching oscillator strengths for CH₃OH, HNO₃, HCOOH, and H₂O–H₂O. The calculated AVDZ, AVTZ, and AVQZ conventional CCSD(T) oscillator strengths and the calculated VDZ-F12 and VTZ-F12 explicitly correlated CCSD(T)-F12 oscillator strengths are included in the supplementary deposit.³² The measurement of absolute oscillator strengths is inherently more difficult than the measurement of absolute absorption frequencies, particularly for overtone transitions. As a result, different experimental investigations and indeed different experimental techniques often result in appreciably different absolute oscillator strengths. To reflect this uncertainty, where possible, we have shown a range of different experimental oscillator strengths in Table XII.

In general, we find that our CCSD(T)-F12b/VQZ-F12 calculated XH-stretching oscillator strengths are in very good agreement with experiment. For CH₃OH, we find that the calculated fundamental, first, second and third overtone OH-stretching oscillator strengths are within the range of experimentally determined oscillator strengths. The fourth overtone OH-stretching oscillator strength of CH₃OH is a factor of 2 smaller than experiment. For HNO₃, we find that the calculated fundamental, first, second and fourth overtone OH-stretching oscillator strengths are within the range of experimentally determined oscillator strengths. Our calculated third overtone OH-stretching oscillator strength of HNO₃ is approximately 4% smaller than the lowest experimental value.

While there have been several experimental investigations of the fundamental and overtone CH- and OH-stretching frequencies of HCOOH,^{49,52,57} only the fundamen-

tal oscillator strengths have been determined.⁵⁸ Formic acid has a strong tendency to form dimers and higher order clusters in the gas phase, which makes it very difficult to independently measure the concentration of HCOOH monomer and hence determine the oscillator strength of the monomeric absorption bands. We find that our calculated fundamental OH-stretching oscillator strength of HCOOH is $\sim 40\%$ smaller than the experimentally determined oscillator strength. For the CH-stretching mode of HCOOH, we find that our calculated fundamental oscillator strength is nearly a factor of 4 smaller than experiment. It is possible that the effect of dimerization has been overestimated in the experimental HCOOH investigation, and that the true concentration of monomeric HCOOH was actually higher, resulting in lower experimental oscillator strengths. However, because the calculated OH-stretching oscillator strength is underestimated by $\sim 40\%$ and the calculated CH-stretching oscillator strength underestimated by a factor of 4, a change in the monomeric HCOOH concentration would only bring one of these two calculated oscillator strengths into agreement with experiment. It is worth noting that this discrepancy between theory and experiment is unlikely due to our simple 1D vibrational model, with VPT2 CH- and OH-stretching fundamental oscillator strengths in excellent agreement (differing by less than 2%) with 1D results at the CCSD(T)/AVTZ level of theory. The OH-stretching frequency of HCOOH is significantly redshifted upon dimerization whereas the CH-stretching frequency is only mildly blueshifted such that the CH-stretching rotational profile of HCOOH and (HCOOH)₂ overlap significantly.^{59,60} Hence, the intensity of the weak CH-stretching transition is likely to be less accurately determined than the corresponding OH-stretching transition.

The fundamental OH(b)-stretching oscillator strength of

H₂O–H₂O measured using He droplet isolation techniques is nearly a factor of 3 smaller than our calculated 1D oscillator strength.⁶¹ We have previously shown at the CCSD(T)/AVTZ level of theory that the fundamental OH(b)-stretching oscillator strength of H₂O–H₂O calculated using a 1D vibrational model is lowered by 20% (5.7×10^{-5}) by inclusion of intramolecular vibrational coupling calculated using a HCAO vibrational model.⁴⁶ The effect of vibrational coupling to the remaining intermolecular vibrational modes has been shown to be even more important with the CCSD(T)/AVTZ fundamental VPT2 oscillator strength calculated to be 2.8×10^{-5} , in good agreement with experiment.⁴²

IV. CONCLUSIONS

We have calculated XH-stretching fundamental and overtone transitions of OH, HF, HCl, CH₃OH, HNO₃, HCOOH, and H₂O–H₂O with a 1D local mode vibrational model. The necessary XH-stretching potential energy and dipole moment curves were calculated *ab initio* using conventional CCSD(T) theory and the newly developed explicitly correlated CCSD(T)-F12 method. We find that the basis set convergence of calculated frequencies and oscillator strengths obtained with the explicitly correlated method is much more rapid than conventional CCSD(T). In general, CCSD(T)-F12 results obtained with a given basis set were found to be of comparable accuracy to conventional CCSD(T) results obtained with a basis set two cardinal numbers larger. For the three diatomic systems, CCSD(T)-F12 frequencies and oscillator strengths obtained with the VTZ-F12 and VQZ-F12 basis sets were found to be in excellent agreement with the CCSD(T)/CBS limit with the VDZ-F12 results only slightly less accurate.

The impressive basis set convergence of the explicitly correlated CCSD(T)-F12 method unfortunately exposes the inherent error of the CCSD(T) method to overestimate frequencies with respect to experiment, which is normally compensated by basis set incompleteness error. To obtain XH-stretching frequencies in closest agreement with experiment we suggest use of conventional CCSD(T) with the aug-cc-pVTZ or aug-cc-pVQZ basis set. This combination of method and basis set appears to fortuitously balance the inherent overestimation error of the CCSD(T) method with the inherent underestimation error due to basis set incompleteness.

The calculated CCSD(T)-F12 XH-stretching frequencies of the diatomic systems were found to be in much better agreement with experiment than the corresponding XH-stretching frequencies of the polyatomic systems. This indicates that even for reasonably well-localized oscillators, inclusion of coupling to other vibrational modes is necessary to accurately calculate vibrational frequencies. Nonetheless we find that in general, calculated 1D local mode XH-stretching oscillator strengths obtained with the CCSD(T)-F12 method are in very good agreement with experiment.

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