

## Factors Contributing to the Accuracy of Harmonic Force Field Calculations for Water

Michael H. Cortez,<sup>§</sup> Nicole R. Brinkmann,<sup>§</sup> William F. Polik,<sup>\*,§</sup> Peter R. Taylor,<sup>†</sup>  
Yannick J. Bomble,<sup>‡</sup> and John F. Stanton<sup>‡</sup>

*Department of Chemistry, Hope College, Holland, Michigan 49423, Department of Chemistry, University of Warwick, Coventry CV4 7AL, United Kingdom, and Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712*

Received November 29, 2006

**Abstract:** An analysis of the major factors affecting the accuracy of harmonic force field computations of water is presented. By systematically varying the level of approximation in the basis set, treatment of electron correlation, core electron correlation, and relativistic correction, the underlying sources of error in the computation of harmonic vibrational frequencies for water were quantified. The convergence error due to wavefunction description with a cc-pVQZ basis set in the absence of electron correlation was  $1.6\text{ cm}^{-1}$ , as determined from extending the Hartree–Fock computations to larger basis sets. The convergence error due to neglecting higher-order electronic correlation terms than are included at the CCSD(T) level using the cc-pVTZ basis set was estimated to be  $4.7\text{ cm}^{-1}$ , as determined from frequency calculations up to CCSDTQ for water and literature results up to CCSDTQP for diatomic molecules. The convergence error due to omitting higher-order diffuse functions than included in aug-cc-pVQZ was found to be  $3.7\text{ cm}^{-1}$ , as determined by adding more diffuse functions in larger basis sets. The error associated with neglecting core electron correlation effects (i.e., “freezing” core electrons) was  $5.0\text{ cm}^{-1}$  and with neglecting relativistic effects was  $2.2\text{ cm}^{-1}$ . Due to a cancellation among these various sources of error, the harmonic frequencies for  $\text{H}_2\text{O}$  computed using the CCSD(T)/aug-cc-pVQZ model chemistry were on average within  $2\text{ cm}^{-1}$  of experimentally inferred vibrational frequencies.

### Introduction

The infrared absorption spectrum of  $\text{H}_2\text{O}$  is important in a variety of applications.  $\text{H}_2\text{O}$  is the third most abundant gaseous species in the universe,<sup>1,2</sup> plays a critical role in the earth’s atmospheric chemistry and radiation trapping,<sup>3–5</sup> and is of great astrophysical interest.<sup>6–10</sup> Even though the vibrational transitions of water have been studied both theoretically and experimentally,<sup>1,2,7,11</sup> currently reported spectra of  $\text{H}_2\text{O}$  contain many unassigned lines and do not

continuously cover the entire spectrum at high resolution.<sup>6,7</sup> Portions of the spectrum of  $\text{H}_2\text{O}$  have been precisely determined experimentally through a variety of techniques over small ranges. Cavity ringdown spectroscopy has been used to study the vibrational spectra of  $\text{H}_2\text{O}$  at 555–604 nm and 810–820 nm vibrational overtone transitions in atmospheric flames.<sup>1,12</sup> Intracavity laser spectroscopy has been used to study the absorption of  $\text{H}_2\text{O}$  near 795 nm.<sup>11</sup> The vibrational overtone spectra of  $\text{H}_2\text{O}$  in the near-infrared, visible, and near-ultraviolet spectrum were also studied by Carleer et al.<sup>2</sup> using Fourier transform spectroscopy.

The potential energy surface (PES) of water has been computed both theoretically and from experimental data to aid in the construction of an absorption spectrum of

\* Corresponding author e-mail: polik@hope.edu.

<sup>§</sup> Hope College.

<sup>†</sup> University of Warwick.

<sup>‡</sup> The University of Texas at Austin.

spectroscopic accuracy for H<sub>2</sub>O. Both Jensen<sup>13</sup> and Polyansky et al.<sup>14</sup> constructed PESs for H<sub>2</sub>O solely from available experimental data. Beardsworth et al.<sup>15</sup> used a nonrigid bender Hamiltonian program to study the rotational–vibrational energy levels of triatomic molecules, including H<sub>2</sub>O. Polyansky et al.<sup>10</sup> computed the PES of H<sub>2</sub>O using MRCI theory and the aug-cc-pVXZ basis sets (X = T, Q, 5, 6). Császár and Mills<sup>16</sup> determined the quartic and sextic force field parameters for H<sub>2</sub>O using CCSD(T)/aug-cc-pVXZ (X = T, Q). Pair potentials for the H<sub>2</sub>O dimer have also been computed using symmetry adapted perturbation theory.<sup>17,18</sup>

The quantification of a PES is an important yet difficult practice in chemistry. Chemical reactions may be modeled as occurring on potential energy surfaces, and with the knowledge of the PES of a molecule, thermodynamic stability, reactivity, and reaction pathways can be predicted before an experiment is performed. The conventional method of modeling a PES is to construct a Taylor series expansion in terms of the displacement from the equilibrium geometry. This PES may then be used to calculate vibrational energy values.<sup>19</sup> Since the harmonic term of the Taylor expansion is a good approximation only at small displacements, higher-order anharmonic corrections are needed away from the equilibrium point.

Equation 1 is a Taylor expansion of the PES about the equilibrium point  $r_e$

$$\begin{aligned}
 U(r) &= \sum_{i=0}^{\infty} \frac{1}{i!} \left( \frac{\partial^i U}{\partial r^i} \right)_{r=r_e} (r - r_e)^i \\
 &= U(r_e) + \left( \frac{\partial U}{\partial r} \right)_{r=r_e} (r - r_e) + \frac{1}{2} \left( \frac{\partial^2 U}{\partial r^2} \right)_{r=r_e} (r - r_e)^2 + \\
 &\quad \sum_{i=3}^{\infty} \frac{1}{i!} \left( \frac{\partial^i U}{\partial r^i} \right)_{r=r_e} (r - r_e)^i + \dots \quad (1)
 \end{aligned}$$

where  $r - r_e$  is the displacement from the equilibrium point, and  $U$  is the potential energy. Assigning the zero of potential energy to the equilibrium structure, the expansion about a minimum of the PES [ $(\partial U / \partial r)_{r=r_e} = 0$ ] results in the quadratic term being the first nonzero term of the expansion. The quadratic term in eq 1 represents the harmonic energy, and the summation of subsequent terms represents the anharmonic corrections.

The harmonic terms of the Taylor expansion dominate the total energy near the equilibrium point, making it critical to compute the harmonic terms accurately. Császár and Mills<sup>16</sup> have observed that the harmonic force constants converge slower with respect to basis set size and theory level than the anharmonic constants, requiring more computational time to obtain the same accuracy. Thus, it is important to understand and determine the accuracy with which the harmonic force constants can be computed.

Previous studies<sup>10,16,20,21</sup> have examined the factors affecting the accuracy of theoretically computed force constants. Császár et al.<sup>16,20</sup> found that the majority of the error in their quadratic force constants for water at the CCSD(T)/aug-cc-pVQZ level of theory was due to core-core and core-valence correlation. They also found that the inclusion of relativistic

effects had marginal effects on the computed force constants. Polyansky et al.<sup>10</sup> examined H<sub>2</sub>O using the aug-cc-pVXZ (XD = Q, 5, 6) basis sets and MRCI theory and found the neglect of core electron correlation for oxygen resulted in 19 cm<sup>-1</sup> residual error in computed vibrational band origins. Partridge and Schwenke<sup>21</sup> studied the effects of core electron correlation of H<sub>2</sub>O at varying levels of theory and basis set size and found that corrections in core electron correlation are insensitive to increases in basis set size with the use of basis sets larger than the aug-cc-pVQZ basis set.

In the literature, only effects of individual factors on the accuracy of computed force constants have been reported. This work presents a comprehensive study of the major factors that affect the accuracy of such computations. By doing so, the underlying sources of error in theoretical computations of PESs can be evaluated and quantified at varying levels of approximation. In addition, insight is gained into the circumstances under which cancellation of errors may be present and the levels of theory and basis set sizes required to compute force constants to a specific accuracy.

The equilibrium geometry of a molecule serves only as the minimum energy reference point to the PES, while harmonic frequencies depend on the precise curvature of the PES near the equilibrium structure. Hence, the computation of vibrational frequencies is a more stringent test of the computational methods. Since the quadratic term is the largest in size and converges the slowest, it is the most important term of the Taylor expansion about the equilibrium geometry and will be the only term computed in this study.

Although diatomic molecules are computationally efficient species to study, they are missing features that yield greater insight into the intricacies of the computations and therefore would limit the applicability of results to arbitrary polyatomic molecules. H<sub>2</sub>O, therefore, was chosen for this study. As a polyatomic molecule, it has more than one vibrational degree of freedom and has both stretching and bending vibrations. H<sub>2</sub>O also exhibits anharmonicities and resonances, although these are not explicitly considered in the present work. H<sub>2</sub>O is also composed of light atoms, making the use of higher methods and larger basis sets feasible. Finally, H<sub>2</sub>O is a well-studied molecule both theoretically and experimentally, thus allowing for sufficient data comparison.

## Computational Methods

All computations were carried out using the MOLPRO<sup>22</sup> and ACES II<sup>23</sup> ab initio programs, except for the calculations including quadruple excitations (CCSDTQ) which were done with the string-based many-body program of Kállay.<sup>24</sup> The computations were performed on a Linux-based cluster of IA32 computers (2.4 GHz Pentium 4 CPU, 1GB RAM, 120 GB disk) and AMD64 computers (dual 2.2 GHz Opteron 248 CPUs, 8GB RAM, 250 GB disk).

Reference wavefunctions for the ground state of H<sub>2</sub>O were calculated at the Hartree–Fock self-consistent field (HF–SCF) level of theory. Dynamical correlation effects were included using the coupled-cluster series, including all single and double (CCSD)<sup>25</sup> and perturbatively applied triple excitations [CCSD(T)].<sup>26,27</sup> Explicit computation of the full set of triple excitations (CCSDT),<sup>28,29</sup> perturbatively applied

**Table 1.** Convergence of the Hartree–Fock Wavefunction for Computed Equilibrium Geometry and Harmonic Frequencies<sup>a</sup>

method	basis	$r_e$	$\theta_e$	$\omega_1$	$\omega_2$	$\omega_3$	$\langle \text{error} \rangle$	$\langle  \Delta  \rangle$	energy
HF	cc-pVDZ	0.946287	104.6130	4113.47	1775.69	4211.79	225.92		−76.02705
HF	cc-pVTZ	0.940604	106.0016	4126.74	1752.89	4226.63	227.69	16.97	−76.05777
HF	cc-pVQZ	0.939601	106.2222	4129.84	1750.47	4229.14	228.75	2.68	−76.06552
HF	cc-pV5Z	0.939572	106.3280	4130.26	1748.19	4230.64	228.63	1.40	−76.06778
HF	cc-pV6Z	0.939582	106.3361	4129.97	1748.03	4230.51	228.44	0.19	−76.06810
experiment <sup>38</sup>		0.9572	104.52	3832.2	1648.5	3942.5			

<sup>a</sup>  $\langle \text{error} \rangle$  represents the average absolute difference between the experimentally inferred and computed harmonic vibrational frequencies.  $\langle |\Delta| \rangle$  represents the average absolute difference in values from the previous set of computed harmonic vibrational frequencies. Bond lengths are in Å; bond angles are in degrees; frequencies,  $\langle \text{error} \rangle$ , and  $\langle |\Delta| \rangle$  are in  $\text{cm}^{-1}$ ; and total electronic energy is in  $E_h$ .

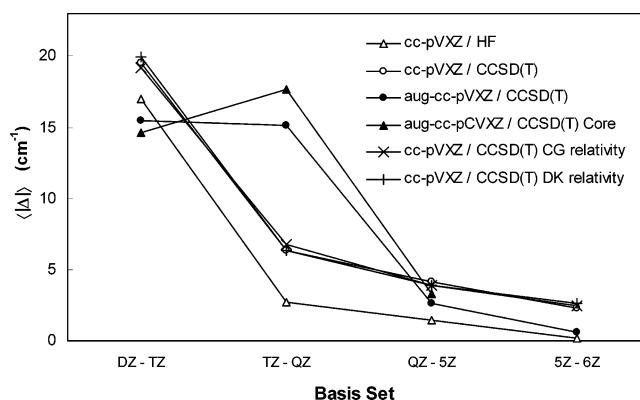
quadruple excitations [CCSDT(Q)],<sup>30</sup> and the full set of quadruple excitations (CCSDTQ)<sup>31,32</sup> were also carried out where feasible. Relativistic effects were analyzed using the Cowan–Griffin<sup>33</sup> (CG) and Douglas–Kroll<sup>34</sup> (DK) methods.

Three families of basis sets were used in the study. The first was Dunning’s correlation-consistent polarized valence basis (cc-pVXZ)<sup>35</sup> sets. For  $\text{H}_2\text{O}$ , the number of basis functions in these basis sets ranged from 24 for cc-pVDZ to 322 for cc-pV6Z. The more extensive augmented correlation-consistent polarized valence basis (aug-cc-pVXZ)<sup>35,36</sup> sets (45–443 basis functions for  $X = \text{D}$  to 6) and the augmented correlation-consistent polarized valence with core basis (aug-cc-pCVXZ)<sup>35–37</sup> sets (45–341 basis functions for  $X = \text{D}$  to 5) were also used.

Each computation included a geometry optimization performed at the respective level of theory and basis set size for the computation. In the core electron correlation computations, all electrons are considered in post-SCF calculations. In all other coupled-cluster computations, the correlation of core electrons was neglected. Vibrational frequencies were computed using finite differences for all computations.

## Results and Discussion

**A. Hartree–Fock Wavefunction.** The convergence of the Hartree–Fock (HF) wavefunction was determined by comparing vibrational frequencies of  $\text{H}_2\text{O}$  computed at the HF level of theory with basis sets from the cc-pVXZ family. The computed equilibrium geometries and harmonic vibrational frequencies are compared to the experimentally inferred equilibrium geometries and harmonic frequencies of Pliva, Spirko, and Papousek<sup>38</sup> in Table 1. The three vibrational modes for  $\text{H}_2\text{O}$  are the symmetric stretch ( $\omega_1$ ), the bend ( $\omega_2$ ), and the antisymmetric stretch ( $\omega_3$ ).  $r_e$  and  $\theta_e$  are the respective equilibrium bond length for the H–O bond and the equilibrium H–O–H angle for the molecule. Computed vibrational frequencies are compared to experimentally inferred frequencies via an average absolute difference between the two sets of values denoted  $\langle \text{error} \rangle$ . Because experimentally inferred frequencies involve fitting data to an assumed Hamiltonian model, some caution is warranted when interpreting  $\langle \text{error} \rangle$ . For example, McCoy and Sibert<sup>39</sup> have demonstrated that harmonic frequencies of water change by approximately  $2 \text{ cm}^{-1}$  when using an eighth-order effective Hamiltonian rather than a second-order effective Hamiltonian. The convergence of computed vibrational frequencies is determined by the convergence of the average absolute difference between adjacent sets of vibrational frequencies denoted  $\langle |\Delta| \rangle$ . Decreasing values of  $\langle |\Delta| \rangle$



**Figure 1.** Average absolute difference ( $\langle |\Delta| \rangle$ ) between computed vibrational frequencies with increasing basis set size. Computations were performed at the varying levels of theory.

for subsequent computations illustrate the convergence of the vibrational frequencies and consequently the convergence of the error associated with the approximation being varied.

When computing energies with the HF method, each electron is assumed to see an averaged distribution of the other electrons. As seen in Table 1, the exclusion of instantaneous electron correlation results in vibrational frequencies approximately  $228 \text{ cm}^{-1}$  in error of experimental frequencies (cc-pVQZ  $\langle \text{error} \rangle = 228.75 \text{ cm}^{-1}$ , cc-pV5Z  $\langle \text{error} \rangle = 228.63 \text{ cm}^{-1}$ , cc-pV6Z  $\langle \text{error} \rangle = 228.44 \text{ cm}^{-1}$ ). As also seen in Figure 1 and Table 1, the average absolute difference,  $\langle |\Delta| \rangle$ , between vibrational frequencies computed with the cc-pVQZ and cc-pV5Z and between frequencies computed with the cc-pV5Z and cc-pV6Z basis sets is within  $1.4 \text{ cm}^{-1}$  and  $0.2 \text{ cm}^{-1}$ , respectively. Consequently, the computed values and the error associated with the HF wavefunction are converged to within  $1.6 \text{ cm}^{-1}$  of the limiting value with the use of the cc-pVQZ basis set ( $\langle |\Delta| \rangle_{\text{QZ-5Z}} + \langle |\Delta| \rangle_{\text{5Z-6Z}} = 1.40 \text{ cm}^{-1} + 0.19 \text{ cm}^{-1} < 1.6 \text{ cm}^{-1}$ ). Therefore, use of basis sets of at least quadruple- $\zeta$  quality should be suitable for high accuracy harmonic frequency computations.

**B. Electron Correlation Level.** The effect of approximating the electron correlation for water was determined through the comparison of vibrational frequencies computed with theories from the coupled-cluster series, which include a systematic increase of electron correlation. The cc-pVTZ basis set was used since the average absolute difference between the vibrational frequencies computed with the HF/cc-pVTZ and HF/cc-pV6Z methods is less than  $5 \text{ cm}^{-1}$ , and the former is 1000 times faster than the latter. To include

**Table 2.** Convergence of Electron Correlation Treatment for Computed Equilibrium Geometry and Harmonic Vibrational Frequencies Computed Using the cc-pVTZ Basis Set<sup>a</sup>

method	basis	$r_e$	$\theta_e$	$\omega_1$	$\omega_2$	$\omega_3$	$\langle \text{error} \rangle$	$\langle \Delta \rangle$	energy
HF	cc-pVTZ	0.940602	106.0016	4127.04	1753.02	4226.94	227.93		-76.05777
CCSD	cc-pVTZ	0.957118	103.8928	3875.94	1678.47	3979.07	36.76	191.17	-76.32456
CCSD(T)	cc-pVTZ	0.959426	103.5821	3840.93	1668.88	3945.54	10.72	26.04	-76.33222
CCSDT	cc-pVTZ	0.959390	103.5906	3841.36	1669.20	3945.31	10.89	0.33	-76.33229
CCSDT(Q)	cc-pVTZ	0.959722	103.5533	3835.06	1668.03	3940.06	8.28	4.24	-76.33265
CCSDTQ	cc-pVTZ	0.959677	103.5581	3835.94	1668.22	3940.73	8.41	0.58	-76.33261
experiment <sup>38</sup>		0.9572	104.52	3832.2	1648.5	3942.5			

<sup>a</sup>  $\langle|\text{error}|\rangle$ ,  $\langle|\Delta|\rangle$ , and units are as described in Table 1. In contrast to Tables 1 and 4–6, all calculations were performed with the ACES II and Kállay programs.

**Table 3.** Average Absolute Differences  $\langle|\Delta|\rangle$  of Harmonic Vibrational Frequencies Using Various Methods and the cc-pVTZ Basis Set<sup>a</sup>

$ \Delta $	HF	CCSD	CCSD(T)	CCSDT	CCSDT(Q)	CCSDTQ
HF	—					
CCSD	191.17	—				
CCSD(T)	217.22	26.04	—			
CCSDT	217.04	25.87	0.33	—		
CCSDT(Q)	221.28	30.11	4.07	4.24	—	
CCSDTQ	220.70	29.53	3.49	3.66	0.58	—

<sup>a</sup> Units are  $\text{cm}^{-1}$ .

the CCSDT, CCSDT(Q), and CCSDTQ computations and to prevent the introduction of extraneous sources of error, all computations for this specific analysis were performed with the ACES II and Kállay programs.<sup>23,24</sup> Table 2 compares the computed equilibrium geometries and harmonic frequencies to experimentally inferred values.<sup>38</sup>

Table 3 describes the convergence of computed harmonic frequencies with the cc-pVTZ basis as a function of coupled-cluster method. The increase in theory from CCSD to CCSDT results in a  $26 \text{ cm}^{-1}$  average absolute difference in vibrational frequencies ( $\langle|\Delta|\rangle_{\text{CCSD}-\text{CCSDT}} = 25.87 \text{ cm}^{-1}$ ) for water, while the increase from CCSDT to CCSDTQ results in only a  $3.66 \text{ cm}^{-1}$  difference. Ruden et al.<sup>40</sup> studied four diatomic molecules (HF,  $\text{N}_2$ ,  $\text{F}_2$ , CO) and found that the average absolute difference in vibrational frequency computed with the cc-pVTZ basis set from CCSD to CCSDT was  $65.7 \text{ cm}^{-1}$  and from CCSDT to CCSDTQ was  $10.9 \text{ cm}^{-1}$ . Similar convergence trends were observed with the cc-pVDZ basis set, and the average convergence for these diatomics from CCSDTQ to CCSDTQP was computed to be only  $1.2 \text{ cm}^{-1}$ . Comparison of these results indicates that the harmonic frequencies of water converge more rapidly with method than these diatomic molecules, suggesting that little improvement in harmonic frequencies would be gained from a CCSDTQP calculation of water. It should be noted that inferences regarding convergence of vibrational frequencies that are based on cc-pVTZ calculations need to be tempered slightly for larger basis sets, as increasing the size of the basis set generally magnifies correlation effects.

Increasing theory from CCSD(T) to CCSDT to fully treat triple excitations results in only a  $0.33 \text{ cm}^{-1}$  difference in harmonic frequencies ( $\langle|\Delta|\rangle_{\text{CCSD(T)}-\text{CCSDT}} = 0.33 \text{ cm}^{-1}$ ) for the triatomic water molecule. This is consistent with the conclusions of Feller and Sordo,<sup>41</sup> who found no significant difference between the two theories when studying 13

diatomic hybrids, and with the previously mentioned study of Ruden et al. Similarly, the difference between CCSDT(Q) and CCSDTQ is only  $0.58 \text{ cm}^{-1}$ , again demonstrating that perturbative treatment of the next higher connected-excitation level is a very effective way to reduce computation time with minimal loss of accuracy.

The remaining average absolute error in harmonic frequencies due to electron correlation associated with the CCSD(T) level is estimated at  $4.7 \text{ cm}^{-1}$ , which arises from the computed difference between CCSD(T) and CCSDTQ,  $\langle|\Delta|\rangle_{\text{CCSD(T)}-\text{CCSDTQ}} = 3.49 \text{ cm}^{-1}$ , and an estimate from the diatomic data of  $1.2 \text{ cm}^{-1}$  for the remaining error.

**C. Valence Electron Description.** The convergence of the correlation consistent wavefunction was determined via the comparison of vibrational frequencies computed at the CCSD(T) level of theory with basis sets from the cc-pVXZ and aug-cc-pVXZ families. While the diffuse functions were developed specifically to provide increased basis set flexibility for charged species, they are often employed for neutral systems in order to yield more accurate results. Table 4 compares the computed vibrational frequencies to the experimentally inferred harmonic frequencies,  $\langle|\text{error}|\rangle$ , of Pliva et al.<sup>38</sup>

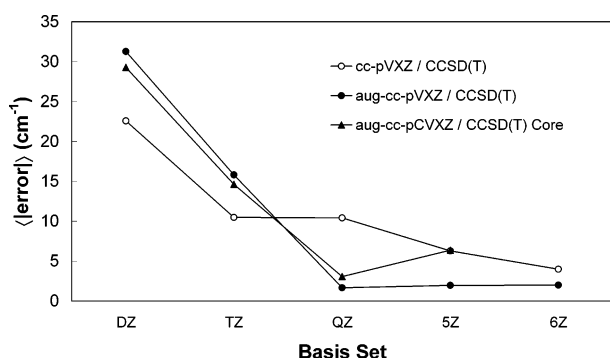
As seen in Figure 2, the cc-pVXZ computations are initially more accurate than their augmented counterparts (cc-pVDZ  $\langle|\text{error}|\rangle = 22.59 \text{ cm}^{-1}$ , aug-cc-pVDZ  $\langle|\text{error}|\rangle = 31.29 \text{ cm}^{-1}$ , cc-pVTZ  $\langle|\text{error}|\rangle = 10.48 \text{ cm}^{-1}$ , aug-cc-pVTZ  $\langle|\text{error}|\rangle = 15.81 \text{ cm}^{-1}$ ). With the use of the two largest ( $X = 5, 6$ ) augmented basis sets though, the computed vibrational frequencies are more accurate than the largest cc-pVXZ basis set (cc-pV6Z  $\langle|\text{error}|\rangle = 3.98 \text{ cm}^{-1}$ , aug-cc-pV5Z and aug-cc-pV6Z  $\langle|\text{error}|\rangle < 2 \text{ cm}^{-1}$ ), supporting the findings of Martin and Taylor<sup>42</sup> who reported that augmented basis sets yield more accurate harmonic frequencies than nonaugmented basis sets for HF and  $\text{H}_2\text{O}$ . In addition, the augmented set, although initially converging slower, converges closer to the basis set limit than the nonaugmented set (cc-pVXZ family  $\langle|\Delta|\rangle_{\text{QZ}-5\text{Z}} = 4.14 \text{ cm}^{-1}$  and  $\langle|\Delta|\rangle_{5\text{Z}-6\text{Z}} = 2.31 \text{ cm}^{-1}$ , aug-cc-pVXZ family  $\langle|\Delta|\rangle_{\text{QZ}-5\text{Z}} = 2.64$  and  $\langle|\Delta|\rangle_{5\text{Z}-6\text{Z}} = 0.56 \text{ cm}^{-1}$ ), as seen in Figure 1. From their study of diatomics, Ruden et al.<sup>40</sup> estimated the remaining basis set error beyond the aug-cc-pV6Z basis set to be conservatively within  $0.5 \text{ cm}^{-1}$ . Thus, with the use of the aug-cc-pVQZ basis set, the error associated with the valence electrons has converged within  $3.7 \text{ cm}^{-1}$  ( $\langle|\Delta|\rangle_{\text{QZ}-5\text{Z}} + \langle|\Delta|\rangle_{5\text{Z}-6\text{Z}} + \langle|\Delta|\rangle_{6\text{Z}-\infty} = 2.64 \text{ cm}^{-1} + 0.55 \text{ cm}^{-1} + 0.5 \text{ cm}^{-1} = 3.7 \text{ cm}^{-1}$ ).



**Table 4.** Convergence of Valence Electron Description for Computed Equilibrium Geometry and Harmonic Vibrational Frequencies Computed Using the CCSD(T) Theory<sup>a</sup>

method	basis	$r_e$	$\theta_e$	$\omega_1$	$\omega_2$	$\omega_3$	$\langle \text{error} \rangle$	$\langle \Delta \rangle$	energy
CCSD(T)	cc-pVDZ	0.966280	101.9127	3821.33	1690.19	3927.29	22.59		-76.24131
CCSD(T)	cc-pVTZ	0.959428	103.5821	3840.65	1668.76	3945.24	10.48	19.57	-76.33222
CCSD(T)	cc-pVQZ	0.957891	104.1159	3844.19	1659.17	3951.11	10.42	6.33	-76.35980
CCSD(T)	cc-pV5Z	0.958041	104.3723	3839.78	1653.24	3949.03	6.28	4.14	-76.36904
CCSD(T)	cc-pV6Z	0.958181	104.4221	3837.00	1651.20	3946.93	3.98	2.31	-76.37202
CCSD(T)	aug-cc-pVDZ	0.966514	103.9366	3786.66	1638.08	3904.59	31.29		-76.27390
CCSD(T)	aug-cc-pVTZ	0.961581	104.1796	3810.41	1645.62	3919.75	15.81	15.48	-76.34233
CCSD(T)	aug-cc-pVQZ	0.958931	104.3646	3830.81	1649.97	3940.39	1.66	15.13	-76.36359
CCSD(T)	aug-cc-pV5Z	0.958416	104.4273	3834.37	1649.97	3944.74	1.96	2.64	-76.37030
CCSD(T)	aug-cc-pV6Z	0.958344	104.4472	3834.70	1649.22	3945.32	2.01	0.56	-76.37256
experiment <sup>38</sup>		0.9572	104.52	3832.2	1648.5	3942.5			

<sup>a</sup>  $\langle|\text{error}|\rangle$ ,  $\langle|\Delta|\rangle$ , and units are as described in Table 1.



**Figure 2.** Average absolute difference ( $\langle|\text{error}|\rangle$ ) between experimentally inferred harmonic frequencies and vibrational frequencies computed using CCSD(T) and increasing basis sets. All electrons were correlated in post-SCF calculations in the CCSD(T) core computation. Correlation of the core electrons was neglected in the other computations.

Comparing computed frequencies for each vibrational mode in Table 4 indicates that the three vibrational modes converge at different rates. As observed by Martin and Taylor,<sup>42</sup> for both the augmented and the nonaugmented basis set families, the vibrational mode corresponding to the symmetric stretch converges faster than the bend or anti-symmetric stretch.

**D. Core Electron Correlation.** The effect of neglecting core electron correlation effects was determined by first characterizing the effect of using basis sets from the aug-cc-pCVXZ family and then characterizing the effect of neglecting core-core and core-valence correlation. The first comparison was made via the average absolute differences,  $\langle|\text{diff}|\rangle$ , between frequencies computed with the aug-cc-pVXZ and aug-cc-pCVXZ families. The contribution due to correlating the core electrons was determined by calculating the average absolute difference,  $\langle|\text{diff}|\rangle$ , between frequencies computed without correlating core electrons (i.e., “frozen core”) [aug-cc-pVXZ/CCSD(T)] and frequencies computed with correlated core electrons (i.e., “all electron”) [aug-cc-pCVXZ/CCSD(T);core]. The convergence of the all electron frequencies,  $\langle|\Delta|\rangle$ , and their error from experimentally inferred frequencies,  $\langle|\text{error}|\rangle$ , was also determined. All values listed above are included in Table 5.

The difference between the frozen core electron computations using basis sets from the aug-cc-pVXZ and aug-cc-

pCVXZ families was less than 1 cm<sup>-1</sup> for most of the computations ( $X = D$   $\langle|\text{diff}|\rangle = 0.36$  cm<sup>-1</sup>,  $X = Q$   $\langle|\text{diff}|\rangle = 0.56$  cm<sup>-1</sup>,  $X = 5$   $\langle|\text{diff}|\rangle = 0.13$  cm<sup>-1</sup>). The change in basis from the aug-cc-pVXZ to the aug-cc-pCVXZ family include the addition of functions that do not describe valence correlation, and hence there is little effect on the computed vibrational frequencies.

The difference between the frozen core and the all electron computations converges to 5.0 cm<sup>-1</sup> with the use the aug-cc-pCVQZ basis set (aug-cc-pCVQZ;core  $\langle|\text{diff}|\rangle = 4.72$  cm<sup>-1</sup>, aug-cc-pCV5Z;core  $\langle|\text{diff}|\rangle = 4.99$  cm<sup>-1</sup>). This independence of basis set when using basis sets of at least quadruple- $\zeta$  quality is consistent with the previous studies<sup>21,40–44</sup> of the contribution from the correlation of core electrons on harmonic frequencies. Since the frequencies from the frozen core and all electron computations converge at virtually the same rate [aug-cc-pCVXZ/CCSD(T)  $\langle|\Delta|\rangle_{\text{TZ-QZ}} = 17.13$  cm<sup>-1</sup>, aug-cc-pCVXZ/CCSD(T);core  $\langle|\Delta|\rangle_{\text{TZ-QZ}} = 17.65$  cm<sup>-1</sup>, aug-cc-pCVXZ/CCSD(T)  $\langle|\Delta|\rangle_{\text{QZ-5Z}} = 3.17$  cm<sup>-1</sup>, aug-cc-pCVXZ/CCSD(T);core  $\langle|\Delta|\rangle_{\text{QZ-5Z}} = 3.34$  cm<sup>-1</sup>], the error associated with neglecting core electron correlation is predicted to be 5.0 cm<sup>-1</sup>.

As seen in Figure 2, when using large basis sets, the error from experiment,  $\langle|\text{error}|\rangle$ , of the vibrational frequencies computed with all electrons correlated is greater than the error of the frequencies computed with frozen core electrons (aug-cc-pCVQZ;core 3.06 cm<sup>-1</sup>, aug-cc-pVQZ 1.66 cm<sup>-1</sup>, aug-cc-pCV5Z;core 6.37 cm<sup>-1</sup>, aug-cc-pV5Z 1.96 cm<sup>-1</sup>). The greater accuracy of the computations with frozen core electrons is presumably due to a cancellation of errors between core electron correlation and inadequacies in correlation treatment.<sup>42</sup> As the error associated with neglecting core electron correlation effects is increasingly accounted for, the other errors associated with the computation become observable. Ruden et al.<sup>40</sup> observed that core correlation computations at the CCSD(T) theory overestimate harmonic frequencies in diatomic molecules. In our study, the correlated core computations significantly overestimate the frequencies of the symmetric and antisymmetric stretches. Previous studies<sup>42,43</sup> suggest this error in the frequency computations of H<sub>2</sub>O and diatomics is due to n-particle space imperfections and contraction errors. The combination of a 30% increase in computational time and a decrease in accuracy when core electrons are correlated results in the

**Table 5.** Magnitude of the Core Electron Correlation Effects at CCSD(T) on Computed Equilibrium Geometry and Harmonic Vibrational Frequencies<sup>a</sup>

method	basis	$r_e$	$\theta_e$	$\omega_1$	$\omega_2$	$\omega_3$	$\langle \text{error} \rangle$	$\langle \text{diff} \rangle$	$\langle \Delta \rangle$	energy
CCSD(T)	aug-cc-pVDZ	0.966514	103.9366	3786.66	1638.08	3904.59	31.29			-76.27390
CCSD(T)	aug-cc-pVTZ	0.961581	104.1796	3810.41	1645.62	3919.75	15.81		15.48	-76.34233
CCSD(T)	aug-cc-pVQZ	0.958931	104.3646	3830.81	1649.97	3940.39	1.66		15.13	-76.36359
CCSD(T)	aug-cc-pV5Z	0.958416	104.4273	3834.37	1649.97	3944.74	1.96		2.64	-76.37030
CCSD(T)	aug-cc-pCVDZ	0.966347	103.9175	3786.43	1638.65	3904.32	31.27	0.36		-76.27686
CCSD(T)	aug-cc-pCVTZ	0.961330	104.1912	3807.57	1645.91	3914.62	18.37	2.75	12.90	-76.34551
CCSD(T)	aug-cc-pCVQZ	0.958969	104.3669	3830.30	1649.07	3940.13	1.61	0.56	17.13	-76.36498
CCSD(T)	aug-cc-pCV5Z	0.958403	104.4296	3834.45	1649.74	3944.82	1.94	0.13	3.17	-76.37092
CCSD(T);core	aug-cc-pCVDZ	0.965881	103.9527	3789.06	1639.13	3907.21	29.27	2.02		-76.31517
CCSD(T);core	aug-cc-pCVTZ	0.960572	104.2891	3813.29	1645.40	3920.66	14.62	1.34	14.65	-76.39966
CCSD(T);core	aug-cc-pCVQZ	0.958098	104.4805	3836.80	1648.46	3947.05	3.06	4.72	17.65	-76.42464
CCSD(T);core	aug-cc-pCV5Z	0.957501	104.5485	3841.21	1649.11	3952.00	6.37	4.99	3.34	-76.43227
experiment <sup>38</sup>		0.9572	104.52	3832.2	1648.5	3942.5				

<sup>a</sup>  $\langle|\text{error}|\rangle$ ,  $\langle|\Delta|\rangle$ , and units are as described in Table 1.  $\langle|\text{diff}|\rangle$ , in  $\text{cm}^{-1}$ , represents the average absolute difference between the vibrational frequencies for each computation and the corresponding aug-cc-pVXZ computation.

**Table 6.** Magnitude of the Relativistic Correction at CCSD(T) for the Equilibrium Geometry and Harmonic Vibrational Frequencies Computed Using the Cowan–Griffin and Douglas–Kroll Relativistic Correction Methods<sup>a</sup>

method	rel	basis	$r_e$	$\theta_e$	$\omega_1$	$\omega_2$	$\omega_3$	$\langle \text{error} \rangle$	$\langle \Delta \rangle$	$\langle \text{diff} \rangle$	energy
CCSD(T)		cc-pVDZ	0.966280	101.9127	3821.33	1690.19	3927.29	22.59			-76.24131
CCSD(T)		cc-pVTZ	0.959428	103.5821	3840.65	1668.76	3945.24	10.48	19.57		-76.33222
CCSD(T)		cc-pVQZ	0.957891	104.1159	3844.19	1659.17	3951.11	10.42	6.33		-76.35980
CCSD(T)		cc-pV5Z	0.958041	104.3723	3839.78	1653.24	3949.03	6.28	4.14		-76.36904
CCSD(T)		cc-pV6Z	0.958181	104.4221	3837.00	1651.20	3946.93	3.98	2.31		-76.37202
CCSD(T)	CG	cc-pVDZ	0.966222	101.8617	3818.34	1690.70	3924.24	24.77		2.18	-76.29280
CCSD(T)	CG	cc-pVTZ	0.959407	103.5122	3837.80	1670.27	3941.91	9.32	19.19	2.56	-76.38380
CCSD(T)	CG	cc-pVQZ	0.957942	104.0503	3841.62	1660.41	3948.46	9.10	6.74	2.15	-76.41153
CCSD(T)	CG	cc-pV5Z	0.958067	104.3095	3837.61	1654.49	3946.73	5.21	3.89	1.91	-76.42078
CCSD(T)	CG	cc-pV6Z	0.958200	104.3602	3834.69	1652.38	3944.49	2.79	2.42	1.98	-76.42382
CCSD(T)	DK	cc-pVDZ	0.966269	101.8564	3817.82	1690.69	3923.78	25.10		2.51	-76.28939
CCSD(T)	DK	cc-pVTZ	0.959341	103.5163	3838.50	1670.26	3942.55	9.37	19.96	2.11	-76.38064
CCSD(T)	DK	cc-pVQZ	0.957938	104.0529	3841.60	1660.35	3948.47	9.07	6.31	2.14	-76.40820
CCSD(T)	DK	cc-pV5Z	0.958071	104.3119	3837.65	1654.22	3946.84	5.17	3.90	1.77	-76.41745
CCSD(T)	DK	cc-pV6Z	0.958195	104.3637	3834.39	1652.37	3944.08	2.55	2.62	2.21	-76.42055
experiment <sup>38</sup>			0.9572	104.52	3832.2	1648.5	3942.5				

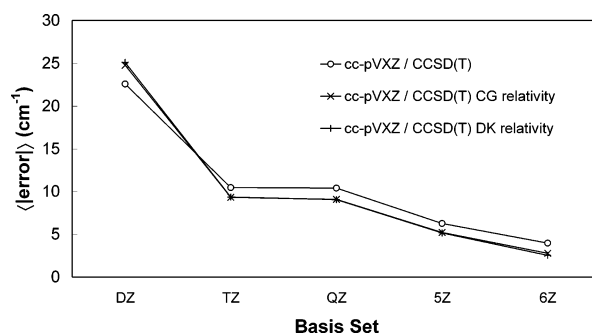
<sup>a</sup>  $\langle|\text{error}|\rangle$ ,  $\langle|\Delta|\rangle$ ,  $\langle|\text{diff}|\rangle$ , and units are as described in Table 5.

conclusion that core electron correlation should be included for only the most rigorous computations.

**E. Relativistic Effects.** The error associated with neglecting relativistic effects was determined by comparing the vibrational frequencies from noncorrected computations to frequencies corrected using either the Cowan–Griffin (CG) method or the Douglas–Kroll (DK) method. The CG approach uses first-order perturbation theory to calculate expectation values for one-electron Darwin and mass-velocity integrals. The DK method performs a free-particle transformation on the Dirac Hamiltonian to produce a no-pair DK operator.

The convergence of the relativistically corrected vibrational frequencies,  $\langle|\Delta|\rangle$ , and the error from the experimentally inferred values of Pliva et al.,<sup>38</sup>  $\langle|\text{error}|\rangle$ , are found in Table 6. The relativistically corrected vibrational frequencies are also compared to the noncorrected frequencies by means of the average absolute difference between the two sets of values,  $\langle|\text{diff}|\rangle$ .

As seen in Figure 3, the difference between the corrected and experimental frequencies is less than the difference



**Figure 3.** Average absolute difference ( $\langle|\text{error}|\rangle$ ) between experimentally inferred harmonic frequencies and relativistically corrected vibrational frequencies computed using CCSD(T) with increasing basis sets. CG computations were performed using the Cowan–Griffin method. DK computations were performed using the Douglas–Kroll method.

between the noncorrected experimental frequencies ( $\langle|\text{error}|\rangle = 6.28 \text{ cm}^{-1}$  and  $3.98 \text{ cm}^{-1}$  for cc-pV5Z and cc-pV6Z, respectively;  $\langle|\text{error}|\rangle = 5.21 \text{ cm}^{-1}$  and  $2.79 \text{ cm}^{-1}$  for cc-pV5Z/CG and cc-pV6Z/CG, respectively;  $\langle|\text{error}|\rangle = 5.17$

**Table 7.** Comparison of Contributing Factors of Uncertainty<sup>a</sup>

factor	cc-pVTZ/ CCSD(T)	aug-cc-pVQZ/ CCSD(T)
HF wavefunction	4.3	1.6
electron correlation method	4.7	4.7
valence electron description	12.8	3.7
core electron correlation	5.0	5.0
relativistic effects	2.2	2.2
RSS	15.3	8.3
$\langle \text{error} \rangle$	10.5	1.7

<sup>a</sup> RSS represents the square root of the sum of the squares of the contributing factors, which estimates the expected error in computed vibrational frequency.  $\langle \text{error} \rangle$  represents the average absolute difference between the experimentally inferred<sup>38</sup> and computed harmonic vibrational frequencies, which estimates the actual error. All units are  $\text{cm}^{-1}$ .

$\text{cm}^{-1}$  and  $2.55 \text{ cm}^{-1}$  for cc-pV5Z/DK and cc-pV6Z/DK, respectively). Also, the convergence of the computed frequencies with respect to changes in the basis set is approximately the same for all three sets of computations [for CCSD(T):  $\langle |\Delta| \rangle_{\text{QZ-5Z}} = 4.14 \text{ cm}^{-1}$ ,  $\langle |\Delta| \rangle_{\text{5Z-6Z}} = 2.31 \text{ cm}^{-1}$ ; for CCSD(T)/CG:  $\langle |\Delta| \rangle_{\text{QZ-5Z}} = 3.98 \text{ cm}^{-1}$ ,  $\langle |\Delta| \rangle_{\text{5Z-6Z}} = 2.42 \text{ cm}^{-1}$ ; for CCSD(T)/CG:  $\langle |\Delta| \rangle_{\text{QZ-5Z}} = 3.90 \text{ cm}^{-1}$ ,  $\langle |\Delta| \rangle_{\text{5Z-6Z}} = 2.62 \text{ cm}^{-1}$ ], as seen in Figure 1. The similarity in convergence of  $\langle |\Delta| \rangle$  and  $\langle \text{error} \rangle$ , respectively, between the relativistically corrected and noncorrected computations can be seen in Figures 1 and 3 where the GC and DK data parallel the noncorrected data. As a result, the difference,  $\langle \text{diff} \rangle$ , between the corrected and the noncorrected vibrational frequencies is consistently in the range of  $1.77 \text{ cm}^{-1}$  to  $2.56 \text{ cm}^{-1}$ , and it is concluded that, on average, there is a  $2.2 \text{ cm}^{-1}$  error associated with neglecting relativistic effects.

**F. Comparison of Different Computations.** The magnitudes of the effect each factor has on the accuracy of two computations are compared in Table 7. The computations were done at the CCSD(T) level of theory with the cc-pVTZ and aug-cc-pVQZ basis sets. In both computations, core electrons were frozen, and relativistic effects were neglected. As previously discussed, the errors associated with using the CCSD(T) theory, neglecting core electron correlation, and neglecting relativistic effects are  $4.7 \text{ cm}^{-1}$ ,  $5.0 \text{ cm}^{-1}$ , and  $2.2 \text{ cm}^{-1}$ , respectively. The error due to the convergence of the Hartree–Fock wavefunction for each computation was determined by the sum of the  $\langle |\Delta| \rangle$  values found in Table 1 of each subsequent computation (for cc-pVTZ:  $\langle |\Delta| \rangle_{\text{TZ-QZ}} + \langle |\Delta| \rangle_{\text{QZ-5Z}} + \langle |\Delta| \rangle_{\text{5Z-6Z}} = 2.68 \text{ cm}^{-1} + 1.40 \text{ cm}^{-1} + 0.19 \text{ cm}^{-1} < 4.3 \text{ cm}^{-1}$ ). Similarly, the error due to the convergence of valence electron description was determined by the sum of  $\langle |\Delta| \rangle$  values (Table 4) of each subsequent computation (for cc-pVTZ:  $\langle |\Delta| \rangle_{\text{TZ-QZ}} + \langle |\Delta| \rangle_{\text{QZ-5Z}} + \langle |\Delta| \rangle_{\text{5Z-6Z}} = 6.33 \text{ cm}^{-1} + 4.14 \text{ cm}^{-1} + 2.31 \text{ cm}^{-1} < 12.8 \text{ cm}^{-1}$ ). The total expected error from experiment of the vibrational frequencies for each computation is represented by the square root of the sum of the squares (RSS) of the errors associated with the contributing factors.

While the cc-pVTZ computation is available for a wide variety of atoms and yields results 175 times faster than the aug-cc-pVQZ computation (minutes vs hours), the expected error associated with the cc-pVTZ calculation is nearly

double (cc-pVTZ RSS =  $15.3 \text{ cm}^{-1}$ , aug-cc-pVQZ RSS =  $8.3 \text{ cm}^{-1}$ ). As seen in Table 7, the actual error from experimental frequencies is 6 times as great for the cc-pVTZ computation (cc-pVTZ  $\langle \text{error} \rangle = 10.5 \text{ cm}^{-1}$ , aug-cc-pVQZ  $\langle \text{error} \rangle = 1.7 \text{ cm}^{-1}$ ). The larger magnitude of the root sum of squares (RSS) of the expected errors in both calculations implies the presence of a cancellation of errors. While cancellation of error is expressed in both computations, the proportionally greater cancellation of error of the aug-cc-pVQZ computation in conjunction with a smaller expected error results in substantially more accurate harmonic frequencies.

## Conclusions

It is important to understand and determine the accuracy to which harmonic force constants can be computed. This work presents a comprehensive study of the major contributing factors affecting the accuracy of such computations through the determination of the underlying sources of error and the evaluation and quantification of the error at varying levels of approximation.

When using basis sets larger than cc-pVQZ, the error associated with the Hartree–Fock wavefunction has converged to  $1.6 \text{ cm}^{-1}$ . Consequently, the associated error can be neglected in corresponding computations. Due to the small difference in values between the CCSD(T) and CCSDT methods ( $\langle |\Delta| \rangle = 0.3 \text{ cm}^{-1}$ ), the CCSD(T) level of theory was chosen for computational efficiency and because of the widespread support of the CCSD(T) method in modern quantum chemistry programs. However, this use of the CCSD(T) theory over the CCSDT(Q), CCSDTQ, or CCSDTQP theories to approximate electron correlation results in a  $5 \text{ cm}^{-1}$  error. It was also found that just as CCSD(T) yields comparable results to CCSDT but at a lower computation cost, CCSDT(Q) is more computationally affordable than CCSDTQ but gives comparable results. Therefore, the possibility of efficiently increasing the accuracy of computations through increased correlation is possible via perturbatively applied quadruples.

The quality of a basis set is one of the most important factors affecting the error associated with computations of vibrational frequencies. Smaller basis sets decrease computational time and demand of computer hardware at the expense of a significant increase in error due to valence electron description. With the use of either the cc-pV5Z or the aug-cc-pVQZ basis set, the error associated with valence electron description has converged within  $3.7 \text{ cm}^{-1}$ , although the augmented basis set yields more accurate results.

The error associated with neglecting core electron correlation effects is determined to be  $5 \text{ cm}^{-1}$  when using basis sets of at least quadruple- $\zeta$  quality. While correlating the core electrons decreases the expected uncertainty in the computation, computational time increases, and the accuracy of the computed frequencies decreases due to the decrease in fortuitous cancellation of errors. Consequently, core electron correlation should be included in only the most rigorous computations. Similarly, while neglecting relativistic effects introduces a  $2 \text{ cm}^{-1}$  error, the decrease in expected error does not outweigh the increase in computational time.

While computations of CCSD(T)/cc-pVTZ quality can be done significantly faster than those of performed at CCSD(T)/aug-cc-pVQZ quality, the substantially smaller expected uncertainty results in vibrational frequencies with a  $2\text{ cm}^{-1}$  accuracy for CCSD(T)/aug-cc-pVQZ computations.

**Acknowledgment.** The authors thank Michael L. Poulblon for constructing and maintaining the computer cluster used for these computations. M.H.C., N.R.B., W.F.P., and the computer cluster were supported by a Cottrell College Science Award of Research Corporation and by the Scholar/Fellow Program of the Camille and Henry Dreyfus Foundation. P.R.T. was supported by the Wolfson Foundation through the Royal Society. Y.J.B. and J.F.S. were supported by the National Science Foundation and the Robert A. Welch Foundation.

### References

- (1) Naus, H.; Ubachs, W.; Levelt, P. F.; Polyansky, O. L.; Zobov, N. F.; Tennyson, J. *J. Mol. Spectrosc.* **2001**, *205*, 117.
- (2) Carleer, M.; Jenouvrier, A.; Vandaele, A. C.; Bernath, P. F.; Mérienne, M. F.; Colin, R.; Zobov, N. F.; Polyansky, O. L.; Tennyson, J.; Savin, V. A. *J. Chem. Phys.* **1999**, *111*, 2444.
- (3) Wayne, R. P. *Chemistry of Atmospheres*, 3rd ed.; Oxford University Press: Oxford, 2000; pp 50–58.
- (4) Callegari, A.; Theulé, P.; Muentner, J. S.; Tolchenov, R. N.; Zobov, N. F.; Polyansky, O. L.; Tennyson, J.; Rizzo, T. R. *Science* **2002**, *297*, 993.
- (5) Ramanathan, V.; Vogelmann, A. M. *Ambio* **1997**, *26*, 38.
- (6) Wallace, L.; Bernath, P.; Livingston, W.; Hinkle, K.; Busler, J.; Guo, B.; Zhang, K. *Science* **1995**, *268*, 1155.
- (7) Polyansky, O. L.; Zobov, N. F.; Viti, S.; Tennyson, J.; Bernath, P. F.; Wallace, L. *Science* **1997**, *277*, 346.
- (8) Griffith, C. A.; Yelle, R. V.; Marley, M. S. *Science* **1998**, *282*, 2063.
- (9) Oppenheimer, B. R.; Kulkarni, S. R.; Matthews, K.; Nakajima, T. *Science* **1995**, *270*, 1478.
- (10) Polyansky, O. L.; Császár, A. G.; Shirin, S. V.; Zobov, N. F.; Barletta, P.; Tennyson, J.; Schwenke, D. W.; Knowles, P. J. *Science* **2003**, *299*, 539.
- (11) Kalmar, B.; O'Brien, J. J. *J. Mol. Spectrosc.* **1998**, *192*, 386.
- (12) Xie, J.; Paldus, B. A.; Wahl, E. H.; Martin, J.; Owano, T. G.; Kruger, C. H.; Harris, J. S.; Zare, R. N. *Chem. Phys. Lett.* **1998**, *284*, 387.
- (13) Jensen, P. *J. Mol. Spectrosc.* **1989**, *133*, 438.
- (14) Polyansky, O. L.; Jensen, P.; Tennyson, J. *J. Chem. Phys.* **1996**, *105*, 6490.
- (15) Beardsworth, R.; Bunker, P. R.; Jensen, P.; Kraemer, W. P. *J. Mol. Spectrosc.* **1986**, *118*, 50.
- (16) Császár, A. G.; Mills, I. M. *Spectrochimica* **1997**, *53*, 1101.
- (17) Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A.; Mas, E. M.; Bukowski, R.; Szalewicz, K. *J. Chem. Phys.* **2000**, *113*, 6702.
- (18) Mas, E. M.; Bukowski, R.; Szalewicz, K.; Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **2000**, *113*, 6687.
- (19) Carney, G. D.; Curtiss, L. A.; Langhoff, S. R. *J. Mol. Spectrosc.* **1976**, *61*, 371.
- (20) Császár, A. G.; Allen, W. D. *J. Chem. Phys.* **1996**, *104*, 2746.
- (21) Partridge, H.; Schwenke, D. W. *J. Chem. Phys.* **1997**, *106*, 4618.
- (22) Werner, H.-J.; Knowles, P. J. *MOLPRO 2002.6*; University of Birmingham: Birmingham, U.K., 2002.
- (23) Stanton, J. F.; Gauss, J. *ACES II*; University of Texas: Austin, TX, 2005.
- (24) Kállay, M.; Surján, P. R. *J. Chem. Phys.* **2001**, *115*, 2945.
- (25) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
- (26) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
- (27) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513; erratum: **1990**, *167*, 609.
- (28) Noga, J.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041; erratum: **1988**, *89*, 3041.
- (29) Scuseria, G. E.; Schaefer, H. F. *Chem. Phys. Lett.* **1988**, *152*, 382.
- (30) Bomble, Y. J.; Stanton, J. F.; Kállay, M.; Gauss, J. *J. Chem. Phys.* **2005**, *123*, 54101.
- (31) Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 4282.
- (32) Oliphant, N.; Adamowicz, L. *J. Chem. Phys.* **1991**, *95*, 6645.
- (33) Cowan, R. D.; Griffin, D. C. *J. Opt. Soc. Am.* **1976**, *66*, 1010.
- (34) Douglas, M.; Kroll, N. M. *Ann. Phys. (N.Y.)* **1974**, *82*, 89.
- (35) Dunnings, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (36) Kendall, R. A.; Dunnings, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (37) Woon, D. E.; Dunnings, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.
- (38) Pliva, J.; Spirko, V.; Papousek, D. *J. Mol. Spectrosc.* **1967**, *23*, 331.
- (39) McCoy, A. B.; Sibert, E. L., III. *J. Chem. Phys.* **1990**, *92*, 1893.
- (40) Ruden, T. A.; Helgaker, T.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **2004**, *121*, 5874.
- (41) Feller, D.; Sordo, J. A. *J. Chem. Phys.* **2000**, *112*, 5604.
- (42) Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1994**, *225*, 473.
- (43) Martin, J. M. L. *Chem. Phys. Lett.* **1995**, *242*, 343.
- (44) Pawłowski, F.; Halkier, A.; Jørgensen, P.; Bak, K. L.; Helgaker, T.; Klopper, W. *J. Chem. Phys.* **2003**, *118*, 2539.

CT600347E