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A Nonparametrized Ab Initio Determination of the Heat of Formation of Hydroxylamine, NH_2OH

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Coupled cluster calculations through noniterative triple excitations were used to compute optimized structures, harmonic vibrational frequencies, atomization energies at 0 K, and heats of formation at 298 K for hydroxylamine (NH_2OH) and three related compounds (NH_3, HNO, and H_2O_2). The use of basis sets as large as augmented sextuple-ζ resulted in small extrapolations to the complete basis set limit in order to achieve chemical accuracy (±1 kcal/mol) in the thermodynamic properties. Complete basis set estimates were determined from several simple extrapolation formulas. In addition, four other corrections were applied to the frozen core atomization energies: (1) a zero-point vibrational correction, (2) a core/valence correlation correction, (3) a Douglas-Kroll-Hess scalar relativistic correction, and (4) a first-order atomic spin−orbit correction. For NH_3 and HNO, we incorporated a fifth correction term intended to approximate the difference between coupled cluster theory and the full configuration interact result. This correction was based on coupled cluster theory through iterative quadruple excitations (CCSDTQ). Excellent agreement with experiment was found for the heats of formation of NH_3, HNO, and H_2O_2. For NH_2OH, the best current estimate of the heat of formation at 298 K is -10.1 ± 0.3 kcal/mol, which falls roughly midway between two experimental values at -12.0 ± 2.4 and -7.9 ± 1.5 kcal/mol.

Introduction

Hydroxylamine, NH_2OH ($^1A'$), is widely used in a number of manufacturing processes, including those of the semiconductor industry. It is a thermally, hygroscopic compound that can decompose explosively above room temperature by internal redox reactions. Since 1999, nine people have lost their lives and scores more have been injured in explosions at hydroxylamine manufacturing facilities in the United States and Japan.[1,2] NH_2OH can react with other oxides of nitrogen, and it is often used as an absorbent in combustion analysis. It is also used in reactions of oximes for the manufacture of caprolactam, a key intermediate in the production of fibers such as nylon. Despite its widespread industrial use and a number of experimental and theoretical studies, hydroxylamine's heat of formation is currently not well established.

To the best of our knowledge there are only two experimentally derived values for the heat of formation of hydroxylamine at 298 K, $\Delta H_{f,298}$. Gurvich et al. reported an indirect determination of the heat of formation of gas-phase NH_2OH at 298 K, of -12.0 ± 2.4 kcal/mol ($\Delta H_{f,0} = -9.6 \pm 2.4$ kcal/mol).[3] These authors combined calorimetric measurements of the heat of solution of solid hydroxylamine with enthalpies of reaction involving various other species in solution and the sublimation energy reported by Back and Betts.[4] Anderson[5] combined the appearance potential reported by Kutina et al.[6] for $NH_2OH \rightarrow HNO^+ + H_2 + e^-$ with his own recommended heat of formation of HNO^+ to arrive at a value of $\Delta H_{f,298} = -7.9 \pm 1.5$ kcal/mol ($\Delta H_{f,0} = -5.5 \pm 2.4$ kcal/mol). Anderson combined this result in a weighted average with Gurvich's value and two theoretical values, to arrive at a recommended value of $\Delta H_{f,298} = -9.6 \pm 2.2$ kcal/mol, ($\Delta H_{f,0} = -7.2 \pm 2.2$ kcal). The theoretical components of Anderson's average included a Gaussian-1[7] determination of the $NH_2{-}OH$ bond energy due to Wiberg[8] combined with experimental heats of formation of NH_2 and OH, $\Delta H_{f,298}(NH_2OH) = -10.6$ kcal/mol, $\Delta H_{f,0} = -8.2$ kcal/mol). The final component in the average consisted of a fourth-order perturbation theory value due to Sana and co-workers ($\Delta H_{f,298} = -11.7$ kcal/mol).[9,10]

The most recent theoretical work on NH_2OH is due to Saraf et al.[11] who reported the results of 44 different levels of theory, ranging from the semiempirical AM1[12] method to large basis set coupled cluster theory with singles, doubles and a quasi-perturbative treatment of connected triple excitations (CCSD(T)),[13−15] Their recommended value of $\Delta H_{f,298} = -11.4 \pm 0.6$ kcal/mol was an average based on the energies of two isodesmic reactions:

$$H_2 + NH_2OH \rightarrow H_2O + NH_3 \qquad (1)$$

$$H_2O + NH_2OH \rightarrow H_2O_2 + NH_3 \qquad (2)$$

calculated at several levels of theory. The underlying assumption involved in the use of isodesmic reactions is that computational errors associated with reactants and products will tend to cancel due to the similarity in bonding. To the extent this is true, it is possible to combine the (presumably) accurate theoretical ΔE_{rxn} with reliable experimental heats of formation for all but the unknown compound, yielding the heat of formation of the species of interest. To calibrate their approach, Saraf et al. performed similar calculations on H_2O_2, where reliable experimental data is available. Because their final average value of -32.9 kcal/mol compared well with the experimental value of -32.5 kcal/mo,l[16] they concluded that their hydroxylamine result should be of comparable accuracy.

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The final average used reaction 2 and a selected subset of the 44 methods. Results from methods whose $\Delta H_{f,298}(NH_2OH)$ values predicted by eqs 1 and 2 differed by more than 1 kcal/mol were discarded, leaving 13 remaining cases. Of these they elected to drop six methods which they felt were inherently less reliable. For example, while the two AM1 values predicted by eqs 1 and 2 differed by only 1 kcal/mol, their magnitude was almost a factor of 3 larger than the heats of formation predicted by any other method. The category of discarded values also includes a variety of density functional methods and second-, third-, and fourth-order perturbation theory. The remaining seven values included six based on empirically parametrized methods, e.g. Gaussian-2 (G2)[17] and Gaussian-3 (G3),[18] and one non-parametrized method, CCSD(T). The recommended $\Delta H_{f,298}(NH_2OH)$ was -11.4 ± 0.6, where the raw values associated with eqs 1 and 2 ranged from -10.61 to -12.18 kcal/mol. It should be noted that, because of the use of methods such as G2 and G3, this result involves two levels of empirical fitting and a variety of adjustable parameters.

The goal of the present work is to obtain an improved estimate of the heat of formation of hydroxylamine. To accomplish this, we will apply a composite theoretical approach that has proven effective for a large number of small-to-medium size chemical systems without relying on isodesmic reactions. Instead, it attempts to reduce the various sources of error in thermochemical calculations to the point where the uncertainty in the answer is on the order of ~1 kcal/mol or, in selected cases, even smaller. By avoiding the use of isodesmic reactions and empirically adjusted parameters, we believe our approach to be more general and potentially more accurate, albeit at far greater computational cost. At the very least, results from the present study are expected to provide a reliable, independent estimate of $\Delta H_{f,298}(NH_2OH)$ to complement the available experimental values and the work of Saraf et al.[11]

The observed level of agreement with experiment for our approach roughly matches the observed degree of convergence in the theoretical methods, i.e., 1 to 2 kcal/mol, as judged by over 150 comparisons with reliable experimental data.[19−32] A statistical analysis of the performance of this approach was facilitated by use of the Environmental and Molecular Sciences (EMSL) Laboratory Computational Results Database. In an effort to further calibrate our approach for hydroxylamine, we will also examine three chemically related compounds, NH_3 ($^1A_1$), HNO ($^1A'$) and H_2O_2 (^1A). In addition to the heats of formation, we report high level calculations of the structures and vibrational frequencies of the four molecules.

Methods

We follow the composite approach that we have developed,[22−30] and provide a summary of the major steps in the calculations. To calculate the molecular heat of formation, we first calculate the total atomization energy of the molecule as described below and then combine this value with known experimental heats of formation of the atoms and use Hess's Law. Foremost among the sources of error in most electronic structure calculations is the error arising from the use of incomplete one-particle basis sets. To minimize this error we perform a series of calculations that approach the complete basis set (CBS) limit and subsequently extrapolate to recover the residual error. This process is facilitated by the systematic nature of the correlation consistent family of basis sets. The diffuse function augmented correlation consistent basis sets are conventionally denoted aug-cc-pVnZ, $n = D - 6$.[33−35] However, for brevity we abbreviate the names to aVnZ. By including additional diffuse functions, we are able to treat chemical systems with highly ionic bonds as accurately as those containing only nonpolar covalent bonds. The largest basis set used in the present study was the aV6Z set, which is a [8s,7p,6d,5f,4g,3h,2i] contraction for elements B−Ne. Only the spherical component subset (e.g. 5-term d functions, 7-term f functions, etc.) of the Cartesian polarization functions are used.

Most calculations were performed with the frozen core CCSD(T) method, which is capable of recovering a large fraction of the valence correlation energy. Although CCSD(T) formally scales as the 7th power of the number of basis functions, efficient implementations enable this method to be used with basis sets that approach the CBS limit. All CCSD(T) calculations in the present work were performed with Gaussian 98[36] or MOLPRO-2002[37] running on an SGI Origin 2000, an IBM Regatta p960 server, or on a Hewlett-Packard workstation. The CCSD(T)/aV6Z calculation on NH_2OH (759 basis functions in C_s symmetry), which required 2 days on two 1.3 GHz IBM Power4 processors, was the largest coupled cluster calculation in the present study. Unless otherwise noted, all calculations invoked the frozen core approximation whereby the nitrogen and oxygen 1s core electrons were excluded from the correlation treatment.

Open shell molecules and atoms were treated with the RCCSD(T) method, which is based on restricted open-shell Hartree−Fock (ROHF) orbitals and imposes a restriction on the coupled cluster amplitudes such that the linear part of the wave function becomes a spin eigenfunction.[38−40] This method is requested in MOLPRO with the keyword "RCCSD(T)".

For most molecules, it is prohibitively expensive to use basis sets capable of reducing the residual basis set truncation error to less than 1 kcal/mol, in a brute force fashion. Despite this, reasonable approximations of the CBS limit can be obtained from a variety of simple extrapolation formulas. These formulas express the energy as a function of either a basis set index (n) or $1/l_{max}$, where l_{max} is the highest angular momentum present in the basis set.[41−48]

No one extrapolation formula has been found to provide the best agreement with very high accuracy estimates of the CBS limit or experiment in every case. Nonetheless, they all offer a significant improvement over the raw CCSD(T) atomization energies, ΣD_e. When the sequence of basis sets must be truncated at the quadruple-ζ level for practical reasons, a 3-point mixed Gaussian/exponential function[44] has been found to perform slightly better, in terms of the mean absolute deviation with respect to experiment (~150 comparisons), than the formulas involving $1/l_{max}$.[35] However, when larger basis set results (e.g., aV5Z, aV6Z, etc.) are available, 2- and 3-point $1/l_{max}$ formulas generally produce results in better agreement with experiment because the basis set saturation conditions implicit in their development are more closely met. Indicative of the variability in performance seen with such formulas, an empirically based simple exponential function has sometimes been found to produce the closest agreement with experiment when extrapolating from aVDZ through aVQZ energies.[31]

Fortunately, in the present study it was possible to use the very large aV6Z basis set for all four molecules, which reduced the basis set truncation error in the raw atomization energies, ΣD_e, to less than 1 kcal/mol. We chose to estimate the CBS limit with one of the 2-point $1/l_{max}$ extrapolation formulas:[45]

$$E(l_{max}) = E_{CBS} + B/(l_{max} + 0.5)^4 \qquad (3)$$

thus further reducing this factor as a source of error in our calculations. Although, strictly speaking, this formula is meant to treat only the correlation component of the energy, we have used it to fit the total CCSD(T) energy. With basis sets of aV6Z quality, the SCF component of ΣD_e has essentially converged, eliminating the need to separately extrapolate the SCF and correlation components. For example, in NH_2OH the difference between the aV6Z restricted Hartree−Fock (RHF) ΣD_e and the value predicted by an exponential CBS extrapolation of the aVQZ, aV5Z, and aV6Z energies is a mere 0.01 kcal/mol. Even the aV5Z basis set result only differs by 0.06 kcal/mol.

As a crude measure of the remaining uncertainty in the CBS atomization energies we have adopted the spread in the results obtained from eq 3, the mixed exponential/Gaussian formula and a simple exponential function.[41−43] In many cases, the mixed exponential/Gaussian formula atomization energies are bracketed from below by the exponential result and from above by the $1/l_{max}$ formula. With basis sets as large as aV6Z, both the difference between the raw and CBS extrapolated values and the spread among the three CBS estimates are reassuringly small. This lends confidence to our belief that the basis set truncation error has been reduced significantly below the 1 kcal/mol level. In selected cases, we also consider a $1/l_{max}{}^3$ extrapolation formula.[47]

In addition to addressing the 1-particle basis set error, it is necessary to apply several smaller corrections in order to obtain accurate atomization energies. In most cases, the largest of these is the correction for core/valence (CV) effects, associated with the inclusion of inner shell electrons in the correlation treatment. Our CV calculations were performed with the cc-pCVQZ basis sets of Woon and Dunning[49] at the CCSD(T) level of theory. Previous work suggests that this basis set should be capable of predicting CV corrections within 0.1 kcal/mol of the CBS limit. For the current set of four molecules, the largest CV correction is < 0.7 kcal/mol. For other small-to-medium size systems this correction can easily exceed 7 kcal/mol.[22]

A correction must also be applied for scalar relativistic effects, ΔE_{SR}, which we obtained from spin-free, one-electron Douglas-Kroll-Hess[50−52] (DKH) CCSD(T) calculations using quadruple-ζ basis sets recontracted for DKH calculations and denoted VQZ_DK.[53] In the present case, this correction was on the order of 0.5 kcal/mol or less (and of opposite sign to ΔE_{CV}), although for larger systems it can exceed our target accuracy of ±1 kcal/mol. The sign of the DKH corrections obtained in this work are opposite to the ΔE_{CV} correction, i.e., they decrease the atomization energies. Tests of the accuracy of this approach against other basis sets and levels of theory indicate that it should be accurate to ± 0.1 kcal/mol.

Another correction is necessary in order to account for atomic spin−orbit effects, ΔE_{SO}. This correction arises from the failure of most electronic structure programs to properly treat the lowest energy multiplet of the dissociated atoms. The atomic spin−orbit corrections, ΔE_{SO}, were based on the tables of C. E. Moore.[54] There is no correction for the nitrogen atom, and oxygen has a value of 0.22 kcal/mol. Since the atomic spin−orbit corrections lower the energy of the atomic asymptotes, they result in a decrease of the computed atomization energy. The CV, scalar relativistic, and atomic spin−orbit corrections are assumed to be additive to the CBS (valence) extrapolated total electronic atomization energies.

Zero-point vibrational energies, ΔE_{ZPE}, are needed to convert vibrationless atomization energies to $\Sigma D_0°$, and ultimately to heats of formation at 298 K, $\Delta H_{f,298}°$. In the current study we used zero-point energies obtained from quartic force fields for NH_3 and HNO.[55,56] The inversion splitting in NH_3 is small, 0.7 cm^{-1}, and, therefore, will not affect the zero-point energy.[57,58] For H_2O_2 we estimated the zero-point energy by averaging the values obtained from the CCSD(T)/aVTZ harmonic frequencies, $0.5\Sigma\omega_i$, and experimental fundamentals, $0.5\Sigma\nu_i$,[59] as suggested by Grev et al.[60] In a previous study we compared the 1:1 averaging of harmonic and fundamental frequencies for 31 molecules for which accurate anharmonic zero-point energies were available in the literature. The root-mean-square errors were 0.23 (aVDZ), 0.11 (aVTZ), and 0.09 (aVQZ) kcal/mol.[25] We also tested a 3:1 weighting, which should perform better on purely formal grounds, providing that very accurate harmonic frequencies are available. When CCSD(T)/aVDZ frequencies were used, the 3:1 weighting produced slightly poorer results than the 1:1 weighting. Finally, for NH_2OH the zero-point energy was based solely on the CCSD(T)/aVDZ harmonic frequencies, as no experimental data was available.

The correlation-consistent basis set sequence provides an effective, systematic approach to addressing the 1-particle basis set expansion problem, at least for small-to-medium size chemical systems. Unfortunately, an analogous approach to the n-particle expansion problem poses greater difficulties. Since the majority of accurate, nonparametrized thermochemistry calculations are today based on the CCSD(T) method, what is ideally sought is a practical means of estimating the full configuration interaction (FCI) correction to the CCSD(T) result, ΔE_{FCI}. The FCI wave function represents the exact solution of the molecular Schrödinger equation for any fixed 1-particle basis set, but with an $n!$ dependence on the number of basis functions it is impractical for all but small molecules and small basis sets. This situation is unlikely to change soon. It may well be that for molecules of interest, the magnitude of ΔE_{FCI} will be much less than our target accuracy and can, therefore, be ignored. However, at present too little is known of ΔE_{FCI} to draw that conclusion. For very high accuracy work, such as the recent investigation of the enthalpy of formation of OH and the bond dissociation energy of water, the evidence suggests that some estimate of ΔE_{FCI} will be required.[29,30] Identifying a method superior to CCSD(T) is difficult, in part, because of the high level of accuracy demonstrated by this method and the already steep computational scaling ($\sim n^7$) associated with it.

One approach to estimating ΔE_{FCI} involves the construction of a sequence of approximate wave functions that smoothly converges to the FCI limit, followed by an extrapolation to recover the remaining correlation energy in a manner analogous to the 1-particle basis set extrapolations. An example of this approach is the coupled cluster continued fraction, CCSD(T)-cf, extrapolation of Goodson,[61] which combines Hartree−Fock, CCSD, and CCSD(T) energies with a simple formula for approximating the FCI energy. Tests involving 39 small chemical systems for which FCI energies were available showed that the success of the method depended strongly on the nature of the molecular system to which it was applied. For systems where many-body perturbation theory converged monotonically (referred to by Goodson as "class A" systems) the CCSD(T)-cf total energies were always closer to the FCI result than CCSD(T), although sometimes the differences were very small. For systems where perturbation theory did not converge monotonically, or diverged, the level of agreement between CCSD(T)-cf and FCI was noticeably worse. In six out of 19 cases the CCSD(T)-cf energy was further from the FCI value than CCSD(T).[26,32]

Rather than rely upon an extrapolation procedure, another approach to approximating ΔE_{FCI} would be to identify a level of theory that more closely approximated the FCI result than

TABLE 1: A Comparison of Full CI and Various Coupled Cluster Energies for Atoms and Small Molecules[a]

system	basis	method	E	Δ^b	system	basis	method	E	Δ^b
N (^{4}S)	VTZ	CCSD	−54.511990	2879	N (^{4}S)	VQZ	CCSD	−54.521520	3492
		CCSD(T)	−54.514334	535			CCSD(T)	−54.524415	597
		CCSDT	−54.514825	4			CCSDT	−54.524955	57
		CCSDTQ	−54.514868	1			CCSDTQ	−54.525012	0
		FCI	−54.514869				FCI	−54.525012	
O (^{3}P)	VTZ	CCSD	−74.970679	3490	O (^{3}P)	VQZ	CCSD	−74.989434	4379
		CCSD(T)	−74.973688	481			CCSD(T)	−74.993244	569
		CCSDT	−74.974117	52			CCSDT	−74.993740	73
		CCSDTQ	−74.974168	1			CCSDTQ	−74.993811	2
		FCI	−74.974169				FCI	−74.993813	
F (^{2}P)	VTZ	CCSD	−99.616568	3968	NH_3 ($^1A_1$)	VTZ[c]	CCSD	−56.423473	6581
		CCSD(T)	−99.620216	320			CCSD(T)	−56.429601	453
		CCSDT	−99.620475	61			CCSDT	−56.429795	259
		CCSDTQ	−99.620535	1			CCSDTQ	−56.430042	12
		FCI	−99.620536				FCI[d]	−56.430054	
OH ($^2\Pi$)	VTZ[e]	CCSD	−75.632375	5757	H_2O ($^1A_1$)	VTZ[f]	CCSD	−76.310051	7353
		CCSD(T)	−75.637557	575			CCSD(T)	−76.317001	403
		CCSDT	−75.637963	169			CCSDT	−76.317088	316
		CCSDTQ	−75.638131	1			CCSDTQ	−76.317396	8
		FCI[d]	−75.638132				FCI[d]	−76.317404	

[a] Open shell CCSD(T) calculations were performed with the RCCSD(T) method. All CCSDT and CCSDTQ calculations were performed with ROHF orbitals but without spin restriction in the coupled cluster portion of the calculation. [b] Difference with respect to FCI energy (μE_h). [c] VDZ(2s) on H, VTZ on N. $r_{NH} = 1.0149$ Å, $\angle HNH = 106.3998°$, $\angle HHNH = 113.1694°$. [d] Obtained with a sparsity-driven full CI calculation. The estimated uncertainty in the total energy is approximately $5 - 10\ \mu E_h$. [e] $r_{OH} = 0.9715$ Å. [f] VDZ on H, VTZ on O. $r_{OH} = 0.9594$ Å, $\angle HOH = 103.6°$.

CCSD(T). As already mentioned, CCSD(T) scales as $n,^7$ making it a very computationally expensive method when combined with large basis sets. We expect that still higher level methods, which entail even more severe scaling, will be limited for use with only double- and triple-ζ basis sets for molecules other than simple diatomics. Our experience with very high order methods suggests that basis sets of at least triple-ζ quality are needed in order to estimate the ΔE_{FCI} correction with acceptable accuracy.[21] Conclusions drawn from double-ζ calculations may differ qualitatively from those obtained from better quality basis sets.

In an effort to identify a method capable of reliably predicting the effect of correlation recovery beyond CCSD)T), we have recently examined the CCSDT,[62,63] CCSD(TQ)[64,65] and Brueckner doubles with perturbative triples and quadruples, BD(TQ)[64] techniques.[21,23,32,66] Tests showed that all three of these methods failed to provide uniform improvement over CCSD(T) when computing atomization energies. For example, the BD(TQ) method failed in three out of nine comparisons with FCI atomization energies to improve upon CCSD(T). In two other cases, the BD(TQ) method as implemented in Gaussian 98 ended in aborted runs.

Because CCSDT proved incapable of reliably improving upon CCSD(T), in the present work we turn our attention to the next higher method in the coupled cluster sequence, CCSDTQ.[67] On the basis of the findings of Kucharski and Bartlett, who compared CCSDTQ against small basis set FCI for four small molecules,[67] we anticipate that this method may be capable of accurately estimating ΔE_{FCI}. However, as an iterative $\sim n^{10}$ method, it is likely to be prohibitively expensive for our purposes. CCSDTQ calculations were performed with NWChem using an approach developed by Hirata.[68]

In Table 1, we compare a variety of coupled cluster total energies against FCI values for the O, N, and F atoms and three small molecules. All of the calculations were based on restricted open-shell Hartree−Fock (ROHF) orbitals, but the spin restriction was removed in the CCSDTQ portion of the calculation. The level of agreement with FCI monotonically improves along the sequence CCSD, CCSD(T), CCSDT, and CCSDTQ. For the atoms and OH, the CCSDTQ energies fall within 2 μE_h of FCI. For H_2O and NH_3, the differences are 8 and 12 μE_h larger, respectively. Since the FCI energies for H_2O and NH_3 were obtained with the Knowles sparsity-driven, determinant-based FCI program,[69] which introduces an uncertainty in the total energies of 5−10 μE_h, the actual CCSDQT errors for these two molecules may be smaller than Table 1 implies.

TABLE 2: Coupled Cluster Atomization Energy Errors (kcal/mol) Relative to Full CI

system	basis	method	$\Delta E_{FCI}{}^a$	system	basis	method	$\Delta E_{FCI}{}^a$
H_2O ($^1A_1$)	VTZ	CCSD	−2.42	NH_3 ($^1A_1$)	VTZ	CCSD	−2.32
		CCSD(T)	0.05			CCSD(T)	0.05
		CCSDT	−0.17			CCSDT	−0.13
		CCSDTQ	−0.01			CCSDTQ	−0.01
OH ($^2\Pi$)	VTZ	CCSD	−3.31				
		CCSD(T)	−0.06				
		CCSDT	−0.08				
		CCSDTQ	0.01				

[a] $\Delta E_{FCI} = \Sigma D_e$ (approximate) $-\ \Sigma D_e$ (FCI).

Absolute accuracy in total energies is not a prerequisite for accurate thermochemistry due to its reliance on energy differences. Table 2 compares coupled cluster ΣD_e errors relative to their FCI counterparts, ΔE_{FCI}, for H_2O, NH_3, and OH. It is apparent that when truncated at the singles and doubles level, coupled cluster theory is incapable of accurate thermochemistry. CCSD is only marginally superior to second-order perturbation theory, on the basis of a statistical analysis of the data contained in the EMSL Computational Results Database. The introduction of triple excitations dramatically improves agreement with FCI. CCSD(T) benefits from a balanced cancellation of errors between molecules and atoms. It displays smaller errors than CCSDT for all three molecules. This agrees with our previous experience with CCSDT and comes despite the fact that the CCSDT total energies lie closer to the FCI energies. CCSDTQ is in nearly exact agreement with the FCI results, with errors of ±0.01 kcal/mol. Although the body of data is admittedly very small, it would appear that CCSDTQ is capable of very accurately reproducing FCI atomization energies, at least in the vicinity of the equilibrium geometry. Kucharski and Bartlett found that as they stretched the OH bonds in H_2O to $1.5r_e$, the error in the total energy increased to $\sim$140 μE_h (0.09 kcal/mol).[67]

TABLE 3: CCSD(T) Electronic Atomization Energies (kcal/mol), Bond Lengths (Å), and Bond Angles (°)[a]

system	basis set	ΣD_e	r_{NH}	∠HNH	∠HHNH
NH_3 ($^1A_1$)[b]	aVDZ	276.56	1.0237	105.9	112.2
	aVTZ	291.53	1.0149	106.4	113.2
	aVQZ	295.43	1.0126	106.6	113.5
	aV5Z	296.50	1.0123	106.6	113.5
	aV6Z[c]	296.91	1.0122	106.6	113.5
	aV6Z+CV[d]		1.0107	106.7	113.8
	CBS($1/l_{max}$)	297.4 ± 0.2			
	expt.[e]		1.0116	106.7	
	expt.[f]		1.0124	106.67	
	expt.[g]		1.025	107	
	expt.[h]		1.0180	107.3	

system	basis set	ΣD_e	r_{NO}	r_{OH}	∠HNO
HNO ($^1A'$)	aVDZ	183.43	1.2256	1.0660	107.7
	aVTZ	197.52	1.2151	1.0554	108.0
	aVQZ	202.47	1.2116	1.0535	108.0
	aV5Z	203.88	1.2103	1.0533	108.1
	aV6Z[c]	204.50	1.2095	1.0532	108.1
	aV6Z+CV[d]		1.2076	1.0518	108.1
	CBS($1/l_{max}$)	205.2 ± 0.2			
	expt.[i]		1.212 ± 0.001	1.063 ± 0.002	108.6 ± 0.2
	expt.[j]		1.239 ± 0.005	1.020 ± 0.020	114.4 ± 2

system	basis set	ΣD_e	r_{OO}	r_{OH}	∠OOH	∠HOOH
H_2O_2 (^1A)	aVDZ	247.07	1.4604	0.9689	100.0	111.9
	aVTZ	261.91	1.4610	0.9665	99.8	112.2
	aVQZ	266.42	1.4535	0.9635	100.0	112.7
	aV5Z	267.61	1.4515	0.9624	100.0	112.7
	aV6Z[c]	268.11	1.4510	0.9619	100.0	112.7
	aV6Z+CV[d]		1.4498	0.9609	100.1	115.1
	CBS($1/l_{max}$)	268.6 ± 0.2				
	expt.[k]		1.456	0.967	102.3	119.1

system	basis set	ΣD_e	r_{NO}	r_{OH}	r_{NH}	∠NOH	∠ONH	∠HONH
NH_2OH ($^1A'$)	aVDZ	330.15	1.4628	0.9671	101.7	1.0269	102.9	125.6
	aVTZ	350.14	1.4498	0.9621	101.9	1.0177	103.4	125.1
	aVQZ	356.07	1.4430	0.9591	102.1	1.0155	103.6	125.0
	aV5Z	357.67	1.4394	0.9573	102.1	1.0150	103.6	125.0
	aV6Z	358.33	1.4408	0.9563	102.1	1.0149	103.6	125.0
	aV6Z+CV[d]		1.4377	0.9554	102.3	1.0136	103.7	124.9
	CBS($1/l_{max}$)	359.0 ± 0.3						
	G2	359.4						
	G3	358.1						
	CBS-Q	359.6						
	expt.[l]		1.453	0.962	101.4	1.016	103.2	

[a] Unless otherwise indicated, all calculations were performed using the frozen core approximation. The atomization energies are with respect to RCCSD(T) atoms. Symmetry equivalencing of the p_x, p_y, and p_z orbitals was not imposed in the atomic calculations. The CBS($1/l_{max}$) entries were obtained from eq 3 using the aV5Z and aV6Z energies. [b] NH_3 CCSD(T) atomization energies are based on total energies from Dixon et al., ref. [77]. [c] Bond lengths estimated from an exponential fit of the aVTZ through aV5Z bond lengths. Bond angles adopted from the aV5Z values. [d] Core/valence correction obtained at the CCSD(T)/CVQZ level of theory. [e] Duncan and Mills, ref. [70]. [f] NIST/JANAF, ref. [16]. [g] Hoy et al., ref. [71]. [h] Spirko and Kraemer, ref. [76]. These values correspond to Fit I in Table 2. [i] Dalby, ref. [72]. [j] Bancroft, ref. [73]. [k] Pelz et al., ref. [74]. [l] Tsunekawa, ref. [75].

Unfortunately, given the scarcity of molecular FCI energies, it is difficult to perform a more comprehensive calibration of the CCSDTQ method.

Despite its high accuracy, the CCSDTQ method is unlikely to be widely adopted for correcting CCSD(T) atomization energies due to its high computational costs, unless an efficient parallel implementation can be developed that scales to large numbers of processors. A single-point CCSDTQ calculation on NH_3 with the VTZ(N)/VDZ(H) basis set required approximately 9 days of wall clock time on two IBM 1.3 GHz Power4 processors.

Results and Discussion

Frozen core CCSD(T) electronic atomization energies and optimized geometries are given in Table 3, along with the available experimental data for the latter.[16,70−76] The NH_3 atomization energies were based on total energies from Dixon et al.,[77] but differ slightly from the values reported by these authors because of their use of the R/UCCSD(T) method for the nitrogen atom. The effects of core/valence correlation on the optimized geometrical parameters was evaluated at the CCSD(T)(full)/CVQZ level. The aV6Z basis set is sufficiently flexible that its atomization energies fall within 0.5−0.7 kcal/mol of the CBS limit predicted by eq 3. Use of the $1/l_{max}^3$ extrapolation results in ΣD_e values that are 0.1−0.2 kcal/mol larger, falling within the error bars we have adopted. We have also computed the atomization energy of NH_2OH with the Gaussian-2 (G2),[17] Gaussian-3 (G3),[18] and CBS-Q[78] composite methods, which are based on a combination of ab initio calculations and empirical corrections. All three methods predict values within ±1 kcal/mol of the frozen core CCSD(T)/CBS result.

TABLE 4: CCSD(T) Harmonic and Experimental Frequencies (cm^{-1})

system	basis	a_1	e	a_1	e
NH_3	aVDZ	1070.1	1649.7	3433.9	3571.4
	aVTZ	1063.7	1671.1	3463.9	3592.5
	aVQZ	1058.3	1678.6	3473.7	3603.6
	expt.(ω)[a]	1030	1689.9	3503	3591.6
	expt.(ω)[b]	1022	1691	3504	3577
	expt.(ω)[c]		1678 ± 6	3485 ± 11	3624 ± 12
	expt.(ω)[d]		1684 ± 8	3478 ± 12	3597 ± 8
	expt.[e]	950	1627	3337	3444

system	basis	a′	a′	a′
HNO	aVDZ	1520.2	1577.5	2904.8
	aVTZ	1553.9	1625.4	2962.2
	expt.[f]	1505	1593	3039

system	basis	a	a	b	a	a	b
H_2O_2	aVDZ	393.0	842.3	1301.8	1409.1	3752.5	3752.9
	aVTZ	412.5	897.3	1312.9	1415.6	3773.7	3775.7
	expt.[e]	371	877	1266	1402	3599	3608

system	basis	a”	a′	a′	a”	a′	a′	a′	a”	a′
NH_2OH	aVDZ	397.9	888.7	1153.2	1317.0	1396.2	1636.6	3412.2	3502.2	3801.2

[a] Harmonic frequencies, Hoy et al., ref. [71]. [b] Harmonic frequencies, Duncan and Mills, ref. [70]. [c] Harmonic frequencies, Coy and Lehmann, ref. [79]. [d] Harmonic frequencies, Lehmann and Coy, ref. [80]. [e] Shimanouchi, ref. [59]. [f] NIST-JANAF Tables, ref. [16].

In general, the predicted r_e bond lengths are in good agreement with the r_e and r_0 experimental values. In all cases, the inclusion of core/valence effects results in a small contraction of the bond lengths by amounts ranging from −0.0015 Å to −0.0031 Å. For NH_3 our best value of r_{NH} (1.0107 Å), obtained at the CCSD(T)/aV6Z+CV level of theory, is 0.0017 Å shorter than the best CCSD(T) value quoted by Martin et al.[55] Compared to experimental r_e(NH) values, the best current value is only 0.0009 Å shorter than the value reported by Duncan and Mills[70] and 0.0143 Å shorter than the value of Hoy et al.[71] Agreement with the more recent experimental value of Spirko and Kraemer (1.0180 Å) is noticeably poorer.[76] Differences for bond lengths between two first-row atoms in the larger molecules, e.g., N−O, are somewhat larger, falling into the 0.005 Å to 0.015 Å range.

Good agreement with experiment was also found for the normal-mode frequencies listed in Table 4.[16,59,70,71,79,80] For NH_3 the CCSD(T) harmonic frequencies and experimentally derived harmonic frequencies are within 30 cm^{-1} of each other. The difficult-to-describe “umbrella mode” has a CCSD(T)/aVQZ frequency of 1058.3 cm^{-1}, 28 cm^{-1} larger than the harmonic frequency reported by Hoy et al.[71] and 36 cm^{-1} larger than value of Duncan and Mills.[70] This mode appears to be sensitive to the basis set, since the best CCSD(T)/VQZ value (1084.1 cm^{-1}) reported by Martin et al.[55] was significantly larger than the value obtained in the present work. Martin et al. also reported the effect of core/valence correlation at the QCISD(T)/[5s,4p,2d,1f/3s,2p] level of theory. For the umbrella mode, the core/valence correction is 9 cm^{-1}, which brings the theoretical values into better agreement with experiment.

For HNO, where no experimental harmonic frequencies are available, the difference between the theoretical harmonics and experimental fundamentals is slightly larger than with NH_3, being ≤50 cm^{-1}. A similar level of agreement was found for H_2O_2.

Of potential interest for NH_2OH is the role of the inversion and torsion about the N−O bond on the zero-point energy. The trans structure for NH_2OH is the global minimum and a cis structure with the H(O) bisecting the NH_2 hydrogens is also a minimum but is 4.7 kcal/mol above the trans structure at the local density functional theory level with a triple-ζ basis set. The gauche structure is not a minimum. We also optimized two planar structures, one with all atoms in the plane and one with the H(O) atom in a plane perpendicular to the plane containing the other atoms. The former structure, 16.6 kcal/mol above the trans, has two imaginary frequencies corresponding to the NH_2 inversion motion and torsion about the N−O bond. The latter structure has one imaginary frequency corresponding to the NH_2 inversion motion and is 8.2 kcal/mol above the trans. The inversion barrier is higher than that in NH_3 which is calculated to be 3.5 kcal/mol at this level as compared to an experimental value of 5.8 kcal/mol. The N−O rotation barrier must be above 4.7 kcal/mol. These results show that the barriers to rotation and inversion are high enough that they will not produce a sizable splitting to the zero-point energy.

Zero-point corrected atomization energies, ΣD_0, and enthalpies of formation at 0 K, $\Delta H_{f,0}°$, and at 298 K, $\Delta H_{f,298}°$, are listed in Table 5 along with the individual components contributing to these properties and the experimental values, where available. The agreement between theory and experiment is excellent for NH_3, HNO, and H_2O_2. For NH_3, the upper limit of the theoretical $\Delta H_{f,298}°$ value (−10.7 ± 0.2 kcal/mol) just overlaps the lower limit of the experimental value (−11.0 ± 0.1 kcal/mol) quoted in the NIST/JANAF Tables.[16]

Previously, we reported a full CI calculation on NH_3 with a mixed basis set consisting of VDZ(2s) on H and VTZ on N.[77] At 1.4 × 10^9 determinants, this calculation was at the limits of our software and hardware capabilities. The quoted ΔE_{FCI} value of +0.28 kcal/mol was in error due to the use of an incorrect atomic energy. The correct value, when dissociating to R/UCCSD(T) atoms is +0.05 kcal/mol. When dissociating to RCCSD(T) atoms, as we have chosen to do in the present work, the correction becomes −0.05 kcal/mol. Despite the use of an incorrect FCI correction, a different description of the atomic asymptotes (RCCSD(T) vs R/UCCSD(T)) and a different approach to the scalar relativistic correction (CISD/VQZ vs DKH/VQZ_DK), the $\Sigma D_0(NH_3)$ value reported by Dixon et al.[77] (276.52 ± 0.17 kcal/mol) is (probably fortuitously) in almost exact agreement with the present result. We have replaced the

TABLE 5: Theoretical and Experimental Enthalpies of Formation (kcal/mol)

NH_3 ($^1A_1$)	ΣD_0	$\Delta H_{f,0}{}^0$	$\Delta H_{f,298}{}^0$
ΣD_e RCCSD(T)(FC)/CBS(l_{max})[a]	297.4 ± 0.2		
ΔE_{ZPE}[b]	−21.33		
ΔE_{CV} RCCSD(T)/CVQZ	0.60		
ΔE_{SR} DKH CCSD(T)/VQZ	−0.24		
ΔE_{FCI}[c]	−0.03		
Total	276.4 ± 0.2	−9.0 ± 0.2	−10.7 ± 0.2
G2		−9.1	−10.8
G3		−8.5	−10.2
CBS-Q		−8.3	−10.0
expt.[d]		−9.3 ± 0.1	−11.0 ± 0.1
HNO ($^1A'$)	**ΣD_0**	**$\Delta H_{f,0}{}^0$**	**$\Delta H_{f,298}{}^0$**
ΣD_e RCCSD(T)(FC)/CBS(l_{max})[a]	205.2 ± 0.2		
ΔE_{ZPE}[e]	−8.56		
ΔE_{CV} RCCSD(T)/CVQZ	0.39		
ΔE_{SR} DKH CCSD(T)/VQZ	−0.27		
ΔE_{SO}[f]	−0.22		
Total	196.5 ± 0.2	26.4 ± 0.2	25.7 ± 0.2
G2		24.4	23.7
G3		27.1	26.4
CBS-Q		26.1	25.4
expt.[g]		24.5 ± 2.5	23.8 ± 2.5
expt.[h]			25.8 ± 1.0
expt.[i]			21.4 ± 2.8
expt.[j]		26.3 ± 0.03	25.6 ± 0.03
expt.[k]			24.4 ± 2.5
expt.[l]			25.6 +0.6/−0.1
H_2O_2 (^1A)	**ΣD_0**	**$\Delta H_{f,0}{}^0$**	**$\Delta H_{f,298}{}^0$**
ΣD_e RCCSD(T)(FC)/CBS(l_{max})[a]	268.6 ± 0.2		
ΔE_{ZPE}[m]	−16.24		
ΔE_{CV} RCCSD(T)/CVQZ	0.35		
ΔE_{SR} DKH CCSD(T)/VQZ	−0.36		
ΔE_{SO}[e]	−0.43		
Total	251.9 ± 0.2	−30.7 ± 0.2	−32.2 ± 0.2
G2		−30.8	−32.3
G3		−29.9	−31.3
CBS-Q		−31.3	−32.8
expt.[d]		−31.0	−32.5
NH_2OH ($^1A'$)	**ΣD_0**	**$\Delta H_{f,0}{}^0$**	**$\Delta H_{f,298}{}^0$**
ΣD_e RCCSD(T)(FC)/CBS(l_{max})[a]	359.0 ± 0.3		
ΔE_{ZPE}[n]	−25.02		
ΔE_{CV} RCCSD(T)/CVQZ	0.67		
ΔE_{SR} DKH CCSD(T)/VQZ	−0.45		
ΔE_{SO}[e]	−0.22		
Total	334.0 ± 0.3	−7.6 ± 0.3	−10.1 ± 0.3
G2	334.6	−8.2	−10.7
G3	333.4	−7.0	−9.5
CBS-Q	334.0	−7.6	−10.1
expt.[o]		−9.6 ± 2.4	−12.0 ± 2.4
expt.[p]			−7.9 ± 1.5
expt./theory[q]			−9.6 ± 2.2
expt./theory[r]			−11.4 ± 0.6

[a] CBS extrapolation with the $1/l_{max}$ formula (eq 3a) using the aV5Z and aV6Z basis set energies. The uncertainty is taken from the spread in the exponential, mixed and $1/l_{max}$ extrapolations. [b] Anharmonic zero-point energy based on a quartic force field reported by Martin, ref. [55]. [c] Estimated full CI correction based on a mixed basis set CCSDTQ calculation: cc-pVTZ (N) and cc-pVDZ(H). [d] NIST-JANAF, ref. [16]. [e] Anharmonic zero-point energy based on a quartic force field reported by C. E. Dateo et al., ref. [56]. [f] Atomic spin−orbit correction. [g] NIST-JANAF, ref. [16]. Error bars are from Anderson, ref. [5]. The NIST/JANAF Tables do not quote any error bars. [h] Value derived by Anderson, ref. [5], using results from Adams et al., ref. [82]. [i] Value derived by Anderson, ref. [5] ,using results from Kutina et al., ref. [6]. [j] Dixon et al., ref [83]. [k] Gurvich et al., ref. [3], with error bars from Anderson, ref. [5]. [l] Anderson recommended value, ref. [5]. [m] Based on the average of the zero-point energies from the CCSD(T)/aVTZ harmonic frequencies and the experimental fundamentals. [n] Based on the CCSD(T)/aVDZ harmonic frequencies. [o] Gurvich et al., ref. [3], indirectly based on the heat of formation of solid hydroxylamine and the heat of sublimation. [p] Kutina et al., ref. [6]. [q] Anderson recommended value, ref. [5], based on a weighted average of four theoretical and experimental estimates ranging from −7.9 to −12.0 kcal/mol. [r] Saraf et al., ref. [11], based on two isodesmic reactions involving a combination of experimental and theoretical data and an analysis of the error in comparable calculations on H_2O_2.

explicit FCI-based correction with one based on a CCSDTQ calculation using a mixed VDZ(H)/VTZ(N) basis set. This basis set differs from the basis set used in the older FCI calculation in that it includes p functions on H for a total of 45 basis functions. The CCSDTQ estimate of the FCI correction to the CCSD(T) atomization energy is −0.03 kcal/mol, a value that is very close to the explicit FCI result with the slightly smaller basis set. By way of comparison, the CCSDT correction is 0.13

kcal/mol, showing once again that the approximate treatment of triple excitations in CCSD(T) can be a more accurate approximation to FCI that the iterative triples method.

The aVDZ through aV5Z total energies for HNO were taken from Dixon et al.[81] The aV6Z results are from this work. Compared with the present $\Delta H_{f,0}°$ value of 26.4 ± 0.2 kcal/mol, the earlier work reported values of 26.4 and 26.7 kcal/mol, obtained with a mixed Gaussian/exponential and eq 3. There are numerous $\Delta H_{f,298}°$ experimental values, which fall into the range 21.4 to 25.8 kcal/mol[3,5,6,16,82,83] and bracket our value of $\Delta H_{f,298}° = 25.7 \pm 0.2$ kcal/mol. A CCSDTQ calculation with the VDZ basis set predicted a surprisingly large 0.87 kcal/mol increase in the atomization energy. This suggests that the ΔE_{FCI} correction may be larger than expected. However, we have chosen not to apply this correction to our final recommended value for HNO because double-ζ quality basis set results can be misleading because they often do not reflect the true size of the correction.

For H_2O_2 the NIST/JANAF Tables list a heat of formation at 298 K of −32.5 kcal/mol, compared to our theoretical value of −32.2 ± 0.2 kcal/mol. No experimental error bars were quoted. Thus, for all three of the molecules chosen to calibrate our approach, the level of agreement with experiment is such that the theoretical results either fall within the experimental error bars or very close to them. Based on these findings, we expect comparable accuracy when this approach is applied to NH_2OH.

As seen in Table 5, the present $\Delta H_{f,298}°(NH_2OH)$ value of −10.1 ± 0.3 kcal/mol falls essentially midway between the experimental values reported by Gurvich et al. (−12.0 ± 2.4 kcal/mol)[3] and by Kutina et al. (−7.9 ± 1.5 kcal/mol).[6] The error bars quoted by Gurvich et al. encompass our result. It also falls within the −9.6 ± 2.2 kcal/mol range reported by Anderson, which was obtained from a weighted average of experimental and theoretical values. Our value is in good agreement with the CCSD(T)/VQZ value of Saraf et al.[11] obtained through the use their isodesmic reaction 2 (−10.61 kcal/mol). However, the value recommended by Saraf et al. (−11.4 ± 0.6 kcal/mol) is seen to be slightly larger in magnitude than our result.

It is of interest to compare the sizes of the various small corrections to the atomization energies. The ΔE_{CV} corrections range from 0.35 kcal/mol for H_2O_2 to 0.67 kcal/mol for NH_2OH, and the ΔE_{SR} corrections range from −0.24 kcal/mol for NH_3 to −0.45 kcal/mol for NH_2OH. The ΔE_{SO} corrections range from 0.0 kcal/mol for NH_3 to −0.43 kcal/mol for H_2O_2. Thus the sum of these corrections can lead to small changes either positive or negative in the total atomization energies. For these size molecules, the corrections are small and ignoring them would lead to errors of ±0.5 kcal/mol, but for larger molecules, they cannot be ignored.

We evaluated the three isodesmic reaction energies used by Saraf et al. by using our calculated heats of formation at 0 K and the calculated heats of formation of H_2 (0.02 kcal/mol) and H_2O (−57.0 ± 0.3 kcal/mol) obtained at the same level as given above.[84] The corresponding experimental values for $\Delta H_f{}^0(H_2)$ and $\Delta H_f{}^0(H_2O)$ are 0.00 and −57.10 kcal/mol. The calculated isodesmic reaction energies with our heats of formation at 0 K are −58.4 kcal/mol and −24.9 kcal/mol for reactions 1 and 2, respectively, and −83.3 kcal/mol for the following test reaction given by Saraf et al.

$$H_2 + H_2O_2 \rightarrow 2H_2O \qquad (4)$$

with an experimental value of −83.3 kcal/mol for reaction 4 for comparison. We note that the G2, G3, and CBS-Q values for $\Delta H_{f,298}°(NH_2OH)$ obtained from the isodesmic reactions 1 and 2 are −11.78 (G2(1)), −11.53 (G2(2)), −11.15 (G3(1)), −11.28 (G3(2)), −12.18 (CBS-Q(1)), and −11.16 (CBS-Q(2)) kcal/mol, respectively, showing a range of about 1 kcal/mol and all at least 1 kcal/mol more negative than our value. The G2, G3, and CBS-Q values for $\Delta H_{f,298}°(H_2O_2)$ obtained from isodesmic reaction 4 are −32.83 (G2), −32.74 (G3), and −33.60 (CBS-Q) kcal/mol as compared to our value of −32.2 kcal/mol and the experimental value of −32.5 kcal/mol. These results suggest that the isodesmic reaction approach coupled with the various more approximate G2, G3, and CBS-Q methods can do no better than 1 kcal/mol and that the CBS-Q method coupled with the isodesmic reaction approach has errors for these simple systems of 2 kcal/mol in some cases. The raw G2, G3, and CBS-Q values show better agreement with our calculated values with all three of these calculated heats of formation within 1 kcal/mol of our calculated value for NH_3, H_2O_2, and NH_2OH. For HNO, the G3 and CBS-Q values are within 1 kcal/mol of our calculated value, but the G2 value differs by 2 kcal/mol.

Conclusion

A composite theoretical approach based on large basis set coupled cluster calculations corrected for core/valence, scalar relativistic, and atomic spin−orbit effects was used to determine the structures, harmonic vibrational frequencies, and the heats of formation of NH_3, HNO, H_2O_2, and NH_2OH. Structures and frequencies were found to be in good agreement with experiment. The excellent level of agreement with experiment for the heats of formation of NH_3, HNO, and H_2O_2 argues that our approach should be capable of predicting the heat of formation of NH_2OH within our target range of ±1 kcal/mol. For NH_2OH the best current estimate of the heat of formation at 298 K is −10.1 ± 0.3 kcal/mol, which falls roughly midway between two experimental values at −12.0 ± 2.4 and −7.9 ± 1.5 kcal/mol.

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(84) $\Sigma D_e = \Sigma D_e$ RCCSD(T)(FC)/CBS(l_{max}) + ΔE_{CV} RCCSD(T)/CVQZ + ΔE_{SR} DKH CCSD(T)/VQZ + ΔE_{SO} + ΔE_{ZPE}. $\Sigma D_e(H_2) = 109.48 + 0.00 + 0.00 + 0.00 - 6.20 = 103.28$ kcal/mol. $\Sigma D_e(H_2O) = 232.55 + 0.44 - 0.27 - 0.22 - 13.26 = 219.24$ kcal/mol.