The Role of Anharmonicity in Hydrogen-Bonded Systems: The Case of Water Clusters

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S Supporting Information

ABSTRACT: The nature of vibrational anharmonicity has been examined for the case of small water clusters using second-order vibrational perturbation theory (VPT2) applied on second-order Møller–Plesset perturbation theory (MP2) potential energy surfaces. Using a training set of 16 water clusters (H_2O)_{n=2–6,8,9} with a total of 723 vibrational modes, we determined scaling factors that map the harmonic frequencies onto anharmonic ones. The intermolecular modes were found to be substantially more anharmonic than intramolecular bending and stretching modes. Due to the varying levels of anharmonicity of the intermolecular and intramolecular modes, different frequency scaling factors for each region were necessary to achieve the highest accuracy. Furthermore, new scaling factors for zero-point vibrational energies (ZPVE) and vibrational corrections to the enthalpy (ΔH_{vib}) and the entropy (S_{vib}) have been determined. All the scaling factors reported in this study are different from previous works in that they are intended for hydrogen-bonded systems, while others were built using experimental frequencies of covalently bonded systems. An application of our scaling factors to the vibrational frequencies of water dimer and thermodynamic functions of 11 larger water clusters highlights the importance of anharmonic effects in hydrogen-bonded systems.

1. INTRODUCTION

It has long been recognized that comparison of calculated harmonic vibrational frequencies (ω) with observed fundamental frequencies (ν) requires an empirical correction to account for vibrational anharmonicity and inherent errors in the electronic structure calculations.^{1–12} There are three main reasons for scaling calculated harmonic vibrational frequencies to approximate experimental frequencies. First, scaling corrects for deviation from the harmonic oscillator model as a consequence of anharmonicity. The deviation could be mild in the case of high-frequency stretching modes where the vibrational potential around the equilibrium geometry of the molecule is deep and well-described by a harmonic oscillator potential. The difference between this harmonic potential and the more appropriate Morse potential is small, and a simple scaling factor goes a long way in reducing the disparity between the two. However, there are extreme cases of anharmonicity where the “vibrational” potential has multiple shallow minima and the motion is better described as an internal rotation, ring inversion, or a pseudorotation.^{13–17} This is most common in low-frequency modes and cannot be easily remedied by introducing scaling factors. In cases where the harmonic approximation works well, a second reason for using scaling factors is that they can correct for the incompleteness of the basis set and electron correlation treatment that is inherent in the most practical quantum mechanical calculations. Scaling factors allow one to perform vibrational frequency analysis using a modest basis set and electron correlation method and to improve the quality of the calculated frequencies by scaling with a prescribed multiplicative factor. A third source of error in harmonic vibrational frequencies is the coupling of different modes, but accounting for these requires the calculation of coupled (as opposed to independent normal mode) vibrational wave functions. In principle,

methods like vibrational configuration interaction (VCI)^{18–20} and the Huang–Braams–Bowman (HBB)²¹ potential can give exact vibrational wave functions, but they are not practical for systems with more than 10 atoms.

Anharmonic correction for rigid and semirigid systems typically amounts to 3–5% of harmonic frequencies computed using second-order Møller–Plesset perturbation theory (MP2) and Becke, three-parameter, Lee–Yang–Parr (B3LYP) methods and about 10% using Hartree–Fock (HF) methods with modest basis sets. Errors in harmonic vibrational frequencies are systematic, and it is possible to determine scaling factors by comparing calculated frequencies with experimental ones. Most scaling factors reported in the literature make use of large databases of experimental vibrational frequencies to systematically improve harmonic frequencies. By least-squares fitting of harmonic frequencies to experimental frequencies, many scaling factors have been suggested for a host of methods and basis sets. Radom et al.^{4,7} have obtained scaling factors for vibrational frequencies, zero point vibrational energies (ZPVE) and vibrational enthalpies (ΔH_{vib}) and entropies (S_{vib}). They suggested different scaling factors for high- and low-frequency modes, with the high modes being scaled by 0.95–0.97 and the inverse of the low modes being scaled by 1.01–1.04 for MP2 theory with aug-cc-pVNZ basis sets where $N = D - Q$. A similar work by Sinha et al.⁵ suggests split scaling of fundamental modes and low-frequency modes. The recommended fundamental and inverse low-frequency scaling factors for MP2 theory were 0.9604 and 1.0999 for the aug-cc-pVDZ basis set, 0.9557 and 1.0634 for the aug-cc-pVTZ basis set, and 0.9601 and 1.0698 for the aug-cc-pVQZ basis set. Halls et al.¹² have determined frequency scaling factors for various

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methods along with the Sadlej pVTZ electric property basis set and found that dual scaling improves agreement between computed and observed vibrational frequencies better than a single uniform scaling. Wong¹¹ has looked at the performance of different density functionals and recommended scaling factors for each. As noted by Irikura et al.,^{6,8,9} even though the uncertainty in most scaling factors is larger than typically acknowledged, empirical scaling of frequencies almost universally marks an improvement over plain harmonic ones. Nevertheless, the effectiveness of empirical scaling is still being debated in the literature.^{22–25}

While the works discussed above introduce uniform or separate scaling factors for different regions of the vibrational spectrum to correct harmonic vibrational frequency, Borowski's effective scaling frequency factor (ESFF)^{26–28} method and Pulay's scaled quantum mechanical (SQM)²⁹ force field approaches scale individual vibrational frequencies or force constants depending on the nature of the local modes (ESFF) or the internal coordinates (SQM) contributing to each vibrational mode. Both ESFF and SQM have been shown to reduce the root-mean-square (RMS) deviation between scaled vibrational frequencies and experimental frequencies impressively when applied for density functional methods with various basis sets.^{26–28,30,31} Even though SQM has been successfully applied to hydrogen-bonded acid dimers,^{30–33} its use has been limited to date.

All the empirical scaling schemes described so far are derived from training sets of small covalently bound molecules for which experimental frequencies are readily available. None of these training sets include the experimental vibrational frequencies of even water dimers: the prototypical hydrogen-bonded system with a resolved vibrational spectrum. Thus, their applicability to hydrogen-bonded systems, like water clusters, is highly questionable even though they have been routinely employed in the literature.^{34–38}

Each water cluster $(\text{H}_2\text{O})_n$ has $3n$ high-frequency intramolecular vibrational modes corresponding to the symmetric stretch, asymmetric stretch and bending of each monomer. As water clusters form from individual monomers, the $6n - 6$ translational and rotational degrees of freedom of the monomers turn into low-frequency intermolecular vibrational modes. Experimental intramolecular vibrational frequencies are available for $(\text{H}_2\text{O})_n$, however the intermolecular modes remain murky due to the coupling of low-frequency vibrational modes with each other and rotational degrees of freedom. Moreover, the experimental spectra are taken with the water clusters in different matrices that shift and broaden the spectral lines of the clusters in ways that are difficult to interpret. Perhaps the one exception is the water dimer whose 12 experimental vibrational frequencies have been resolved with the help of theoretical calculations.^{37,39–41} Therefore, in the absence of reliable experimental intermolecular frequencies, it is imperative that one relies on theoretical anharmonic calculations to correct harmonic vibrational frequencies.

Many approaches have been developed to incorporate anharmonic effects in vibrational wave function calculations. One popular approach is vibrational second-order perturbation theory (VPT2) where anharmonic corrections are calculated from higher (third and fourth) order derivatives of the potential energy surface along the normal mode coordinates. The cubic and semi-diagonal quartic force constants are calculated by finite differentiation of the Hessian along the normal mode coordinates.^{42,43} It has the advantage of being affordable (albeit substantially more expensive than a harmonic calculation), and it is often the only practical approach for most systems of interest. If one has analytical second derivatives of the energy, then the necessary third and fourth derivatives can be computed easily using finite differentiation. For

a system with N_m normal modes, the cost is $2N_m + 1$ times that of a single harmonic vibrational calculation. Because each of the Hessian calculations on the $2N_m + 1$ displaced geometries can be run separately, VPT2 calculations are amenable to parallelization. The main drawback of VPT2 is that it is subject to the problem of near degeneracies (resonances) just like all other perturbation theory.

In a manner analogous to electronic wave function methods, grid-based methods start with the vibrational self-consistent field (VSCF) approach, where each normal mode couples with all other modes in an average way.^{44–46} Higher order correlation between the modes is included via second-order perturbation theory (VMP2), configuration interaction (VCI), or coupled-cluster (VCC) theory. These methods give good anharmonic frequencies for fundamental modes and overtones resulting from them, and they can account for coupling of different modes. They can however be expensive as they scale nonlinearly with the number of normal modes and the number of modes being correlated.⁴⁷ The cost of a VPT2 calculation scales linearly with the number of normal modes, and it is typically at least an order of magnitude cheaper than VSCF and its correlation corrected analogs. Another downside of VSCF is that it often gives unreasonable anharmonic frequencies for large amplitude, low-frequency modes, like the intermolecular modes of hydrogen-bonded systems.^{48–50} Aside from these two popular schemes, harmonically coupled anharmonic oscillator (HCAO),⁵¹ *ab initio* molecular dynamics,⁵² P_VMWCI2,⁵³ and HBB⁵⁴ have been used to account for anharmonicity in hydrogen-bonded systems.

Most of the literature on the vibrational frequencies of water clusters attempts to look at the red shift in the bonded O–H stretching modes of gas-phase water clusters relative to the gas-phase monomer.^{36,55,56} Aside from the water dimer,⁵⁷ there has been little work done on the effect of anharmonicity on vibrational modes of water clusters. Diri et al.⁵⁸ have evaluated the effect of anharmonic correction of the binding energy and ZPVE of $(\text{H}_2\text{O})_{n=2–6}$ using MP2 and B3LYP theories with VPT2. Dunn et al.³⁷ showed that harmonic frequencies calculated using HF theory are more amenable to scaling than those computed using MP2. Njagic and Gordon⁵⁰ have looked at the effect of the anharmonicity of vibrational modes on thermodynamic functions of small- and medium-size molecules, including the water dimer using VSCF. They concluded that vibrational anharmonicity and coupling of modes have a substantial effect on the ZPVE as well as thermodynamic functions. They suggest expressing the normal mode displacement vectors in internal instead of Cartesian coordinates to get reasonable VSCF anharmonic frequencies for modes that involve bending and torsional motion. For the case of the water dimer, casting the potential energy surface in internal coordinates improves the agreement between calculated and experimental low-frequency modes remarkably. Correlation corrected vibrational mean field theory (cc-VSCF) has also been applied to hydrogen-bonded systems.^{48,49} Kjaergaard et al.⁵⁷ have examined the performance of VPT2, VSCF, cc-VSCF, and HCAO for the water dimer. Their results show that VSCF, cc-VSCF, and HCAO perform well for O–H stretches but are somewhat erratic for intermolecular modes. VPT2 works well for all vibrational modes, even though it does not perform as well as HCAO for O–H stretching frequencies. Begue et al.⁵³ have benchmarked different anharmonic approaches and found VPT2 to be consistently applicable to water clusters, while other approaches had many pitfalls. Similarly, Torrent-Sucarrat et al.⁵⁹ have studied the role of vibrational anharmonicity in hydrogen-bonded complexes formed between the hydroperoxyl radical and formic, acetic, nitric, and sulfuric acids. They conclude that VPT2 anharmonic frequencies computed over

B3LYP/6-31+G(d,p) and B3LYP/6-311+G(2d,2p) PES agree well with experiment. Watanabe et al.⁶⁰ used a scaled hypersphere search (SHS) by polynomial fitting of the intramolecular potential energy function of water clusters to get fundamental frequencies that were very close to experimental values. A recent application of these different anharmonic treatments to $(\text{HF})_{n=2-4}$ showed that VPT2, VSCF, and cc-VSCF perform comparably for high-frequency stretching modes, but the latter two were unreliable for low-frequency intermolecular modes.⁴⁷ Dykstra has looked at anharmonic effects on zero point energies of weakly bound molecular clusters including the water dimer and trimer and concluded that the effect is large when there are multiple minima on the intermolecular potential energy surface.⁶¹

Low-frequency modes are generally much more anharmonic than high-frequency ones. They also couple with each other as well as rotational degrees of freedom, thus making theoretical treatments and experimental spectral resolutions daunting. Since low-frequency modes contribute the most to the thermal correction to the enthalpy and entropy of a system, even small deviations in these modes lead to large errors in free energies. As a result, researchers have been somewhat reluctant to use calculated harmonic frequencies to estimate free energies of weakly bound clusters, particularly at high temperatures where the errors would be most pronounced.⁶²

On the basis of existing literature, VPT2 is the most appropriate and affordable approach for evaluating the role of anharmonicity in large water clusters. Even though recent works by Barone et al.^{63,64} advocate the use of density functional methods with modest basis sets to calculate VPT2 anharmonic frequencies, we chose to use an MP2 wave function because it has been shown to be the most affordable and accurate method for studying water clusters. The aug-cc-pVDZ basis set has the necessary diffuse and polarization functions to describe hydrogen bonding well, and it is often used to determine optimal geometries and harmonic vibrational frequencies. MP2 calculations with correlation consistent basis sets, when extrapolated to the CBS limit, capture all the important features of small water clusters.⁶⁵⁻⁸⁰ MP2/aug-cc-pVDZ harmonic vibrational frequencies have been used for benchmark quality works on water clusters as large as $(\text{H}_2\text{O})_{17}$ due to their affordability.⁸⁰ Therefore, appropriate scaling factors for the MP2/aug-cc-pVDZ level of theory are especially important.

In this paper, we demonstrate the need to use separate scaling factors for intermolecular vibrational modes of hydrogen-bonded clusters. For the commonly used MP2/aug-cc-pVDZ level of theory, we provide a set of frequency scaling factors for harmonic frequencies as well as the ZPVE and vibrational corrections to the enthalpy and entropy. Using 723 VPT2 anharmonic frequencies calculated for $(\text{H}_2\text{O})_{n=2-6,8,9}$, scaling factors for the harmonic vibrational frequencies have been determined. The intermolecular modes ($\omega < 1100 \text{ cm}^{-1}$) are found to be substantially more anharmonic than intramolecular bending ($1100 \text{ cm}^{-1} < \omega < 1800 \text{ cm}^{-1}$) and stretching modes ($\omega > 1800 \text{ cm}^{-1}$), suggesting that the use of different frequency scaling factors for each region in correcting the harmonic vibrational modes is appropriate. Similarly, by comparing the harmonic and anharmonic ZPVE, vibrational contribution to the enthalpy (ΔH_{vib}) and entropy (S_{vib}), scaling factors are calculated. These different scaling approaches are applied to the water dimer system in order to evaluate the importance of anharmonicity and the validity of the rigid rotor-harmonic oscillator (RRHO) model. The transferability of the recommended scaling factors to other levels of theory and hydrogen-bonded systems is also discussed.

Figure 1. The 16 water clusters included in this study.

2. METHODOLOGY

The clusters included in this study are the water dimer (2- C_s), trimer (3-UUD), tetramers (4- S_4 , 4- C_i), pentamer (5-Cyclic), hexamers (6-Cyclic-chair, 6-Book-1, 6-Cage, 6-Prism, 6-Book-2, 6-Bag, 6-Cyclic-boat-1, 6-Cyclic-boat-2), octamers (8- D_{2d} , 8- S_4), and one nonamer (9- D_{2dDD}). The optimized structures are shown in Figure 1. These 16 clusters have a total of 723 harmonic vibrational modes. The geometry optimizations and harmonic vibrational frequencies were computed using MP2/aug-cc-pVDZ with analytical gradients and Hessians. To avoid numerical problems in subsequent anharmonic frequency calculations, tight convergence criteria was enforced for both the geometry optimization and the Hessian calculations. We denote VPT2 anharmonic calculations on MP2/aug-cc-pVDZ potential energy function as VPT2/MP2/aVDZ for the sake of brevity. For these anharmonic calculations, the necessary third and fourth derivatives were determined by finite differentiation of analytic Hessians with respect to nuclear displacements along each normal mode. The default $0.0250 \text{ \AA}^{43}$ step size is appropriate for rigid and semirigid systems, but it gives erratic anharmonic frequencies for the larger water clusters even after our geometries and energies were converged very tightly. A step size that gave the most reasonable anharmonic frequencies for $(\text{H}_2\text{O})_{n=2-6,8,9}$ is $0.0050 \text{ \AA}$.

One unintended consequence of using small step sizes is that it reduced the number of resonances encountered in VPT2 calculation. One of the shortcomings of VPT2 is that it suffers in handling Fermi (that affect modes coupled by cubic force constants) and Darling–Dennison resonances (which affect modes coupled by quartic force constants and Coriolis coupling constants).⁸¹ We used the default cutoffs for Fermi and Darling–Dennison resonances. Gaussian 09 A.02⁸² removes resonances in an automated way as prescribed by Martin et al.^{83,84} All computations are performed using the Gaussian 09 A.02⁸² software package on a 128-core SGI Altix 3700 Bx2. There are differences in anharmonic frequencies calculated using Gaussian 03 B.02,⁸⁵ Gaussian 09 A.02, and CFOUR.⁸⁶ In the interest of consistency, all our calculations are performed using Gaussian 09 A.02.⁸²

Of the 16 clusters we studied, 4 hexamers had one or more anharmonic frequencies that are abnormally small compared to

Figure 2. The differing anharmonicity in the three classes of VPT2/MP2/aug-cc-pVDZ vibrational modes of water clusters $(\text{H}_2\text{O})_{2-6,8,9}$.

the harmonic analog. These outliers have individual scaling factors ($\lambda_i = \nu_i/\omega_i$) that lie outside of three standard deviations (σ) from the average λ of each class. Since these anomalous frequencies introduce large uncertainty, they have been removed from the scaling scheme. Scaling factors are calculated in a manner that is partly different from previous works.^{3-5,7} First, while others have used the inverse of frequencies to calculate scaling factors for low-frequency modes, we find such an approach to massively skew the scaling factors toward those of the lowest (and most error prone) frequency modes. Scaling the inverse of the frequency may be appropriate for covalently bonded systems where the anharmonicity rarely exceeds 10% even for low-frequency modes, but it gives unreasonably low-scaling factors and large errors when applied to the highly anharmonic intermolecular modes of our water clusters. Since we preemptively separate low-frequency intermolecular modes into their own class, deriving the frequency scaling factors using the normal frequencies works reasonably well. Second, the ZPVE scaling factors in our case are determined by scaling the harmonic ZPVE against an estimate of the true ZPVE in a manner suggested by Barone et al.⁴² Third, to get scaling factors for ΔH_{vib} and S_{vib} , previous works used least-squares fitting of frequencies to minimize the residual between the experimental and theoretical ΔH_{vib} and S_{vib} . We have looked at two approaches: (a) scaling the harmonic ΔH_{vib} and S_{vib} against their anharmonic analogs directly and (b) determining frequency scaling factors that minimize the residual of ΔH_{vib} and S_{vib} . The merits and downsides of both approaches are discussed.

3. RESULTS AND DISCUSSION

3.1. Classification of Vibrational Frequencies. Each water cluster $(\text{H}_2\text{O})_n$ has $2n$ high-frequency intramolecular stretching modes, n intramolecular bending modes, and $6n - 6$ low-frequency intermolecular modes. In this study, there are 723 vibrational modes of which 182 correspond to monomer stretching, 91 to monomer bending, and 450 to low-frequency intermolecular motion. Removing a few anomalous anharmonic frequencies leaves us with 703 vibrational frequencies of which 435, 271, 88, and 178 are intermolecular, intramolecular, bending, and stretching modes, respectively. As illustrated in Figure 2, the distribution of the ratio of anharmonic to harmonic frequencies ($\lambda = \nu^f/\omega^h$) for the water clusters in this study shows three

distinct groupings. The stretching modes which lie above 3000 cm^{-1} are not particularly anharmonic; as can be seen from the $\lambda \sim 0.95$, one would need to match the harmonic frequencies to the fundamentals. The bending modes are even less anharmonic, needing a scaling factor of $\lambda \sim 0.97$ to match fundamentals. In contrast, the low-frequency intermolecular modes have a larger and more spread anharmonicity. Figure 2 demonstrates the need to use separate multiplicative factors to scale the different classes of frequencies. Johnson et al.⁹ outline the three conditions that need to be met to form a class of frequencies as “(1) the bias (λ) for the target frequency is believed to be of similar value to those in the class; (2) the (estimated) biases in the class have an approximately normal and acceptably narrow distribution; (3) the number of vibrational frequencies in the class is reasonably large.” Our grouping of the water clusters frequencies into two or three classes satisfies the conditions listed above. The frequencies can be classified into intermolecular ($\omega^h < 1100 \text{ cm}^{-1}$) and intramolecular ($\omega^h > 1100 \text{ cm}^{-1}$) modes, and that scheme will be designated as two-split scaling. Alternatively, the frequencies can be grouped into intermolecular ($\omega^h < 1100 \text{ cm}^{-1}$), bending ($1100 \text{ cm}^{-1} < \omega^h < 1800 \text{ cm}^{-1}$), and stretching ($\omega^h > 1800 \text{ cm}^{-1}$) modes, in a scheme we will call three-split scaling. A comparison of uniform scaling with the two- and three-split scaling schemes is performed below.

3.2. Scaling Vibrational Frequencies. Given N MP2/aVDZ harmonic frequencies (ω^h) and VPT2/MP2/aVDZ anharmonic fundamental frequencies (ν^f), an optimal scaling factor, λ can be found by using the least-squares procedure minimizing the residual (Δ) which is defined as

$$\Delta = \sum_{i=1}^N (\lambda \omega_i^h - \nu_i^f)^2 \quad (1)$$

The λ that minimizes the residual is

$$\lambda = \frac{\sum_{i=1}^N \omega_i^h \nu_i^f}{\sum_{i=1}^N (\omega_i^h)^2} \quad (2)$$

How well this scaling factor improves the harmonic frequencies is assessed by evaluating the root-mean-square error (RMSE) of the scaled frequency relative to the anharmonic fundamental:

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N (\lambda \omega_i^h - \nu_i^f)^2} \quad (3)$$

$$\text{RMSE} = \sqrt{\frac{\Delta}{N}}$$

The uncertainty associated with the scaling factor λ is a critical measure of the confidence and applicability of the scaling scheme, as shown repeatedly by Irikura et al.^{6,8,9} The uncertainty $\sigma(\lambda)$ is defined as

$$\sigma(\lambda) = \sqrt{\frac{\Delta}{\sum_{i=1}^N (\omega_i^h)^2}} \quad (4)$$

As noted already, there are many ways to calculate frequency scaling factors. Table 1 shows the scaling factors for uniform, two- and three-split scaling schemes for each separate water

Table 1. Individual Scaling Factors for MP2/aug-cc-pVDZ Harmonic Frequencies Relative to VPT2/MP2/aug-cc-pVDZ Anharmonic Frequencies of $(\text{H}_2\text{O})_{n=2-6,8,9}$

	uniform	two-split scaling		three-split scaling		
	λ (all)	λ ($\omega < 1100$)	λ ($\omega > 1100$)	λ ($\omega < 1100$)	λ ($1100 < \omega < 1800$)	λ ($\omega > 1800$)
2- C_s	0.954	0.831	0.955	0.831	0.972	0.953
3-UUD	0.951	0.811	0.955	0.811	0.970	0.953
4- C_i	0.952	0.875	0.955	0.875	0.976	0.952
4- S_4	0.952	0.878	0.954	0.878	0.980	0.952
5-Cyclic	0.950	0.880	0.952	0.880	0.972	0.950
6-Cyclic-chair ^a	0.950	0.876	0.953	0.876	0.971	0.951
6-Book-1	0.950	0.880	0.953	0.880	0.979	0.950
6-Cage	0.948	0.864	0.951	0.864	0.974	0.949
6-Prism	0.947	0.872	0.950	0.872	0.983	0.946
6-Book-2 ^a	0.947	0.878	0.949	0.878	0.969	0.947
6-Bag	0.947	0.876	0.950	0.876	0.975	0.947
6-Cyclic-boat-1 ^a	0.949	0.864	0.952	0.864	0.967	0.951
6-Cyclic-boat-2 ^a	0.949	0.863	0.952	0.863	0.964	0.950
8- S_4	0.944	0.888	0.946	0.888	0.982	0.943
8- D_{2d}	0.944	0.885	0.947	0.885	0.983	0.943
9- D_{2d} DD ^a	0.944	0.884	0.946	0.884	0.978	0.943
overall	0.948	0.876	0.950	0.876	0.975	0.949

^a Have individual scaling factors ($\lambda_i = \nu_i / \omega_i$) that lie outside 3σ of the average λ .

Table 2. Collective Scaling Factors for MP2/aug-cc-pVDZ Harmonic Frequencies Relative to VPT2/MP2/aug-cc-pVDZ Anharmonic Frequencies of $(\text{H}_2\text{O})_{n=2-6,8,9}$ ^a

	nature of mode	scaling factor (λ)	uncertainty [$\sigma(\lambda)$]	RMSE (cm^{-1})
Uniform Scaling				
λ (all)	all	0.948	0.019	39
Two-Split Scaling				
λ ($\omega < 1100$)	intermolecular	0.876	0.036	17
λ ($\omega > 1100$)	intramolecular	0.950	0.012	36
Three-Split Scaling				
λ ($\omega < 1100$)	intermolecular	0.876	0.036	17
λ ($1100 < \omega < 1800$)	intramol. bending	0.975	0.010	17
λ ($\omega > 1800$)	intramol. stretching	0.949	0.007	25

^a Using 703, 435, 271, 88, and 178 frequencies for all, intermolecular, intramolecular, bending, and stretching modes, respectively, after removing outlying frequencies from an initial set of 723, 450, 273, 91, and 182 modes.

cluster and all 15 clusters combined. The individual scaling factors do not vary substantially among the clusters, with the dimer and the trimer being slight outliers. The overall scaling factors are given in Table 2. Applying a uniform scaling factor of 0.948 ± 0.019 leads to an RMSE of 39 cm^{-1} . It is clear that the high-frequency stretching modes are dominating this scaling factor, as evidenced by the scaling factor of 0.949 ± 0.007 we get just for the stretching modes alone. In the two-split scaling scheme, we get a scaling factor of 0.876 ± 0.036 for the 435 intermolecular modes and 0.950 ± 0.012 for the 271 intramolecular modes. The larger uncertainty in the intermolecular scaling factor is due to the diverse range of anharmonicity in the low-frequency modes, as can be seen in the frequency range $\omega^h < 1100 \text{ cm}^{-1}$ in Figure 2. The RMSE of the two-split scaling scheme is lower than that of the uniform scaling. In the three-split scaling, we derive values of 0.876

± 0.036 for the 435 intermolecular modes, 0.975 ± 0.010 for the 88 intramolecular bending modes, and 0.949 ± 0.007 for the 178 intramolecular stretching modes. The RMSE for this scheme is lower than that of the uniform and two-split scaling approaches. The distribution of the error in each scheme, defined as the difference between the scaled harmonic and anharmonic frequency, is shown in Figure 3. Figure 3a shows that the harmonic frequencies exceed anharmonic ones by as much as 260 cm^{-1} , and the error distribution is large. Applying the scaling schemes substantially improves the agreement with the anharmonic frequencies, as illustrated in Figure 3b. The three-split scaling has the lowest average error and narrowest error distribution.

Our scaling factors for the intramolecular modes (0.950 ± 0.012) in the two-split scaling scheme are comparable to those in the literature which are constructed by least-squares fitting of theoretical

Figure 3. Error distribution of unscaled (a) and scaled (b) MP2/aVDZ harmonic vibrational frequencies of $(\text{H}_2\text{O})_{2-6,8,9}$ relative to VPT2/MP2/aVDZ anharmonic frequencies. Please note that different abscissa scales are used in (a) and (b).

harmonic vibrational frequencies to experimental fundamental frequencies of covalently bonded molecules. For the MP2/aVDZ level of theory, Merrick et al. report scaling factors of 0.9615 and 0.9614 for fundamental frequencies using the F1 and F1'' set of frequencies.⁷ Sinha et al. similarly recommend a scaling factor of 0.9604 based on a database of 41 common organic molecules.⁵ There are two reasons for the slight differences between our scaling factors and those from the literature. First, we are comparing harmonic frequencies against calculated anharmonic frequencies, while the literature references compare against experimental fundamental frequencies. Second, we are using a database of hydrogen-bonded water clusters, while those in the literature rely on a set of small covalently bonded molecules.

The most stark difference between our scaling scheme and others is the scaling factor for the low-frequency intermolecular modes. Merrick et al. use inverse frequency scaling and obtain scaling factors of 1.0418 and 1.0338 for the F1 and F1'' set of frequencies for the MP2/aVDZ level of theory.⁷ Using the same approach on a database of 41 organic molecules, Sinha et al. get scaling factors for MP2/aVDZ low frequencies ($\omega^h < 1000 \text{ cm}^{-1}$) of 1.0999.⁵ We did not use inverse frequency scaling because it is unduly biased toward the lowest frequency modes which are very anharmonic and error prone. For the database of covalently bonded molecules that Merrick and Sinha used, the level of anharmonicity in

the lowest frequency modes is not as severe as ours. So, it would make sense to use an inverse frequency scaling factor to overcome the dominance of the high-frequency modes in the direct scaling scheme. We circumvent that dominance by grouping our frequencies into three classes and determining separate scaling factors for each class.

3.3. Scaling of ZPVE. Provided how important quantum mechanical ZPVE corrections are to most chemical systems, a proper scaling factor for ZPVEs is crucial. As demonstrated by Grev et al.,² ZPVE scaling factors are different from plain frequency scaling factors due to the presence of anharmonicity. The harmonic and fundamental ZPVE for a molecule with N_m vibrational modes are given by

$$\text{ZPVE}^h = \frac{1}{2} \sum_{i=1}^{N_m} \omega_i^h \quad (5)$$

$$\text{ZPVE}^f = \frac{1}{2} \sum_{i=1}^{N_m} \nu_i^f \quad (6)$$

Since our calculated anharmonic fundamental corresponds to the $\nu(0 \rightarrow 1)$ transition frequency and not the energy of $\nu(0)$, we cannot get the anharmonic ZPVE by simply plugging the fundamental frequency into the ZPVE expression in eq 6. The true ZPVE lies somewhere in between ZPVE^h and ZPVE^f and various approximations to it have been given in the literature.^{2,87} A commonly used estimate of the true ZPVE is

$$\text{ZPVE} = \chi_0 + \frac{1}{2}(\text{ZPVE}^h + \text{ZPVE}^f) - \frac{1}{4} \sum_{i=1}^{N_m} \chi_{ii} \quad (7)$$

where χ_0 is a small anharmonic correction and χ_{ii} are the diagonal elements of the anharmonicity matrix. With an estimate of the true ZPVE in hand, we can derive a scaling factor that maps the harmonic ZPVE to it. For a database of N_{mols} molecules, the residual of the harmonic and true ZPVE is

$$\Delta = \sum_{i=1}^{N_{\text{mols}}} (\lambda(\text{ZPVE}_i^h) - \text{ZPVE}_i)^2 \quad (8)$$

The λ that minimizes the residual is

$$\lambda = \frac{\sum_{i=1}^{N_{\text{mols}}} (\text{ZPVE}_i^h)(\text{ZPVE}_i)}{\sum_{i=1}^{N_{\text{mols}}} (\text{ZPVE}_i^h)^2} \quad (9)$$

The RMSE and uncertainty are then given by

$$\text{RMSE} = \sqrt{\frac{\Delta}{N_{\text{mols}}}} \quad (10)$$

$$\sigma(\lambda) = \sqrt{\frac{\Delta}{\sum_{i=1}^{N_{\text{mols}}} (\text{ZPVE}_i^h)^2}} \quad (11)$$

The anharmonic fundamental (ν_i^f), χ_0 , and χ_{ii} terms can be determined from the quadratic, cubic, and semidiagonal quartic force constants calculated using VPT2. Of the 16 clusters in our training set, we have removed 5 because they had one or more abnormally low anharmonic frequencies. For the remaining 11 water clusters, Table 3 shows the scaling factor for each cluster and the set overall. All the scaling factors are in a narrow range

Table 3. Scaling Factors for the MP2/aug-cc-pVDZ Harmonic ZPVE of Water Clusters^{a,b}

	ZPVE ^{harmonic}	ZPVE ^{anharmonic c}	ZPVE ^{anharmonic} /ZPVE ^{harmonic}
2-C _s	28.88	28.23	0.978
3-UUD	45.50	44.31	0.974
4-C _i	61.59	60.19	0.977
4-S ₄	61.78	60.27	0.976
5-Cyclic	77.36	75.40	0.975
6-Book-1	93.59	91.20	0.974
6-Cage	93.96	91.48	0.974
6-Prism	94.16	91.78	0.975
6-Bag	93.38	90.95	0.974
8-S ₄	127.57	124.76	0.978
8-D _{2d}	127.57	124.90	0.979
λ			0.976
$\sigma(\lambda)$			0.002
RMSE/cluster			0.18

^a Four hexamers (Cyclic-chair, Book-2, Cyclic-boat-1, and Cyclic-boat-2) and the D_{2d}DD nonamer are excluded because they had individual scaling factors ($\lambda_i = \nu_i / \omega_i$) that lie outside 3σ of the average λ . ^b In kcal/mol. ^c Estimate of the true ZPVE calculated using eq 7.

Table 4. Scaling Factors for the MP2/aug-cc-pVDZ Harmonic ΔH_{vib} (298.15 K) of Water^a

	$\Delta H_{\text{vib}}^{\text{h}}$ (298.15 K) ^a	$\Delta H_{\text{vib}}^{\text{f}}$ (298.15 K) ^a	$\Delta H_{\text{vib}}^{\text{f}}/\Delta H_{\text{vib}}^{\text{h}}$ (298.15 K)
2-C _s	1.92	2.10	1.096
3-UUD	3.03	3.49	1.154
4-C _i	4.51	5.01	1.112
4-S ₄	4.40	4.82	1.096
5-Cyclic	6.27	6.95	1.109
6-Book-1	7.74	8.49	1.096
6-Cage	7.51	8.39	1.118
6-Prism	7.46	8.33	1.117
6-Bag	7.82	8.70	1.112
8-S ₄	9.75	10.71	1.098
8-D _{2d}	9.75	10.69	1.097
λ_H			1.106
$\sigma(\lambda_H)$			0.011
RMSE/cluster ^b			0.07

^a Four hexamers (Cyclic-chair, Book-2, Cyclic-boat-1, and Cyclic-boat-2) and the D_{2d}DD nonamer are excluded because they had individual scaling factors ($\lambda_i = \nu_i / \omega_i$) that lie outside 3σ of the average λ . ^b In kcal/mol.

between 0.97 and 0.98. Our overall scaling factor of 0.976 ± 0.002 is close to the 0.9675^5 and 0.9878^7 reported in the literature from databases of small covalently bonded molecules. Considering that ZPVE is dominated by high-frequency modes, the proximity between our scaling factors and those from the literature (which have a larger number of high-frequency modes) is not surprising.

3.4. Scaling of Vibrational Corrections to the Enthalpy and Entropy. Given the vibrational energy levels of a molecule, we can calculate the vibrational partition function $Q_{\text{vib}}(T)$ and the

finite temperature vibrational correction to the enthalpy [$\Delta H_{\text{vib}}(T) = H_{\text{vib}}(T) - H_{\text{vib}}(0)$] and entropy [$S_{\text{vib}}(T)$]. The vibrational and rotational contributions to the partition function employ the canonical rigid rotor-harmonic oscillator (RRHO) equations.^{15,88} In the harmonic oscillator model, the vibrational energy levels of each mode are evenly spaced, and we can get compact expressions for $Q_{\text{vib}}(T)$ and the finite temperature corrections:

$$Q_{\text{vib}} = \prod_i \left(\frac{1}{1 - e^{-\mu_i}} \right) \quad (12)$$

$$\Delta H_{\text{vib}}(T) = RT \sum_i \left(\frac{\mu_i}{e^{\mu_i} - 1} \right) \quad (13)$$

$$S_{\text{vib}}(T) = R \sum_i \left[\frac{\mu_i}{e^{\mu_i} - 1} - \ln(1 - e^{-\mu_i}) \right] \quad (14)$$

where $\mu_i = \hbar c \omega_i / k_B T$, R is the universal gas constant, $\hbar$ is Planck's constant, c is the speed of light, and ω_i is the harmonic frequency in wavenumbers. The anharmonic partition function is not amenable for such simplifications, and it has terms that include the anharmonicity constant. Anharmonic energy levels are not evenly spaced as is the case for a harmonic oscillator. One would need to sum over all the anharmonic energy levels to calculate the partition function, but the perturbation theory is prone to failures in predicting higher vibrational energy levels. To overcome these limitations, Truhlar and Isaacson⁸⁹ have proposed an approximation called simple perturbation theory (SPT) which retains a form like the harmonic expression above but uses anharmonic frequencies and ZPVEs:

$$Q_{\text{vib}} = \frac{\exp\left(\frac{-\text{ZPVE}}{k_B T}\right)}{\prod_i (1 - e^{-\mu_i})} \quad (15)$$

where $\mu_i = \hbar c \nu_i / k_B T$, $\hbar$ is Planck's constant, c is the speed of light, ν_i is the anharmonic frequency in wavenumbers, and ZPVE is the true zero point vibrational energy correction shown in eq 7. SPT has been shown to compare well with methods summing over anharmonic energy levels for linear and nonlinear molecules in the small anharmonicity limit.^{81,89–91} In modes like torsions, ring inversions, and internal rotations where the vibrational potential differs markedly from that of a single well harmonic oscillator, the SPT approximation will not work well. Kurtén et al.⁹² have recently generalized the solution to a one-dimensional system in the small anharmonicity limit to n -dimensions and successfully applied it to $(\text{H}_2\text{SO}_4)(\text{H}_2\text{O})_{n=1-2}$ and $(\text{HSO}_4^-)(\text{H}_2\text{O})_{n=1-2}$. Their more complicated anharmonic expressions contain terms including the anharmonicity constant, and they do predict vibrational enthalpies and entropies that differ substantially from those of SPT for hydrogen-bonded systems. Nevertheless, since their expressions have not been rigorously tested on a variety of systems, we will use the SPT approximation here. The SPT thermal corrections to the enthalpy and the entropy look similar to their harmonic analogs except we use the fundamental frequency ($\mu_i = \hbar c \nu_i / k_B T$) in this case:

$$\Delta H_{\text{vib}}(T) = RT \sum_i \left(\frac{\mu_i}{e^{\mu_i} - 1} \right) \quad (16)$$

$$S_{\text{vib}}(T) = R \sum_i \left[\frac{\mu_i}{e^{\mu_i} - 1} - \ln(1 - e^{-\mu_i}) \right] \quad (17)$$

There are two approaches to determine appropriate scaling factors for $\Delta H_{\text{vib}}(T)$ and $S_{\text{vib}}(T)$. One can calculate the harmonic and anharmonic $\Delta H_{\text{vib}}(T)$ and $S_{\text{vib}}(T)$ for each molecule first and seek scaling factors (λ_H and λ_S) that minimize the residuals:

$$\Delta_H = \sum_{i=1}^{N_{\text{mols}}} [\lambda_H \Delta H_{\text{vib},i}(T, \omega^h) - \Delta H_{\text{vib},i}(T, \nu^f)]^2 \quad (18)$$

$$\Delta_S = \sum_{i=1}^{N_{\text{mols}}} [\lambda_S S_{\text{vib},i}(T, \omega^h) - S_{\text{vib},i}(T, \nu^f)]^2 \quad (19)$$

This method is easy to apply, and below is an analytic form for the scaling factors:

$$\lambda_H = \frac{\sum_{i=1}^{N_{\text{mols}}} \Delta H_{\text{vib},i}(T, \omega^h) \Delta H_{\text{vib},i}(T, \nu^f)}{\sum_{i=1}^{N_{\text{mols}}} [\Delta H_{\text{vib},i}(T, \omega^h)]^2} \quad (20)$$

$$\lambda_S = \frac{\sum_{i=1}^{N_{\text{mols}}} S_{\text{vib},i}(T, \omega^h) S_{\text{vib},i}(T, \nu^f)}{\sum_{i=1}^{N_{\text{mols}}} [S_{\text{vib},i}(T, \omega^h)]^2} \quad (21)$$

The RMSE and uncertainty in the scaling factors are calculated simply:

$$\text{RMSE}_H = \sqrt{\frac{\Delta_H}{N_{\text{mols}}}} \quad (22)$$

$$\text{RMSE}_S = \sqrt{\frac{\Delta_S}{N_{\text{mols}}}} \quad (23)$$

$$\sigma(\lambda_H) = \sqrt{\frac{\Delta_H}{\sum_{i=1}^{N_{\text{mols}}} [\Delta H_{\text{vib},i}(T, \omega^h)]^2}} \quad (24)$$

$$\sigma(\lambda_S) = \sqrt{\frac{\Delta_S}{\sum_{i=1}^{N_{\text{mols}}} [S_{\text{vib},i}(T, \omega^h)]^2}} \quad (25)$$

Please note that the thermal correction to the enthalpy here excludes the ZPVE, since the ZPVE has been scaled separately in the previous subsection. Here $\Delta H_{\text{vib}}(T) = H_{\text{vib}}(T) - H_{\text{vib}}(0)$. Since the ZPVE makes up a large part of the $H_{\text{vib}}(T)$ at most relevant temperatures, scaling $H_{\text{vib}}(T)$ would closely resemble scaling of the ZPVE. Thus, we are scaling the vibrational correction to the enthalpy excluding the ZPVE.

Table 4 shows the scaling factors for $\Delta H_{\text{vib}}(T)$ determined using the procedure above. With the exception of the water trimer, the ratio of anharmonic to harmonic $\Delta H_{\text{vib}}(298.15 \text{ K})$ is between 1.09 and 1.11. A scaling factor exceeding unity makes sense here because harmonic vibrational frequencies and $\Delta H_{\text{vib}}(T)$ have an inverse relationship; as we scale down the harmonic frequencies,

Table 5. Scaling Factors for the MP2/aug-cc-pVDZ Harmonic $S_{\text{vib}}(298.15 \text{ K})$ of Water Clusters^{a,b}

	$S_{\text{vib}}^h(298.15 \text{ K})^b$	$S_{\text{vib}}^f(298.15 \text{ K})^b$	$S_{\text{vib}}^f(298.15 \text{ K})/S_{\text{vib}}^h(298.15 \text{ K})$
2- C_2	12.17	13.95	1.147
3-UUD	17.59	21.24	1.207
4- C_2	29.16	33.16	1.137
4- S_4	27.37	30.63	1.119
5-Cyclic	43.06	50.06	1.163
6-Book-1	52.37	59.84	1.143
6-Cage	48.19	56.21	1.166
6-Prism	47.44	55.44	1.169
6-Bag	52.94	62.54	1.181
8- S_4	61.33	69.49	1.133
8- D_{2d}	61.20	68.87	1.125
λ_S			1.150
$\sigma(\lambda_S)$			0.021
RMSE			0.945

^a Four hexamers (Cyclic-chair, Book-2, Cyclic-boat-1, and Cyclic-boat-2) and the D_{2d} DD nonamer are excluded because they had individual scaling factors ($\lambda_i = \nu_i / \omega_i$) that lie outside 3σ of the average λ . ^b In cal/mol/K.

the $\Delta H_{\text{vib}}(T)$ is scaled up. The overall scaling factor of 1.106 ± 0.011 works well as evidenced by the RMSE of 0.07 kcal/mol for the 11 clusters in this study. Table 5 shows the scaling factor for $S_{\text{vib}}(298.15 \text{ K})$ for the individual clusters and the collective group. All the scaling factors lie within the range of 1.12–1.21. Considering how sensitive the entropy is to the low-frequency modes (which are scaled down by 0.876), it should not come as a surprise that the entropy is scaled up by 10–20%. The overall scaling factor for this scheme is 1.150 ± 0.021 with an RMSE of 0.95 cal/mol/K.

The approach just outlined for scaling $\Delta H_{\text{vib}}(T)$ and $S_{\text{vib}}(T)$ has the advantage that it gives a simple multiplicative factor that can be applied directly to harmonic $\Delta H_{\text{vib}}(T)$ and $S_{\text{vib}}(T)$. An alternative approach that has been advocated in the literature seeks frequency scaling factors that minimize the residuals:

$$\Delta_H = \sum_{i=1}^N [\Delta H_{\text{vib}}(T, \lambda_H \omega_i^h) - \Delta H_{\text{vib}}(T, \nu_i^f)]^2 \quad (26)$$

$$\Delta_S = \sum_{i=1}^N [S_{\text{vib}}(T, \lambda_S \omega_i^h) - S_{\text{vib}}(T, \nu_i^f)]^2 \quad (27)$$

There is no analytic expression for the scaling factors, and they have to be determined numerically. The RMSE and uncertainty in the scaling factors are calculated in the same way as frequencies and ZPVEs. Along the same lines, it would make sense to separate the vibrational modes into three classes and scale each group independently. However, the vibrational corrections to both the enthalpy and entropy are overwhelmingly dominated by the low-frequency modes. Figure 4 shows a plot of $\Delta H_{\text{vib}}(298.15 \text{ K})$ and $S_{\text{vib}}(298.15 \text{ K})$ as a function of vibrational frequency. Vibrational modes of frequency exceeding 1100 cm^{-1} (i.e., intramolecular modes) make a very minimal contribution to $\Delta H_{\text{vib}}(298.15 \text{ K})$ and $S_{\text{vib}}(298.15 \text{ K})$. The contribution of the intramolecular modes to the enthalpy and entropy for small water clusters is typically around 1%, which is below 0.1 kcal/

mol. So, it is not necessary to separate the frequencies into classes and scale them differently.

Since low-frequency modes are the dominant contributors to ΔH_{vib} and S_{vib} , the frequency scaling factors that minimize ΔH_{vib} and S_{vib} residuals are similar to the scaling factor for low-frequency modes. Tables 6 and 7 show the frequency scaling factors for ΔH_{vib} and S_{vib} at temperatures ranging from 50 K to 373.15 K. At low temperatures, there is only enough thermal energy to populate all the ground vibrational levels of all the modes and the excited vibrational levels of the low-frequency modes. So, we see ΔH_{vib} and S_{vib} frequency scaling factors that reflect the scaling factor for low-frequency modes (0.876). As more thermal energy is available at higher temperatures, the excited vibrational levels of more modes start contributing, and the ΔH_{vib} and S_{vib} frequency scaling factors increase. At temperatures below 373.15 K, the ΔH_{vib} and S_{vib} frequency scaling factors are less than 0.870 and 0.845, respectively.

The uncertainty in the ΔH_{vib} frequency scaling factors is large, particularly at low temperatures, but the RMSE is very small. For the S_{vib} frequency scaling factors, both the uncertainty and the RMSE are small. Our scaling factors differ significantly from those in the literature which are intended for covalently bonded systems. Unlike our ΔH_{vib} (298.15 K) frequency scaling factor of 0.866 ± 0.040 , Sinha et al.⁵ and Merrick et al.⁷ report values of 0.9473 and 1.0359, respectively. Our S_{vib} (298.15 K) frequency scaling factor of 0.841 ± 0.016 is different from Sinha et al.'s⁵ 0.9049 and Merrick et al.'s⁷ 1.0452, respectively. Our RMSE is in general comparable to the two cited above.

The two approaches we have used to scale ΔH_{vib} and S_{vib} (scaling ΔH_{vib} and S_{vib} themselves or the vibrational frequencies that enter the ΔH_{vib} and S_{vib} expressions) are equivalent, but scaling the frequencies is advocated in this case because that approach is more rigorous. It also happens to be the approach taken by others in the literature.^{4,5,7}

3.5. Assessment of the Scaling Factors. The performance of the scaling factors reported above is evaluated in two ways. First, the vibrational scaling factors are applied to the water dimer, and the resulting vibrational frequencies are compared with experimental,

harmonic, and anharmonic frequencies. While the small RMSEs reported in Table 2 and the narrow error distribution shown in

Table 6. Frequency Scaling Factors for $\Delta H_{\text{vib}}(T)$ for Water Clusters at the MP2/aug-cc-pVDZ Level of Theory^a

T (K)	scaling factor (λ_H)	uncertainty [$\sigma(\lambda_H)$]	RMSE (kcal/mol)
50	0.806	0.117	0.00
100	0.835	0.087	0.00
150	0.851	0.069	0.01
200	0.860	0.055	0.01
250	0.865	0.045	0.01
273.15	0.866	0.042	0.01
298.15	0.868	0.039	0.01
300	0.868	0.039	0.01
350	0.871	0.034	0.01
373.15	0.872	0.033	0.01

^a Using 703 frequencies after removing outliers from an initial set of 723 frequencies.

Table 7. Frequency Scaling Factors for $S_{\text{vib}}(T)$ for Water Clusters at the MP2/aug-cc-pVDZ Level of Theory^a

T (K)	scaling factor (λ_S)	uncertainty [$\sigma(\lambda_S)$]	RMSE (cal/mol/K)
50	0.790	0.040	0.06
100	0.815	0.028	0.08
150	0.828	0.023	0.09
200	0.836	0.020	0.10
250	0.841	0.018	0.10
273.15	0.843	0.017	0.11
298.15	0.844	0.016	0.11
300	0.844	0.016	0.11
350	0.847	0.015	0.11
373.15	0.848	0.014	0.11

^a Using 703 frequencies after removing outliers from an initial set of 723 frequencies.

Figure 4. ΔH_{vib} and S_{vib} as a function of frequency at $T = 298.15$ K. Low-frequency modes contribute most greatly to ΔH_{vib} (left axis) and S_{vib} (right axis).

Table 8. Comparison of Calculated Harmonic,^a Scaled Harmonic,^{b–d} and Anharmonic^e Frequencies^f with Experimental^g Values for the Water Dimer

mode ^h	harmonic ^a	scaled			anharmonic ^e	experiment ^g
		uniform ^b	two-split ^c	three-split ^d		
donor torsion	127	121	112	112	108	88
acceptor wag	148	140	130	130	123	103
acceptor twist	151	143	132	132	124	108
intermol. stretch	184	174	161	161	152	143
in-plane bend	358	339	313	313	328	311
out-of-plane bend	639	605	560	560	514	523
ν_2 (a)	1624	1539	1543	1583	1581	1599
ν_2 (d)	1643	1557	1561	1601	1593	1616
ν_1 (d)	3704	3511	3520	3515	3554	3601
ν_1 (a)	3796	3597	3607	3602	3614	3660
ν_3 (d)	3904	3700	3710	3705	3720	3735
ν_3 (a)	3925	3720	3730	3725	3730	3745
RMSE	98	53	41	36	25	

^a MP2/aug-cc-pVDZ harmonic frequencies. ^b MP2/aug-cc-pVDZ harmonic frequencies scaled by 0.948. ^c MP2/aug-cc-pVDZ harmonic frequencies scaled by 0.876 and 0.950 for the inter- and intramolecular modes, respectively. ^d MP2/aug-cc-pVDZ harmonic frequencies scaled by 0.876, 0.975, and 0.949 for the intermolecular, bending, and stretching modes, respectively. ^e VPT2/MP2/aug-cc-pVDZ anharmonic frequencies. ^f In cm^{-1} . ^g See ref 37 and references therein. ^h ν_1 for symmetric stretching; ν_2 for bending; and ν_3 for asymmetric stretching. The use of (a) signifies hydrogen-bond acceptor water, and the (d) signifies the hydrogen-bond donor water.

Figure 3 speak to the reliability of our scaling approach, a comparison with experimental frequencies answers questions about the validity of using calculated anharmonic frequencies as proxies for experimental ones. Second, the ZPVE, ΔH_{vib} , and S_{vib} scaling factors are applied to 11 water clusters, and their effectiveness in reproducing anharmonic numbers is assessed.

3.5.1. Vibrational Scaling Factors Applied to $(\text{H}_2\text{O})_2$. The water dimer is a prototypical hydrogen-bonding system that has been the subject of extensive theoretical and experimental investigations. It remains the only water cluster for which all the experimental vibrational frequencies are available. Thus, it serves as an ideal system for assessing the performance of the harmonic, anharmonic, and scaled harmonic approaches outlined in Section 3.2.

A comparison of the theoretical harmonic and anharmonic frequencies and intensities of the water dimer against the experimental analogs has been performed by the research groups of Shields,³⁷ Jordan,⁵⁸ and Kjaergaard⁵⁷ among others. We perform a similar assessment on the MP2/aVDZ frequencies and scaling schemes in Table 8. The RMSE in the harmonic frequencies relative to experiment is large (98 cm^{-1}), but scaling it by different factors brings sizable improvements. As discussed earlier, using uniform scaling factors does not correct for the varying anharmonicity in the harmonic frequencies. Using the two- and three-split scalings gives substantially better agreement with experiment, with RMSEs of 41 and 36 cm^{-1} , respectively. The experimental frequencies are closer to the anharmonic frequencies ($\text{RMSE} = 25 \text{ cm}^{-1}$) than they are to the harmonic ones ($\text{RMSE} = 98 \text{ cm}^{-1}$). That observation further validates our decision to use calculated anharmonic frequencies as proxies for experimental frequencies. In the case of larger water clusters whose vibrational spectra are not resolved fully, calculated anharmonic frequencies serve an indispensable role.

3.5.2. ZPVE, ΔH_{vib} , and ΔS_{vib} Scaling Factors Applied to $(\text{H}_2\text{O})_{n=2-6,8}$. Here, we want to evaluate: (a) the ability of our scaling factors to map harmonic values onto anharmonic ones and (b) the magnitude of the anharmonic correction to the ZPVE,

ΔH_{vib} , and S_{vib} . The scaled harmonic ZPVE is calculated by multiplying the harmonic ZPVE by 0.976 (see Table 3), while the harmonic and anharmonic values are determined using eqs 5 and 7, respectively. For ΔH_{vib} and S_{vib} , the harmonic and anharmonic values are computed using eqs 16 and 17. The scaled harmonic values require proper frequency factors for $T = 298.15 \text{ K}$. Looking at Tables 6 and 7, those factors are $\lambda_H = 0.868$ and $\lambda_S = 0.844$ for ΔH_{vib} and S_{vib} . The harmonic frequencies are scaled by these factors before being input into eqs 16 and 17 to get the scaled harmonic ΔH_{vib} and S_{vib} .

Figure 5a–c displays a comparison of ZPVE, ΔH_{vib} (298.15 K), and S_{vib} (298.15 K) for 11 water clusters. It is quite evident that application of our scaling factors works remarkably well in mapping the harmonic values to their anharmonic analogs. Starting with the ZPVE, the largest absolute difference between the scaled harmonic and anharmonic value is only 0.39 kcal/mol for the S_4 octamer. This difference is small compared to the largest absolute difference between the harmonic and anharmonic ZPVE, which is 2.82 kcal/mol for the same S_4 octamer. The absolute difference between the scaled harmonic and anharmonic ZPVE ranges from 0.05 to 0.39 kcal/mol, while that between the harmonic and anharmonic values is 0.65 to 2.82 kcal/mol. Considering the magnitude of the ZPVE spans $\sim 28 \text{ kcal/mol}$ for the water dimer to $\sim 125 \text{ kcal/mol}$ for the octamer, the scaled harmonic value is matching the anharmonic one within 0.5% or less.

For ΔH_{vib} (298.15 K), we again see that our scaled harmonic value agrees remarkably well with the anharmonic value. The absolute difference between the scaled harmonic and anharmonic values ranges from 0.01 to 0.16 kcal/mol, while that between the harmonic and anharmonic values is 0.18 to 0.96 kcal/mol. Likewise, our scaled harmonic S_{vib} (298.15 K) is in great agreement with the anharmonic values. The absolute difference between the scaled harmonic and anharmonic value is in the range of 0.01–2.68 cal/mol/K, while the harmonic and anharmonic values differ by as much as 9.60 cal/mol/K.

Figure 5. Comparison of harmonic, scaled harmonic and anharmonic ZPVE(a), ΔH_{vib} (b) and S_{vib} (c) for 11 water clusters at 298.15 K. The harmonic and anharmonic frequencies are calculated using [VPT2]/MP2/aug-cc-pVDZ level of theory. We used a scaling factor of 0.976 to get the scaled harmonic ZPVE. The scaled harmonic ΔH_{vib} and S_{vib} are calculated using harmonic vibrational frequencies scaled by 0.868 and 0.844, respectively.

The apparent gap between the harmonic and anharmonic values for ZPVE and ΔH_{vib} and S_{vib} in Figure 5 is indicative of the importance of anharmonicity. The anharmonic correction, which we define as the difference between the harmonic and anharmonic values as a percentage of the anharmonic value, is 1.8–2.7% for the ZPVE, 8.7–13.4% for the ΔH_{vib} , and 10.7–17.2% for the S_{vib} . Given such large anharmonic corrections, it is very important that one accounts for them. More importantly, when scaling factors are used to correct for anharmonicity, it is essential that the proper scaling factors are used. Applying scaling factors intended for covalently bonded systems to hydrogen-bonded clusters could lead to large errors, even though we have not attempted to quantify them here.

3.6. Transferability of the Scaling Factors. The vibrational scaling factors we have determined are strictly intended for application to the MP2/aVDZ harmonic vibrational frequencies of water clusters. Even though our training set contains vibrational frequencies for $(\text{H}_2\text{O})_{n=2-6,8,9}$, the scaling factors should be applicable to larger water clusters. At the very least, they should perform better than conventional frequency scaling factors that are based on training sets of covalently bonded systems. The transferability of these scaling factors to other

hydrogen-bonded systems requires further investigation. Our preliminary look at sulfuric acid hydrates, $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_{n=1-2}$ yielded reasonable VPT2 fundamental frequencies (see Tables S17 and S18 of the Supporting Information) indicating that a scaling scheme similar to that we devised for water clusters can be developed. However, it is not as trivial to partition the vibrational frequencies into physically meaningful classes (such as intramolecular stretching, intramolecular bending, and intermolecular modes) as it is for water clusters. That is because nine of H_2SO_4 vibrational modes lie below 1000 cm^{-1} , which is in the same region as the hydrogen-bonded intermolecular modes. Thus, one would need to develop an algorithm to determine whether certain low-frequency modes are primarily intramolecular H_2SO_4 modes or intermolecular modes. While such an approach is certainly possible, it borders on the territory of other scaling methods like SQM and ESFF which are better equipped to handle such cases.

4. CONCLUSION

Using a training set of 16 water clusters with a combined 723 vibrational frequencies, we have determined scaling factors for vibrational frequencies, ZPVEs, $\Delta H_{\text{vib}}(T)$, and $S_{\text{vib}}(T)$ at the MP2/aug-cc-pVDZ level of theory. Our scaling factors were determined by comparing harmonic vibrational frequencies with VPT2 anharmonic fundamentals. For vibrational frequencies, it is important to separate the modes into different classes because of the varying range of anharmonicities. The disparity between our scaling factors and those derived from databases of covalently bonded systems highlights the need to use different scaling factors for hydrogen-bonded systems. The application of our scaling factors to the water dimer binding energy illustrates the importance of accounting for anharmonic effects. Our scaling factors can readily be applied to calculations on water clusters using the MP2/aug-cc-pVDZ level of theory, but their applicability to other hydrogen-bonded systems has yet to be tested. While VPT2 or the three-split scaling methods are the most reliable techniques for calculating anharmonic frequencies, the relatively good agreement using a single scaling factor supports the conclusions obtained from past studies of water cluster free energies.^{93,94}

■ ASSOCIATED CONTENT

S Supporting Information. All the MP2/aVDZ optimized geometries, energies, VPT2/MP2/aVDZ harmonic and fundamental frequencies for $(\text{H}_2\text{O})_{n=2-6,8,9}$ and $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_{n=1-2}$. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Supporting Information for:

The Role of Anharmonicity in Hydrogen Bonded
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Table S1: (H₂O)₂-Cs geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₂ C _s E[MP2/aVDZ]= -152.5302069 a.u.				Harmonic	Anharmonic
6				127	108
dimer				148	123
O	0.003386	0.000000	1.003796	151	124
H	0.765355	0.000000	0.411918	184	152
H	-0.764306	0.000000	0.406268	358	328
O	-2.467024	0.000000	-0.546582	639	514
H	-3.003066	-0.762684	-0.291013	1624	1581
H	-3.003066	0.762684	-0.291013	1643	1593
				3704	3554
				3796	3614
				3904	3720
				3925	3730

Table S2: (H₂O)₃-UUD geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₃ UUD E[MP2/aVDZ]= -228.8088005 a.u.				Harmonic	Anharmonic
9				156	128
3-UUD				172	144
H	-0.606830	-1.095067	0.024601	184	156
O	-1.478308	-0.659353	-0.057842	192	163
H	-2.036784	-1.080040	0.606958	233	177
O	1.310442	-0.949283	-0.050209	217	187
H	1.225115	0.024305	-0.001049	340	269
H	1.982185	-1.177920	0.603515	349	309
O	0.165110	1.606239	0.065606	441	360
H	-0.637413	1.048368	0.022543	568	433
H	0.079627	2.223414	-0.671526	664	586
				858	663
				1631	1592
				1634	1592
				1658	1593
				3575	3419
				3633	3464
				3641	3476
				3890	3700
				3894	3705
				3896	3708

Table S3: (H₂O)₄-S₄ geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₄ S ₄ E[MP2/aVDZ]= -305.0894329 a.u.				Harmonic	Anharmonic
12				49.958	45.75
4-S ₄				78.917	70.52
H	1.214527	2.216388	0.764022	209.193	185.25
O	1.023132	1.651613	0.005269	199.363	182.71
H	1.561716	-0.042153	0.004066	235.054	202.32
H	0.042152	1.561715	-0.004066	235.054	202.32
O	1.651615	-1.023133	-0.005269	252.417	221.88
H	2.216390	-1.214529	-0.764021	252.417	221.89
H	-0.042154	-1.561717	-0.004066	259.03	231.64
O	-1.023134	-1.651612	0.005269	288.225	252.95
H	-1.214531	-2.216387	0.764021	400.093	346.13
H	-1.561714	0.042152	0.004066	431.342	384.29
O	-1.651612	1.023132	-0.005269	447.982	398.04
H	-2.216387	1.214529	-0.764021	447.982	398.05
				748.337	694.58
				819.328	718.26
				819.329	718.27
				989.556	837.26
				1636.002	1595.31
				1651.185	1616.18
				1651.185	1616.18
				1681.262	1658.55
				3395.65	3249.86
				3486.321	3316.26
				3486.321	3316.28
				3523.551	3349.67
				3884.226	3692.17
				3885.528	3694.36
				3884.929	3694.37
				3884.929	3693.04

Table S4: (H₂O)₄-C_i geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₄ C _i E[MP2/aVDZ]= -305.0879996 a.u.				Harmonic	Anharmonic
12				29.112	31.038
4-ci				72.479	61.307
H	1.475188	-2.109404	0.673441	188.505	152.386
O	1.179124	-1.547316	-0.052830	203.743	179.53
H	1.547906	0.190137	0.010773	205.829	179.264
H	0.195931	-1.569030	-0.008950	240.037	209.142
O	1.552007	1.174235	0.054619	244.422	201.629
H	2.175745	1.451261	-0.627398	253.194	221.183
H	-0.195934	1.569029	0.008950	253.596	186.068
O	-1.179128	1.547318	0.052820	269.056	198.351
H	-1.475182	2.109406	-0.673453	385.66	351.967
H	-1.547909	-0.190137	-0.010781	402.176	348.066
O	-1.552011	-1.174236	-0.054610	485.384	443.256
H	-2.175741	-1.451248	0.627419	532.397	472.718
				663.276	634.864
				751.611	690.42
				829.298	700.425
				950.757	796.543
				1647.799	1604.8
				1649.005	1609.547
				1670.445	1627.668
				1680.001	1648.607
				3407.226	3268.108
				3486.798	3325.211
				3502.566	3339.072
				3529.946	3362.762
				3885.796	3695.285
				3886.6	3695.668
				3887.156	3691.255
				3887.539	3695.947

Table S5: (H₂O)₅-Cyclic geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₅ Cyclic E[MP2/aVDZ]= -381.3647344 a.u.				Harmonic	Anharmonic
15				23.483	19.545
5-cyclic				42.464	32.803
H	-0.972759	-1.684129	-0.084067	62.567	49.666
H	2.526700	-1.272626	0.968055	65.39	43.205
O	-0.204724	-2.296294	-0.177775	180.843	157.233
O	-2.266352	-0.528691	0.097773	193.115	137.635
H	-1.938217	0.400557	0.073642	200.039	147.745
H	-2.782296	-0.590427	0.910681	228.527	169.05
O	-1.185952	1.982012	-0.081836	235.965	205.269
H	-1.400137	2.719681	0.501615	240.589	206.84
H	-0.200693	1.928468	-0.070905	266.553	214.871
O	1.533013	1.731673	-0.048325	295.769	248.8
H	1.786163	0.783446	0.052976	299.557	260.721
H	2.007636	2.025999	-0.835448	302.504	266.5
O	2.125877	-0.922617	0.163277	410.579	375.47
H	1.306860	-1.457570	0.034316	429.896	375.877
H	-0.355647	-2.755632	-1.012842	453.163	400.484
				466.338	415.693
				512.63	468.686
				721.191	669.636
				787.07	716.823
				865.438	744.253
				881.125	769.378
				984.4	857.331
				1640.467	1598.058
				1652.082	1621.863
				1660.213	1636.922
				1681.013	1627.78
				1688.845	1602.13
				3353.788	3144.346
				3433.326	3275.333
				3442.183	3282.28
				3486.953	3313.942
				3494.005	3324.797
				3882.765	3689.378
				3884.968	3689.106
				3886.789	3694.497
				3886.981	3696.495
				3888.698	3699.29

Table S6: (H₂O)₆-Cyclic chair geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₆ Cyclic-chair E[MP2/aVDZ]= -457.6397288 a.u.				Harmonic	Anharmonic
18				30.111	14.673
6-cyclic-chair				30.111	14.726
H	-0.831866	2.210850	-0.030212	46.581	23.007
O	0.014001	2.706065	-0.141981	46.581	22.771
H	-0.109130	3.222499	-0.947495	53.624	37.388
H	1.498701	1.825830	0.030840	84.66	59.936
O	-2.336529	1.365123	0.142274	158.866	142.157
H	-2.845374	1.516451	0.947814	182.032	148.22
H	-2.330579	0.385009	0.030202	207.528	158.008
O	-2.350467	-1.340878	-0.142819	207.532	158.432
H	-1.498700	-1.825828	-0.030850	215.862	187.994
H	-2.735917	-1.705653	-0.948478	215.863	187.901
O	-0.014002	-2.706068	0.141981	267.289	201.522
H	0.109123	-3.222494	0.947501	267.292	201.952
H	0.831864	-2.210852	0.030215	295.106	238.832
O	2.336527	-1.365122	-0.142266	299.417	267.349
H	2.330579	-0.385006	-0.030202	299.418	267.318
H	2.845381	-1.516459	-0.947798	331.906	294.916
O	2.350470	1.340882	0.142805	418.876	373.305
H	2.735919	1.705653	0.948466	438.01	381.737
				438.013	381.548
				458.151	408.346
				465.082	423.499
				465.083	423.401
				781.972	710
				803.871	716.86
				803.873	716.873
				900.771	783.664
				900.775	782.382
				978.33	840.525
				1635.857	1579.52
				1648.262	1627.048
				1648.262	1621.4
				1678.842	1624.586
				1678.843	1624.577
				1696.931	1622.203
				3348.465	3145.832
				3420.613	3276.028
				3420.615	3276.04
				3475.999	3304.401
				3476	3304.399
				3494.118	3320.114
				3887.079	3695.808
				3887.151	3695.801
				3887.151	3695.699
				3887.585	3699.897
				3887.585	3699.797
				3887.996	3696.371

Table S7: (H₂O)₆-Book-1 geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₆ Book-1 E[MP2/aVDZ]= -457.6418357 a.u.				Harmonic	Anharmonic
18				27.784	16.954
6-book-1				38.786	29.743
H	3.587741	5.431675	4.279365	55.58	46.161
H	4.099179	5.244158	5.738394	69.498	55.939
H	6.184675	5.081186	4.706913	87.655	77.592
H	7.554866	5.712418	4.979451	155.642	125.967
H	7.139008	7.896633	4.985358	182.029	158.487
H	8.512417	7.867699	4.283524	189.464	157.992
H	4.957618	8.810819	5.597089	198.218	172.251
H	4.881584	7.418557	4.933387	227.824	198.432
H	3.803815	4.808027	8.033109	236.666	206.61
H	4.931421	4.005915	7.333809	254.05	208.726
H	6.909855	4.031200	6.465899	255.276	215.672
H	6.905003	2.684257	7.240083	279.262	247.545
O	4.293859	5.700184	4.879957	289.398	247.165
O	7.094090	4.847207	4.962753	297.991	264.35
O	8.032034	7.491761	5.031418	311.099	270.55
O	5.364980	8.271329	4.908550	387.276	347.533
O	6.606979	3.599541	7.305362	403.125	357.057
O	4.017277	4.363336	7.203678	442.628	410.865
				453.943	407.544
				480.956	437.979
				543.016	475.286
				616.587	521.773
				730.608	648.548
				754.782	666.495
				837.913	728.964
				858.437	753.348
				907.688	808.225
				1025.417	900.824
				1631.551	1614.821
				1644.984	1607.997
				1647.123	1614.034
				1666.651	1625.812
				1678.307	1635.642
				1707.409	1670.153
				3285.43	3068.04
				3362.287	3169.735
				3414.879	3265.397
				3515.719	3355.648
				3570.074	3397.803
				3586.175	3415.438
				3734.822	3546.317
				3877.443	3685.701
				3882.208	3691.765
				3884.865	3693.115
				3886.254	3693.712
				3888.919	3697.177

Table S8: (H₂O)₆-Cage geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₆ Cage E[MP2/aVDZ]= -457.6426191 a.u.				Harmonic	Anharmonic
18				45.07	32.093
6-cage				57.615	45.372
H	0.063746	1.370228	-0.535519	74.365	63.774
O	0.593274	1.729598	0.229481	98.837	86.396
H	0.508196	2.689491	0.179344	123.264	96.798
H	2.159040	0.826090	0.162036	149.371	123.754
H	-1.628481	0.235804	-1.244624	184.474	148.671
O	2.811279	0.098384	0.056408	197.565	133.566
H	1.683728	-1.219015	-0.321381	211.26	171.496
H	3.298495	0.077966	0.889701	224.525	199.508
O	0.851442	-1.722144	-0.484056	233.817	198.349
H	1.128737	-2.606198	-0.753349	243.556	210.998
H	-0.285241	-0.446030	-1.532575	244.769	217.693
H	-0.188665	-1.097262	1.091688	260.953	201.103
O	-0.755781	0.397638	-1.659951	287.883	257.516
O	-0.684248	-0.493866	1.675160	305.397	262.619
H	-2.247829	-0.249640	0.785869	387.678	350.781
H	-0.266370	0.366609	1.492462	403.029	359.416
O	-2.892720	0.022876	0.094390	431.297	394.262
H	-3.651893	-0.562557	0.198037	456.762	398.055
				473.176	422.689
				530.529	473.539
				563.87	457.095
				636.411	525.675
				692.193	582.996
				736.134	656.229
				800.473	697.038
				818.053	701.345
				879.1	752.889
				1011.608	889.284
				1638.827	1613.202
				1647.951	1598.668
				1660.551	1618.276
				1674.142	1621.972
				1681.586	1636.154
				1696.477	1653.73
				3224.341	2980.609
				3442.128	3298.695
				3483.361	3315.976
				3533.046	3348.784
				3590.729	3410.274
				3670.838	3490.487
				3723.936	3520.726
				3761.534	3555.326
				3877.668	3684.213
				3880.204	3691.726
				3883.441	3690.355
				3894.506	3708.601

Table S9: (H₂O)₆-Prism geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₆ Prism E[MP2/aVDZ]= -457.6430159 a.u.				Harmonic	Anharmonic
18				62.863	45.158
6-prism				70.995	56.732
H	0.280085	-1.115676	-1.505747	75.109	62.578
O	1.233799	-1.200715	-1.323362	88.293	60.929
H	1.541956	-0.278331	-1.281840	99.802	71.03
H	-0.441637	-0.685016	1.573766	146.494	113.207
O	-1.408814	-0.468633	1.450722	169.963	155.623
H	-1.851253	-0.760546	2.256739	175.017	150.095
H	1.288019	-1.285926	0.546403	212.202	183.105
O	1.213913	-0.927730	1.459038	222.945	198.351
H	1.611248	-0.048005	1.336866	237.83	206.345
H	-2.314717	-1.355258	-1.690243	247.886	221.089
O	-1.650089	-0.778247	-1.294237	280.032	245.043
H	-1.753027	-0.882003	-0.324695	288.271	256.298
H	-1.315577	1.367221	-0.914751	295.211	264.947
O	-0.976746	1.863882	-0.152405	359.327	298.119
H	-1.243438	1.290115	0.590232	368.823	317.683
H	0.792641	1.741734	-0.176619	426.906	371.215
O	1.734212	1.447372	-0.158826	429.806	364.518
H	2.256902	2.248508	-0.284693	467.712	403.243
				491.655	416.761
				539.367	480.621
				556.226	467.648
				620.964	525.49
				646.301	540.675
				691.826	566.087
				735.644	640.107
				848.193	788.543
				898.6	779.728
				1040.425	940.258
				1635.773	1606.005
				1648.623	1611.303
				1655.344	1605.427
				1673.696	1623.863
				1690.321	1653.755
				1709.327	1740.965
				3196.981	2949.949
				3437.538	3279.441
				3534.651	3303.495
				3565.241	3366.748
				3667.047	3487.273
				3677.388	3481.929
				3754.628	3546.137
				3771.545	3578.604
				3805.122	3604.428
				3879.817	3687.202
				3883.907	3692.713
				3885.128	3692.285

Table S10: (H₂O)₆-Book-2 geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₆ Book-2 E[MP2/aVDZ]= -457.6414447 a.u.				Harmonic	Anharmonic
18				23.148	2.588
6-book-2				30.76	19.265
O	2.305230	1.271784	-0.403092	40.5	37.999
H	3.223784	1.463814	-0.178001	68.645	46.964
H	2.286365	0.298477	-0.587624	85.795	68.629
O	2.025571	-1.399657	-0.678701	153.552	123.61
H	1.775147	-1.804813	-1.518038	190.23	165.967
H	1.242649	-1.534250	-0.085401	205.171	178.941
O	-0.089941	-1.445594	1.017708	210.101	182.116
H	-0.072179	-0.521941	1.323776	223.618	199.601
H	-0.930735	-1.500142	0.516594	237.071	207.952
O	-2.367388	-1.241556	-0.605451	251.524	221.758
H	-3.264516	-1.467065	-0.330597	261.723	225.28
H	-2.355823	-0.260300	-0.654295	269.755	230.683
O	-2.008184	1.505372	-0.534949	285.671	251.81
H	-1.750468	1.979067	-1.335618	290.529	261.119
H	-1.242086	1.602725	0.069499	298.742	238.775
O	0.162802	1.465119	1.220103	389.004	352.594
H	0.267342	2.075080	1.960340	408.911	343.277
H	1.014174	1.501505	0.715029	438.343	395.511
				454.005	419.054
				534.342	469.953
				569.3	510.973
				641.683	552.738
				735.916	658.229
				764.676	674.951
				809.39	682.591
				838.307	759.964
				873.898	764.836
				984.818	854.284
				1638.954	1610.144
				1651.162	1596.516
				1656.297	1597.282
				1673.822	1657.14
				1691.713	1591.74
				1702.181	1651.307
				3285.636	3012.266
				3368.044	3124.785
				3408.869	3249.66
				3501.846	3341.809
				3569.866	3398.507
				3583.246	3408.763
				3739.62	3549.213
				3880.092	3687.594
				3881.297	3692.73
				3881.709	3691.074
				3883.806	3691.242
				3886.533	3691.528

Table S11: (H₂O)₆-Bag geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₆ Bag E[MP2/aVDZ]= -457.6406749 a.u.				Harmonic	Anharmonic
18				34.52	19.143
6-bag				43.441	31.32
O	-1.019343	1.600534	-0.468309	52.14	41.607
H	-0.031108	1.700552	-0.379547	63.739	46.097
H	-1.327825	2.455286	-0.793754	80.113	60.845
O	-0.097581	-1.934622	0.494430	155.041	96.86
H	-0.531324	-1.349998	1.145244	174.66	137.822
H	-0.594348	-1.748932	-0.326266	185.945	157.03
O	1.634535	1.716180	-0.186563	194.017	165.697
H	1.952634	2.102384	0.639466	201.3	168.357
H	1.959619	0.779768	-0.155356	205.069	146.157
O	2.346927	-0.868300	0.051856	218.758	183.217
H	2.787546	-1.374963	-0.640749	245.5	215.611
H	1.489115	-1.339457	0.215377	285.615	254.277
O	-1.323517	0.196773	1.963586	288.876	257.572
H	-2.190946	0.206283	2.385829	314.605	285.37
H	-1.403622	0.795711	1.195308	322.694	267.99
O	-1.342826	-0.864363	-1.818698	388.466	347.655
H	-1.339402	0.052150	-1.475837	405.281	362.158
H	-2.236756	-1.008062	-2.151951	443.571	408.86
				484.817	417.319
				496.936	441.206
				557.555	518.588
				636.672	496.85
				663.871	560.178
				711.639	590.752
				776.378	696.028
				863.18	782.337
				948.345	837.053
				997.88	898.908
				1645.187	1597.598
				1648.32	1603.742
				1657.721	1610.457
				1674.334	1641.726
				1696.022	1670.427
				1699.205	1646.646
				3211.049	2992.082
				3311.609	3082.679
				3386.12	3171.372
				3585.022	3419.37
				3614.997	3441.465
				3637.066	3461.929
				3697.503	3496.235
				3872.081	3681.372
				3873.447	3685.329
				3886.013	3695.856
				3891.367	3700.597
				3894.538	3704.123

Table S12: (H₂O)₆-Cyclic boat-1 geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₆ cyclic-boat-1 E[MP2/aVDZ]= -457.63818 a.u.				Harmonic	Anharmonic
18				20.632	5.326
6-cyclic-boat-1				29.793	17.605
O	-0.964938	-2.122656	-0.415391	36.674	24.765
H	-1.160652	-2.908291	-0.939494	41.638	28.852
H	0.020007	-2.083012	-0.371327	45.019	6.897
O	1.753649	-1.961908	-0.326495	74.246	60.284
H	2.091172	-1.036763	-0.383746	168.773	142.763
H	2.209985	-2.338977	0.435549	197.07	142.454
O	2.667259	0.604895	-0.471102	199.348	138.665
H	2.174156	1.241812	0.097603	207.464	140.864
H	2.698781	1.018903	-1.341761	219.026	180.294
O	-2.289078	0.235629	-0.747605	224.92	191.747
H	-2.267440	0.461980	-1.685016	240.454	130.761
H	-1.814645	-0.626202	-0.681259	267.169	210.066
O	1.284203	2.253456	1.200608	268.854	176.138
H	1.492450	3.190094	1.298353	289.945	255.479
H	0.299201	2.213141	1.158437	299.053	263.03
O	-1.431881	2.122870	1.026545	320.224	283.156
H	-1.748791	1.446036	0.382684	412.288	366.754
H	-1.934270	1.945135	1.831000	416.294	369.825
				441.534	397.626
				457.205	419.658
				501.671	441.132
				504.502	465.801
				740.979	689.511
				757.24	674.255
				824.446	732.625
				874.557	760.472
				904.051	746.86
				960.929	801.559
				1640.725	1607.48
				1644.672	1610.356
				1657.483	1629.177
				1673.981	1622.035
				1684.891	1587.678
				1693.258	1614.259
				3353.965	3116.798
				3417.468	3264.902
				3428.51	3282.241
				3473.869	3307.755
				3485.114	3320.139
				3496.019	3329.18
				3884.526	3692.077
				3884.719	3693.035
				3888.955	3697.741
				3889.176	3698.464
				3890.025	3703.308
				3890.089	3700.526

Table S13: (H₂O)₆-Cyclic boat-2 geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₆ cyclic-boat-2 E[MP2/aVDZ]= -457.6379985 a.u.				Harmonic	Anharmonic
18				21.082	6.192
6-cyclic-boat-2				29.924	16.303
O	-1.038094	-2.228715	-0.562432	36.939	17.379
H	-1.339570	-2.751800	0.190588	41.381	15.693
H	-0.064309	-2.145562	-0.434192	44.09	3.551
O	1.640603	-1.893245	-0.179736	70.979	63.192
H	1.995123	-0.983505	-0.316871	169.645	143.261
H	2.316444	-2.482609	-0.534248	179.452	68.191
O	2.600126	0.644203	-0.487223	181.913	70.343
H	2.163344	1.300520	0.106904	194.051	117.251
H	2.622735	1.073810	-1.350603	218.406	189.601
O	-2.224278	0.218622	-0.776667	220.646	147.006
H	-2.194849	0.426655	-1.718131	230.091	195.415
H	-1.806698	-0.672992	-0.704780	259.364	203.019
O	1.360426	2.435788	1.154653	274.12	217.891
H	1.613419	2.364733	2.083356	286.24	246.945
H	0.383016	2.308201	1.152187	299.802	261.726
O	-1.327847	1.982967	1.104123	320.45	278.326
H	-1.658354	1.367475	0.408385	406.742	374.669
H	-1.995195	2.676393	1.164084	408.123	374.478
				434.615	398.621
				452.49	419.202
				518.71	460.948
				526.839	473.21
				744.265	660.36
				770.941	669.609
				794.93	692.04
				825.69	719.28
				918.2	775.608
				937.767	802.682
				1643.142	1601.187
				1651.868	1621.343
				1660.255	1625.841
				1675.376	1624.769
				1684.61	1569.055
				1695.072	1611.977
				3356.313	3098.671
				3413.577	3266.739
				3436.039	3285.357
				3476.064	3313.884
				3489.321	3321.488
				3500.481	3330.342
				3882.689	3691.082
				3882.759	3691.831
				3887.762	3696.95
				3888.161	3697.692
				3892.784	3704.907
				3892.794	3704.059

Table S14: (H₂O)₈-S4 geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₈ S4 E[MP2/aVDZ]=-610.2105722 a.u.				Harmonic	Anharmonic
24				69.203	54.706
8-S4				73.283	56.288
H	-1.348963	-0.813717	1.532407	74.274	63.439
O	-0.061639	-1.900221	1.365265	74.274	63.403
H	0.752336	-1.381895	1.517644	78.806	65.95
H	0.274391	-2.704981	-2.102680	108.537	93.55
O	2.002094	0.064076	1.476004	164.848	141.267
O	-2.002081	-0.064082	1.476021	165.971	139.435
H	-2.704981	-0.274413	2.102678	165.971	139.45
H	-2.141419	0.008498	-0.419807	174.654	149.77
H	-0.752321	1.381885	1.517657	189.989	166.653
O	0.061652	1.900213	1.365274	207.401	182.177
H	0.008499	2.141413	0.419821	207.892	183.401
H	1.348975	0.813710	1.532397	207.893	183.402
O	1.900213	-0.061646	-1.365275	276.159	252.326
O	-1.900224	0.061649	-1.365262	281.796	254.301
H	-1.381897	-0.752324	-1.517646	289.12	260.482
H	-0.274421	2.704997	-2.102653	292.352	268.364
O	0.064067	-2.002082	-1.476019	292.352	268.279
H	-0.008494	-2.141417	0.419811	305.42	278.815
H	0.813704	-1.348967	-1.532409	305.421	279.027
H	2.141414	-0.008498	-0.419823	317.162	292.318
H	2.705002	0.274410	2.102651	448.977	401.933
O	-0.064082	2.002090	-1.476006	454.833	404.75
H	-0.813716	1.348971	-1.532393	484.399	427.556
H	1.381891	0.752331	-1.517657	484.4	427.465
				505.023	459.581
				558.832	493.129
				558.832	493.222
				567.851	497.561
				624.251	533.533
				668.652	581.487
				690.335	594.01
				690.336	594.062
				727.534	616.114
				727.534	616.07
				741.89	626.016
				827.643	799.891
				975.564	879.393
				975.565	879.361
				1044.677	943.338
				1070.102	965.122
				1635.952	1596.657
				1642.906	1609.015
				1642.906	1609.105
				1657.515	1623.761
				1680.517	1704.929
				1690.188	1643.809
				1690.188	1643.747
				1714.779	1680.84
				3221.746	2963.902
				3246.884	2984.411
				3275.206	3028.786
				3275.208	3028.754
				3602.329	3422.353
				3608.037	3425.331
				3608.037	3425.318
				3618.664	3431.774
				3666.032	3463.437
				3693.072	3484.688
				3693.072	3484.659
				3711.541	3497.777
				3878.265	3685.044
				3878.288	3685.47
				3878.288	3685.333
				3878.364	3685.839

Table S15: (H₂O)₈-D2d geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₈ D2d E[MP2/aVDZ]= -610.2106012 a.u.				Harmonic	Anharmonic
24				70.989	57.224
8-D2d				74.529	64.419
H	2.146397	0.283150	0.351411	75.666	63.657
O	1.917663	0.261579	-1.330631	77.456	67.24
H	1.251793	0.950763	-1.520737	77.456	67.243
H	1.454428	-0.575482	-1.528721	109.549	96.907
O	-0.281248	2.066115	-1.343578	164.163	140.505
O	0.265747	-2.053960	-1.365122	170.915	148.549
O	2.067823	0.267528	1.343824	176.373	150.787
H	-1.471804	0.589098	-1.506726	176.373	150.743
H	-0.286745	2.145950	-0.351158	189.557	167.766
H	-0.401758	2.960443	-1.685082	207.596	184.984
H	0.382283	-2.945195	-1.715962	208.214	181.961
H	-1.269167	-0.937147	-1.514703	208.216	181.962
H	0.282627	-2.142658	-0.373583	271.075	248.922
H	2.962588	0.384533	1.685402	276.47	249.65
H	0.952647	-1.267224	1.506750	278.297	258.535
H	0.591052	1.456387	1.520988	283.471	257.351
O	0.263199	-1.931104	1.310733	283.471	257.351
H	-2.142197	-0.286335	0.373476	301.101	273.351
H	-0.935188	1.253715	1.528843	316.444	289.919
O	-0.248001	1.919354	1.330865	316.445	290.071
H	-0.573594	-1.469898	1.514602	440.545	403.433
O	-2.052239	-0.279577	1.365022	466.768	411.037
O	-1.932776	-0.249724	-1.310820	466.769	410.994
H	-2.943032	-0.399675	1.715786	512.882	461.802
				520.547	460.535
				534.87	482.809
				552.603	481.072
				552.605	481.002
				609.065	524.89
				690.977	593.83
				690.979	593.768
				699.833	609.797
				711.917	601.083
				711.918	601.072
				738.687	632.85
				849.116	798.26
				930.472	832.983
				1031.334	920.736
				1031.335	920.754
				1093.989	975.719
				1641.328	1621.979
				1641.328	1621.971
				1644.984	1609.169
				1652.018	1619.624
				1669.335	1632.65
				1669.335	1632.641
				1697.029	1638.164
				1712.623	1720.299
				3225.633	2966.365
				3250.208	3002.634
				3250.208	3002.636
				3309.627	3067.848
				3601.816	3421.523
				3601.817	3421.434
				3618.37	3432.094
				3620.303	3434.183
				3667.33	3466.507
				3668.089	3466.87
				3713.691	3502.059
				3713.693	3501.982
				3878.584	3686.861
				3878.584	3686.799
				3878.637	3686.276
				3878.71	3686.677

Table S16: (H₂O)₉-D2dDD geometry, harmonic and VPT2 fundamental frequencies

(H ₂ O) ₉ D2dDD E[MP2/aVDZ]= -686.4871616 a.u.				Harmonic	Anharmonic
27				44.991	23.742
9-D2dDD				57.695	34.869
H	-2.588062	0.410981	-0.043732	60.12	41.613
O	-2.424043	-1.268084	0.082306	68.373	54.912
H	-1.854987	-1.407021	0.864333	73.223	59.117
H	-1.858003	-1.534886	-0.668225	73.473	60.109
O	-0.450380	-1.161191	2.129009	79.054	63.239
O	-0.439747	-1.510473	-1.939160	107.829	92.669
O	-2.473271	1.398039	-0.114465	159.86	135.841
H	0.812753	-1.817580	0.903948	167.994	143.666
H	-0.373915	-0.168952	2.098685	168.999	146.174
H	-0.476926	-1.396937	3.064268	172.884	149.138
H	-0.433751	-1.877386	-2.831560	185.134	160.879
H	0.827071	-1.966347	-0.628332	200.837	177.561
H	-0.348657	-0.525289	-2.047874	206.683	179.993
H	-3.362827	1.769117	-0.155826	211.888	186.205
H	-1.109402	1.412133	-1.436340	249.636	170.827
H	-1.136384	1.643393	1.209676	268.719	246.593
O	-0.317621	1.164674	-1.951814	272.696	245.739
H	2.391698	1.263676	-0.069070	278.087	253.79
H	0.400983	1.747816	1.210113	286.02	256.551
O	-0.354217	1.490301	1.774595	293.435	260.906
H	0.428465	1.497786	-1.415258	302.211	272.627
O	1.709086	1.983298	-0.118801	304.255	271.782
O	1.407187	-2.021795	0.156152	316.995	289.427
H	2.204770	2.801206	-0.247852	326.187	296.79
O	3.317878	-0.152237	-0.069170	447.827	413.336
H	2.662905	-0.892808	0.033374	449.83	414.215
H	4.015288	-0.339163	0.570457	458.655	415.191
				495.474	451.479
				516.23	469.147
				519.243	474.496
				543.495	484.433
				561.477	482.799
				599.195	522.908
				623.189	543.691
				671.119	579.765
				697.78	596.475
				705.903	613.675
				711.077	612.463
				717.395	602.852
				751.114	647.068
				833.118	729.579
				887.73	778.241
				926.571	846.065
				975.922	879.909
				1031.154	932.249
				1076.008	952.841
				1640.825	1627.719
				1644.915	1610.515
				1650.971	1607.318
				1658.496	1608.126
				1666.133	1638.174
				1672.141	1640.358
				1689.513	1650.263

	1707.558	1658.948
	1720.898	1683.39
	3221.51	2967.587
	3242.06	2988.781
	3249.258	3010.057
	3304.902	3067.772
	3348.444	3102.794
	3593.662	3414.685
	3597.115	3417.931
	3614.736	3429.498
	3616.959	3430.474
	3658.228	3460.979
	3659.077	3461.287
	3708.475	3497.445
	3708.862	3497.182
	3876.665	3686.273
	3878.173	3686.049
	3878.299	3685.921
	3880.157	3687.105
	3885.346	3695.886

Table S17: H₂SO₄(H₂O) geometry, harmonic and VPT2 fundamental frequencies

H ₂ SO ₄ (H ₂ O) E[MP2/aVDZ]= -775.3458802 a.u.				Harmonic	Anharmonic
10				3887.781	3694.528
H2SO4-H2O				3733.235	3545.039
S	0.594190	-0.065769	0.143077	3722.734	3541.646
O	-0.214132	0.380971	1.295342	3172.862	2945.480
O	1.862273	-0.793093	0.274174	1620.165	1577.788
O	-0.334112	-0.921767	-0.868343	1453.450	1396.675
O	0.864057	1.318115	-0.711711	1330.499	1300.628
H	-1.277205	-0.613504	-0.717426	1172.736	1141.371
H	1.583553	1.115936	-1.338730	1138.873	1126.240
O	-2.688060	0.087604	-0.122458	855.957	831.166
H	-2.287680	0.396082	0.709225	819.075	736.895
H	-3.430800	-0.470822	0.143212	771.369	751.470
				526.735	477.687
				511.707	502.904
				497.648	487.206
				466.156	448.141
				396.599	372.399
				360.305	330.203
				328.152	296.560
				259.267	235.336
				224.939	204.486
				208.898	179.443
				137.960	118.165
				45.977	40.137

Table S18: H₂SO₄(H₂O)₂ geometry, harmonic and VPT2 fundamental frequencies

H ₂ SO ₄ (H ₂ O) ₂ E[MP2/aVDZ]= -851.6269964 a.u.				Harmonic	Anharmonic
13				3884.527	3691.217
H2SO4(H2O)2				3883.685	3690.883
S	0.000001	0.504634	-0.000002	3714.655	3525.088
O	-1.140821	1.219550	-0.606426	3713.239	3520.517
O	1.140821	1.219554	0.606419	3215.067	2983.631
O	-0.541711	-0.506215	1.148028	3197.540	2970.746
O	0.541713	-0.506221	-1.148027	1624.996	1581.114
H	-1.448275	-0.806066	0.844591	1623.617	1580.673
H	1.448277	-0.806070	-0.844588	1447.579	1394.481
O	-2.970177	-0.884504	0.091208	1382.478	1321.975
H	-3.164585	-1.590702	-0.539602	1276.065	1251.246
H	-2.819416	-0.092411	-0.454865	1132.028	1118.696
O	2.970179	-0.884504	-0.091204	875.745	828.584
H	3.164586	-1.590699	0.539610	851.220	768.089
H	2.819417	-0.092409	0.454865	841.460	770.290
				799.446	782.300
				555.162	483.167
				532.784	450.468
				514.718	506.623
				509.025	503.222
				490.017	480.415
				396.624	378.554
				358.798	340.215
				326.295	284.612
				313.603	284.533
				239.285	206.594
				236.115	187.627
				229.115	190.677
				218.636	200.765
				146.685	123.850