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Estimation, Computation, and Experimental Correction of Molecular Zero-Point Vibrational Energies

Gábor I. Csonka,*,[†] Adrienn Ruzsinszky,[‡] and John P. Perdew[‡]

Department of Inorganic Chemistry, Budapest University of Technology and Economics,
H-1521 Budapest, Hungary, and Department of Physics and Quantum Theory Group, Tulane University,
New Orleans, Louisiana 70118

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For accurate thermochemical tests of electronic structure theory, accurate true anharmonic zero-point vibrational energies $\mathrm{ZPVE^{true}}$ are needed. We discuss several possibilities to extract this information for molecules from density functional or wave function calculations and/or available experimental data: (1) Empirical universal scaling of density-functional-calculated harmonic $\mathrm{ZPVE^{harm}}$s, where we find that polyatomics require smaller scaling factors than diatomics. (2) Direct density-functional calculation by anharmonic second-order perturbation theory PT2. (3) Weighted averages of harmonic $\mathrm{ZPVE^{harm}}$ and fundamental $\mathrm{ZPVE^{fund}}$ (from fundamental vibrational transition frequencies), with weights ($^3/_4$, $^1/_4$) for diatomics and ($^5/_8$,$^3/_8$) for polyatomics. (4) Experimental correction of the PT2 harmonic contribution, i.e., the estimate $\mathrm{ZPVE_{PT2}^{true}} + (\mathrm{ZPVE_{expt}^{fund}} - \mathrm{ZPVE_{PT2}^{fund}})$ for $\mathrm{ZPVE^{true}}$. The ($^5/_8$,$^3/_8$) average of method 3 and the additive correction of method 4 have been proposed here. For our database of experimental $\mathrm{ZPVE^{true}}$, consisting of 27 diatomics and 8 polyatomics, we find that methods 1 and 2, applied to the popular B3LYP and the nonempirical PBE and TPSS functionals and their one-parameter hybrids, yield polyatomic errors on the order of 0.1 kcal/mol. Larger errors are expected for molecules larger than those in our database. Method 3 yields errors on the order of 0.02 kcal/mol, but requires very accurate (e.g., experimental, coupled cluster, or best-performing density functional) input harmonic $\mathrm{ZPVE^{harm}}$. Method 4 is the best-founded one that meets the requirements of high accuracy and practicality, requiring as experimental input only the highly accurate and widely available $\mathrm{ZPVE_{expt}^{fund}}$ and producing errors on the order of 0.05 kcal/mol that are relatively independent of functional and basis set. As a part of our study, we also test the ability of the density functionals to predict accurate equilibrium bond lengths and angles for a data set of 21 mostly polyatomic molecules (since all calculated ZPVEs are evaluated at the correspondingly calculated molecular geometries).

1. Introduction

Accurate thermochemical calculations using quantum chemical methods require precise electronic energies, anharmonic zero-point vibrational energies (ZPVEs) for enthalpies at 0 K, and thermal corrections for enthalpies at different temperatures, usually 298.15 K. Recent developments have made it possible to determine total electronic energies to a very high accuracy for small molecules by very expensive methods.[1] These accurate methods require similarly or more accurate ZPVEs. For small molecules, ZPVEs can be measured and calculated at the required level of precision.[2] However, this task is computationally very expensive and/or experimentally very difficult for larger polyatomic molecules. A simple alternative is to calculate the harmonic ZPVE of a molecule by the relatively cheap Hartree−Fock (HF, e.g., HF/6-31G(d)) or density functional theory (DFT) B3LYP[3] or B3PW91[4] models and to scale the calculated ZPVE with an empirical scaling factor to obtain an approximation to the true ZPVE. These scaling factors are based on experimental data for small, mostly diatomic molecules.[5,6] However, using a single scaling factor for a large set of different molecules might lead to an inaccurate ZPVE.[7] For *n*-octane (C_8H_{18}) the difference between scaled (0.8929) HF/6-31G(d) and (0.9854) B3LYP/6-31G(2df,p) true ZPVEs is 4.20 kcal/mol.

Several successful thermochemical methods use a mixture of models to calculate molecular geometry and ZPVE. For example, in the G3 theory[8,9] the geometries are calculated at the second-order Moller−Plesset perturbation theory level with the 6-31G(d) basis set, MP2(FU)/6-31G(d), but the scaled zero-point energies are calculated at the Hartree−Fock level with the 6-31G(d) basis set, HF/6-31G(d). We note that the HF/6-31G(d) scaling factor (0.8929) used in the G3 procedure was based on fitting of experimental vibrational frequencies, not zero-point energies.

Part of the source of error for the nonhydrogen species in the G3 theory results was traced back to the MP2/6-31G(d) geometries used for single-point energies. Use of experimental geometries instead of MP2/6-31G(d) in a small subset of nonhydrogens reduced the deviations in those molecules, but they still remained around 3−4 kcal/mol. The remainder of the error was assigned to basis set deficiencies. To assess the deficiencies in the calculated geometries, Curtiss et al.[10] selected a set of seven second-row nonhydrogen molecules, referred to as set A, from the G3/99 test set. The molecules in this set are PF_3, PF_5, P_4, PCl_5, SO_2, SO_3, and SF_6. Curtiss et al. tested six methods on set A, the MP2(FU)/6-31(d), MP2/6-31(2df,p),

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* Corresponding author. E-mail: csonka@web.inc.bme.hu.
[†] Budapest University of Technology and Economics.
[‡] Tulane University.

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QCISD/6-31G(d), B3LYP/6-31G(d), B3LYP/6-31G(2df,p), and B3LYP/6-311+G(3df,2p) models. The models were also investigated for 14 smaller molecules from the G2/97 test set and N_2H_2 to ensure that the trends in accuracy found for set A hold for other molecules. This set of 15 molecules was referred to as set B.[10] The best results were given with good economy by the B3LYP/6-31G(2df,p) method. This is why the B3LYP/6-31G(2df,p) model was chosen for geometry optimizations instead of the MP2(FU)/6-31G(d) model in the recent G3X and G3SX theories.[10] The B3LYP method has the advantages that it is computationally more efficient and more precise than an MP2 calculation. In these G3X and G3SX methods, the B3LYP/6-31G(2df,p) model was also chosen for the calculation of zero-point energies, to be consistent with the geometry optimization method. A scaling factor of 0.9854 was derived[10] for the B3LYP/6-31G(2df,p) model from fitting the set of zero-point energies compiled by Scott and Radom;[6] see also refs 11 and 12.

It can be observed that different (even false) ZPVE energy calculation methods (e.g., ZPVE derived from a badly scaled HF/6-31G(d) model) might yield only minor changes in the performance of any method (e.g., G3 or B3LYP) that applies a posteriori fitting, because the empirical corrections might partly compensate the imprecision of the zero-point energies. However, for nonempirically derived density functionals the a posteriori fitting is not applicable, and consequently it is advisable to use good quality zero-point energies and molecular geometries to obtain good results for good reason and to show the unbiased performance of the model.

Recent developments in density functional theory (DFT) have shown that nonempirical functionals might provide reasonable results without fitting to the target experimental data. The nonempirical PBE GGA[13] and TPSS meta-GGA[14] functionals show balanced performance in many areas of chemistry and physics. A previous study[15] has shown encouraging results for TPSS, PBE, and their hybrids for bond lengths of 86 neutral diatomics and 10 diatomic cations in the T-96R test set.[15] In that study, all geometry optimizations were carried out using the 6-311++G(3df,3pd) basis set with the options Opt = Tight and Int(Grid = UltraFine). It was observed that TPSS and PBE are among the best performers of their class, and inclusion of the exact exchange is required to obtain improved molecular geometries. The hybrids of PBE (PBEh, with 25% exact exchange)[16] and TPSS (TPSSh, with 10% exact exchange)[14] perform considerably better for molecular geometries than their nonhybrid counterparts. In the previous study[15] it was also found that the TPPS and TPSSh functionals are the best performers for experimental harmonic vibrational frequencies (ω_e) on the T-82F test set of 82 ground-state diatomic molecules. Halls et al.[17] have found that the hybrid DFT methods, B3LYP and B3PW91,[4] with the Sadlej pVTZ basis set, are the most reliable for prediction of harmonic vibrational frequencies, outperforming MP2 at lower cost.

In this paper, we report equilibrium geometries and zero-point energies from the nonempirical PBE[13] GGA and TPSS[14] meta-GGA and their corresponding one-parameter hybrids compared to B3LYP, and experimental results for selected molecules. One aim of this paper is to show the performance and applicability of the nonempirical functionals for molecular geometry and zero-point energy calculations. For testing the performance of a method for molecular geometry, we started from two test sets, A and a modified B (omitting N_2H_2 as it is not a part of the G2/97 test set), as proposed by Curtiss et al.[10] in their G3X theory development. For the fundamental ZPVE, we selected all the molecules that have reliable experimental spectroscopic data available in the Computational Chemistry Comparison and Benchmark Database (CCCBDB).[18] After careful analysis of the experimental frequencies, and comparisons to CCSD(T)/cc-pVTZ results where available and necessary, we retained 123 fundamental ZPVEs for the G2/97,[19] and 25 for the G3−3 test sets.[20] However, experimental harmonic and true ZPVEs are available only for 27 diatomic and 8 polyatomic molecules of these data sets (vide infra).

2. Computational Methodology

The Linux version of the Gaussian03 program[21] was used for all calculations in the current study. We use the B3LYP, B3PW91, PBE, PBEh, TPSS, and TPSSh functionals combined with 6-31G(d), 6-31+G(d), and 6-31+G(d,p) basis sets. For comparison with an earlier G3X and G3SX study,[10] we also use the 6-31G(2df,p) basis set. We use the standard geometry optimization and integration grid criteria. The B3LYP/6-31G(2df,p) ZPVEs are available in the literature, but the geometries were reoptimized and the harmonic ZPVEs were recalculated for this study. We have also performed a series of geometry optimizations and frequency calculations with the options Opt = Tight and Int(Grid = UltraFine); however, we observed no noticeable difference in geometry and zero-point energy for the molecules of the G2-1 test set.

Starting from the optimized geometry, it is possible to build third and semidiagonal fourth derivatives for a model for which analytical second derivatives are available. (In Gaussian03 these are available for any DFT method). Next the anharmonic vibrational frequencies are evaluated by second-order perturbation theory (PT2) using the keyword freq = anharm.[22−27] A recent paper[28] discusses the basis set effects using 12 basis sets from 6-31G(d) up to 6-311+G(d,p). This study reveals that the relatively cheap 6-31+G(d,p) basis set performs very well for harmonic frequency calculations and that B3LYP anharmonicities are in close agreement with the reference values irrespective of basis sets. We also investigated the effect of the 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-31G(2df,p), cc-pVDZ, and cc-pVTZ basis sets for the calculated scaled B3LYP, B3PW91, and PBE ZPVEs found in the CCCBDB[18] for polyatomic molecules. We note that these polyatomic ZPVEs are scaled to the fundamental ZPVEs. Analysis of these ZPVEs shows that the scaling effectively compensates the basis set differences above the 6-31+G(d,p) basis set.

The scaling factor that minimizes the root-mean-square (rms) error, or equivalently the mean square error, is obtained from the following sum: $\sum_i^N(\mathrm{ZPVE}_i^{\mathrm{theor}}\mathrm{ZPVE}_i^{\mathrm{expt}})/\sum_i^N(\mathrm{ZPVE}_i^{\mathrm{theor}})^2$, where $\mathrm{ZPVE}_i^{\mathrm{theor}}$ and $\mathrm{ZPVE}_i^{\mathrm{expt}}$ are the theoretical and experimental ZPVEs of the ith molecule from the set of N molecules.

3. Zero-Point Vibrational Energy

We briefly discuss the problem of obtaining reliable experimental and calculated molecular zero-point vibrational energy (ZPVE). The usual second-order perturbation theory expression for the vibrational energy levels of an asymmetric top molecule is

$$\mathrm{E}(v) = \chi_0 + \sum_r \omega_r\left(v_r + \frac{1}{2}\right) + \sum_r \chi_{rr}\left(v_r + \frac{1}{2}\right)^2 + \sum_r \sum_{s<r} \chi_{rs}\left(v_r + \frac{1}{2}\right)\left(v_s + \frac{1}{2}\right) \quad (1)$$

where ω_r is the harmonic frequency of the rth normal mode of vibration and the χ_{rs} define a square matrix of real (typically negative) anharmonic constants. In eq 1, the sum of the diagonal elements of the anharmonic-constant matrix has been separated from the sum of the off-diagonal elements. The true ZPVE, sometimes denoted as $G(\mathrm{v}_r = 0)$ or simply $G(0)$, can be derived from the condition that all the vibrational quantum numbers v_r for modes r and s are zero:

$$\mathrm{ZPVE}^{\mathrm{true}} = \mathrm{ZPVE}^{\mathrm{harm}} + \chi_0 + \frac{1}{4}\sum_r \chi_{rr} + \frac{1}{4}\sum_r \sum_{s<r} \chi_{rs} \quad (2)$$

In this equation, the sums of the anharmonic constants are negative; consequently the half sum of the harmonic frequencies, the harmonic ZPVE

$$\mathrm{ZPVE}^{\mathrm{harm}} = \frac{1}{2}\sum_r \omega_r \quad (3)$$

is larger than the true ZPVE. The χ_0 term is usually negligible, and it has been neglected in several earlier investigations,[2] but not here (vide infra).

For diatomic molecules, where the matrix χ_{rs} has a single element $\chi = -\omega_e x_e$, eq 2 becomes

$$\mathrm{ZPVE}^{\mathrm{true}} = \mathrm{ZPVE}^{\mathrm{harm}} - \frac{1}{4}\omega_e x_e \ (\text{diatomics}) \quad (4)$$

where $\omega_e x_e$ is the second-order, positive anharmonicity constant. (The higher order terms are generally quite small for diatomics as they are in the Morse oscillator model.) For many diatomic molecules, the experimental harmonic frequencies and the second-order anharmonicity constants are available, so reliable experimental ZPVEs can be calculated. However, for large molecules the determination of the accurate anharmonic force field is extremely difficult, and the experimental ZPVE is rarely known, as noted earlier.

The experimentally readily obtainable fundamental frequencies can be given as

$$\nu_r = G(\mathrm{v}_r = 1) - G(\mathrm{v}_r = 0) \quad (5)$$

These are simply the transition frequencies for the first excitation of the r-th vibrational mode. The half sum of the fundamental frequencies is the so-called fundamental ZPVE,

$$\mathrm{ZPVE}^{\mathrm{fund}} = \frac{1}{2}\sum_r \nu_r = \mathrm{ZPVE}^{\mathrm{harm}} + \sum_r \chi_{rr} + \frac{1}{2}\sum_r \sum_{s<r} \chi_{rs} \quad (6)$$

This $\mathrm{ZPVE}^{\mathrm{fund}}$ is smaller than the true ZPVE of eq 2, because the negative sums have larger coefficients in eq 6. From these equations, it follows that $\mathrm{ZPVE}^{\mathrm{harm}} > \mathrm{ZPVE}^{\mathrm{true}} > \mathrm{ZPVE}^{\mathrm{fund}}$, and for diatomic molecules with no off-diagonal χ_{rs}

$$\mathrm{ZVPE}^{\mathrm{true}} = \mathrm{ZPVE}(^3/_4,{}^1/_4) = \frac{3}{4}\mathrm{ZPVE}^{\mathrm{harm}} + \frac{1}{4}\mathrm{ZPVE}^{\mathrm{fund}} \ (\text{diatomics}) \quad (7)$$

However, for polyatomic molecules the sums of the off diagonal terms in eqs 2 and 6 will shift $\mathrm{ZPVE}^{\mathrm{true}}$ closer to $\mathrm{ZPVE}^{\mathrm{fund}}$. This observation rationalizes the suggestion of Grev et al.[5] to approximate the true ZPVE as the simple average of $\mathrm{ZPVE}^{\mathrm{harm}}$ and $\mathrm{ZPVE}^{\mathrm{fund}}$. This average, $\mathrm{ZPVE}(^1/_2,{}^1/_2)$, is a better approximation to $\mathrm{ZVPE}^{\mathrm{true}}$ than is $\mathrm{ZPVE}^{\mathrm{harm}}$ or $\mathrm{ZPVE}^{\mathrm{fund}}$, and it can be expressed as follows (using eqs 3 and 6):

$$\mathrm{ZPVE}(^1/_2,{}^1/_2) = \frac{1}{2}\mathrm{ZPVE}^{\mathrm{harm}} + \frac{1}{2}\mathrm{ZPVE}^{\mathrm{fund}} = \mathrm{ZPVE}^{\mathrm{harm}} + \frac{1}{2}\sum_r \chi_{rr} + \frac{1}{4}\sum_r \sum_{s<r} \chi_{rs} \quad (8)$$

The error of $\mathrm{ZPVE}(^1/_2,{}^1/_2)$ is (using eqs 2 and 8)

$$\mathrm{ZPVE}(^1/_2,{}^1/_2) - \mathrm{ZPVE}^{\mathrm{true}} = -\chi_0 + \frac{1}{4}\sum_r \chi_{rr} \quad (9)$$

From this it follows that $\mathrm{ZPVE}(^1/_2,{}^1/_2)$ is slightly smaller than the true ZPVE. For small molecules, the error of $\mathrm{ZPVE}(^1/_2,{}^1/_2)$ is smaller than 0.1 kcal/mol. However, this error will increase with the number of vibrational modes, so that in larger molecules this error can be expected to be large. Note also that large negative χ_0 values might compensate or overcompensate for this error (vide infra).

Determination of the elastic constants ω_r, χ_{rr}, and χ_{rs} ($s < r$) from a model fitted to experiment is a problem that becomes rapidly more difficult as the number N of atoms increases. There are $M = 3N - 5$ (linear molecule) or $3N - 6$ (nonlinear molecule) normal modes of vibration, and at most $2M + M(M - 1)/2$ independent elastic constants. For $N = 2$, one finds only one normal mode and only two elastic constants. For $N = 3$, there are 4 (linear) or 3 (nonlinear) normal modes and already at most 14 (linear) or 9 (nonlinear) independent elastic constants. We roughly estimate the error of experimental ZPVEs: less than 0.005 kcal/mol for the directly measured fundamental ZPVE, and 0.02−0.05 kcal/mol for the processed harmonic and true ZPVEs for small polyatomic molecules.

4. A New Estimation of the True Zero-Point Vibrational Energy

The analysis of the above equations led us to propose a more precise estimation for the true ZPVE than the simple average, $\mathrm{ZPVE}(^1/_2,{}^1/_2)$ (eq 8). From the definition of $\mathrm{ZPVE}(^3/_4,{}^1/_4)$ in eq 7 and from eq 6, we find

$$\mathrm{ZPVE}(^3/_4,{}^1/_4) = \mathrm{ZPVE}^{\mathrm{harm}} + \frac{1}{4}\sum_r \chi_{rr} + \frac{1}{8}\sum_r \sum_{s<r} \chi_{rs} \quad (10)$$

The difference of eqs 2 and 10 yields the error of this weighted ZPVE,

$$\mathrm{ZPVE}(^3/_4,{}^1/_4) - \mathrm{ZPVE}^{\mathrm{true}} = -\chi_0 - \frac{1}{8}\sum_r \sum_{s<r} \chi_{rs} \quad (11)$$

From eq 11 it follows that typically $\mathrm{ZPVE}(^3/_4,{}^1/_4)$ is larger than $\mathrm{ZPVE}^{\mathrm{true}}$, as this error is typically positive. We note that the error shown in eq 9 depends on the magnitude of the sum of the diagonal elements of the anharmonic constant matrix, while the error shown in eq 11 depends on the magnitude of the sum of the off-diagonal elements of the anharmonic constant matrix with opposite sign.

Thus, the true ZPVE $- \chi_0$ is bounded by the following two values:

$$\mathrm{ZPVE}(^1/_2,{}^1/_2) \leq \mathrm{ZPVE}^{\mathrm{true}} - \chi_0 \leq \mathrm{ZPVE}(^3/_4,{}^1/_4) \quad (12)$$

We suggest the average of the two bounds as a better approximation to the true ZPVE of a polyatomic molecule:

$$\mathrm{ZPVE}({}^{5}/_{8},{}^{3}/_{8}) = \frac{5}{8}\,\mathrm{ZPVE}^{\mathrm{harm}} + \frac{3}{8}\,\mathrm{ZPVE}^{\mathrm{fund}} \qquad (13)$$

The error of this approximation can be expressed as

$$\mathrm{ZPVE}({}^{5}/_{8},{}^{3}/_{8}) - \mathrm{ZPVE}^{\mathrm{true}} = -\chi_0 + \frac{1}{8}\sum_r \chi_{rr} - \frac{1}{16}\sum_r \sum_{s<r} \chi_{rs} \qquad (14)$$

The advantage of this latter formula over the simple average, $\mathrm{ZPVE}({}^{1}/_{2},{}^{1}/_{2})$, is clearly visible, because, if χ_0 is negligible and $\sum_r \chi_{rr} = {}^{1}/_{2}\sum_r \sum_{s<r} \chi_{rs}$ then this $\mathrm{ZPVE}({}^{5}/_{8},{}^{3}/_{8})$ formula is equal to the true ZPVE. A similar compensation effect cannot arise for $\mathrm{ZPVE}({}^{1}/_{2},{}^{1}/_{2})$. For a set of small polyatomics, we find below that the diagonal and off-diagonal sums in eq 14 do indeed largely cancel one another. Whether this is so for large polyatomics, we cannot say except that it is possible; when the number N of atoms becomes large, eq 2 and each sum in it cannot grow faster than N.

The $\mathrm{ZPVE}^{\mathrm{true}}$ estimates of eqs 8, 10, and 13 are all exact in the limit of vanishing anharmonicity, but eq 10 at least is also valid for strongly anharmonic rare-gas dimers.[29] He_2 is so anharmonic that it has no bound excited vibrational state.

5. Results and Discussion

5.1. Molecular Geometries. We have compared the experimental results used by Curtiss et al.[10] for sets A and B (cf., Table 1) to the experimental data and to the higher-level theoretical results that can be found in the CCCBDB.[18] The discrepancies between the originally used and CCCBDB bond lengths are about 0.01−0.02 Å. For set A, the experimental data used by Curtiss et al.[10] are closer to the high-level results. Consequently, we use the same experimental geometry parameters as Curtiss et al.[10] for set A. However, for the 14 small molecules of set B we have found that several of the experimental geometry parameters used by Curtiss et al.[10] show considerable disagreement with other experimental and high-level theoretical results. The largest discrepancy was found for the Ha-N−Hb angle of N_2H_4. Curtiss et al.[10] used 113.3° for this angle, in contrast with 106° published in the CCCBDB.[18] This latter is in better agreement with high-level calculated results (e.g., CCSD(T)/6-311G(d,p)) and with the B3LYP, TPSS, and TPSSh results. This more than 7° deviation caused a large, insensitive error independent of the selected model in the paper of Curtiss et al.[10]

The inclusion of the LiH bond length in the test somewhat biases the evaluation of the theoretical results, because for this molecule all models provide poor geometry with the 6-31G-(2df,p) basis set, independent of the applied DFT functional. A series of TPSSh calculations with cc-pVNZ basis sets (N = D, T, and Q) yields 1.612, 1.595, and 1.594 Å for the LiH equilibrium distance, showing that triple-ζ or better quality basis sets are required for excellent agreement with the experimental bond length, 1.595 Å (cf., Table 1). The TPSSh/6-311(d,p) model yields a reasonable 1.597 Å equilibrium distance. These results are considerably better than the 1.623 Å equilibrium distance predicted by the expensive TPSSh/6-31(2df,p) model (cf., Table 1). We note that the B3LYP method converges to a too-short 1.589 Å LiH bond length with the same series of cc-pVNZ basis sets, and this is the origin of the apparent better performance of the B3LYP model for LiH in Table 1. For other molecules in set B, the 6-31G(2df,p) basis set is considerably better than it is for LiH, and the basis set error is smaller; e.g., for the HF molecule it is about 0.005 Å.

Previous tests of TPSS and TPSSh for bond lengths were restricted to diatomics and to hydrogen-bonded complexes, so ours are the first such tests for polyatomics. Table 1 shows the results predicted by four theoretical models, B3LYP/6-31G(d), B3LYP/6-31G(2df,p), TPSS/6-31G(2df,p), and TPSSh/6-31G-(2df,p), for test sets A and B. We also compared these results to MP2(FU)/6-31(d), MP2(FC)/6-31(2df,p), and QCISD/6-31G-(d) results published by Curtiss et al.[10] The mean absolute errors (MAEs) in Table 1 for set A show that for bond lengths B3LYP/6-31G(2df,p) and TPSSh/6-31G(2df,p) are the best models (MAE = 0.011 and 0.015 Å, respectively), and even the TPSS/6-31G(2df,p) model is better (MAE = 0.020 Å) than the QCISD/6-31G(d), B3LYP/6-31G(d), and MP2(FU)/6-31(d) models (MAE = 0.022, 0.025, 0.027 Å, respectively).[10] The TPSSh/6-31G(2df,p) results are almost as good as the MP2/6-31(2df,p) results.[10] The two bond angles shown in Table 1 are not sufficient to make a quality order among the models.

The results for set B also indicate improvement of the predictions with increase in basis set size for the B3LYP method except for LiH, where a triple-ζ-quality basis set is necessary for improved results. It was observed by Curtiss et al.[10] that the B3LYP method performs slightly better than the MP2 method. The TPSSh and B3LYP/6-31G(2df,p) models yield the smallest MAE with experiment for bond distances (0.004 Å), and the B3LYP/6-31G(2df,p) model provides the smallest MAE with experiment for bond angles (1.4°), closely followed by the TPSSh method (1.5°).

5.2. Zero-Point Vibrational Energy of Diatomic Molecules. We have collected the experimental harmonic, true and fundamental ZPVEs for 27 diatomic molecules in Table 2. Theoretical models directly provide the harmonic frequencies; thus, we compare first the performance of the selected models for harmonic ZPVE. Table 3 shows the statistics of the results obtained with and without scaling for diatomic molecules. For comparison we also show the HF/6-31G(d) and B3LYP/6-31G-(2df,p) results with scaling factors optimized to obtain the best fit in a least squares sense to experimental harmonic ZPVE results. The mean absolute error (MAE) is frequently used to evaluate the performance of the models, so we include it for comparison. We also present in Table 3 the largest deviations from the experimental ZPVEs (experiment − calculated). We observed that the most negative deviation always occurs for the F_2 molecule. Interestingly, the TPSS method shows a large negative error for H_2 as well. Comparison with the TPSS/6-311++G(3df,3pd) ZPVE[15] shows that this is an exceptionally large basis set error (−0.18 kcal/mol) specific to H_2. A similar large basis set effect was observed for LiF (+0.22 kcal/mol). For other molecules, we observed a good agreement between the TPSS ZPVE obtained with 6-311++G(3df,3pd) and the smaller 6-31G(2df,p) basis sets (MAE = 0.027 kcal/mol). This justifies the use of a smaller basis set. The results in Table 3 show that the best performers for MAE are the scaled PBE/6-31G(2df,p) and the TPSS/6-31G(2df,p) models. In agreement with a previous calculations performed with the considerably larger 6-311++G(3df,3pd) basis set,[15] the best nonscaled model is the TPSSh/6-31G(2df,p). Scaling does not improve the TPSSh results.

Table 4 shows the results obtained for the true ZPVE for the same 27 diatomic molecules. Analysis of the anharmonicity constants in Table 2 (cf., eq 4) shows that there is no linear correlation between ω_e and $\omega_e x_e$, so simple scaling of the harmonic frequencies to obtain the true ZPVE leads to errors. The more correct solution would be the explicit calculation of the anharmonic constant, and application of eq 4.[7] However,

TABLE 1: Equilibrium Bond Lengths and Bond Angles for the Poly- and Diatomic Molecules of Test Sets A and B, from Various Combinations of Density Functionals and Basis Sets (Models)[a]

species	parameter	B3LYP/ 6-31G(d)	B3LYP/6-31G(2df,p)	TPSS/6-31G(2df,p)	TPSSh/6-31G(2df,p)	expt[b]
			Set A			
PF_3	PF	1.596	1.576	1.588	1.579	1.57
	FPF	97.7	97.8	97.7	97.6	97.8
PF_5	PF(ax)	1.597	1.578	1.588	1.580	1.577
	PF(eq)	1.569	1.550	1.562	1.553	1.534
P_4	PP	2.217	2.211	2.208	2.199	2.21
PCl_5	PCl(ax)	2.176	2.157	2.149	2.139	2.19
	PCl(eq)	2.071	2.055	2.054	2.044	2.04
SO_2	SO	1.464	1.443	1.459	1.448	1.432
	OSO	119.1	119.2	119.2	119.1	119.5
SO_3	SO	1.453	1.432	1.447	1.436	1.430
SF_6	SF	1.600	1.575	1.588	1.576	1.564
error[c]	bonds	0.025	0.011	0.020	0.015	
	angles	0.3	0.2	0.2	0.3	
			Set B			
LiH[d]	Li−H	1.621	1.615	1.626	1.623	1.595
CH	C−H	1.133	1.131	1.136	1.132	1.120
CH_4	C−H	1.093	1.092	1.095	1.092	1.089
NH_3	N−H	1.019	1.017	1.024	1.019	1.012
	H−N−H	105.7	105.5	104.5	105.0	106.7
H_2O	O−H	0.969	0.962	0.969	0.965	0.957
	H−O−H	103.6	103.7	102.8	103.2	104.5
HF	F−H	0.934	0.919	0.927	0.922	0.917
C_2H_2	C−C	1.205	1.199	1.206	1.201	1.208
	C−H	1.067	1.062	1.065	1.063	1.061
C_2H_4	C−C	1.331	1.327	1.334	1.330	1.339
	C−H	1.087	1.086	1.089	1.086	1.085
	H−C−H	116.3	116.1	116.1	116.2	117.8
HCN	C−N	1.157	1.152	1.160	1.156	1.156
	C−H	1.07	1.067	1.070	1.068	1.065
CO	C−O	1.138	1.131	1.140	1.135	1.128
H_2CO	C−O	1.206	1.200	1.209	1.204	1.208
	C−H	1.11	1.111	1.114	1.110	1.111
	H−C−H	115.2	115.1	115.1	115.2	116.5
N_2	N−N	1.105	1.099	1.108	1.102	1.098
N_2H_4	N−N	1.437	1.437	1.456	1.444	1.446
	N−Ha	1.017	1.015	1.021	1.017	1.016
	N−Hb	1.022	1.019	1.026	1.021	1.016
	Ha-N−N	106.6	106.8	105.4	106.0	108.9
	Hb-N−N	111.8	111.6	110.7	111.1	108.9
	Ha-N−Hb	106.8	106.6	105.6	106.1	106.0
	Ha-N−N−Hb	90.5	88.6	88.08	88.30	88.9
O_2	O−O	1.215	1.206	1.221	1.210	1.208
error[c]	bonds	0.006	0.004	0.008	0.004	
	angles	1.54	1.35	1.68	1.46	

[a] Bond lengths in Å; bond angles in deg. [b] Experimental values for set A are from: Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **14**, Suppl. No. 1. JANAF Thermochemical Tables, 3rd. ed. Experimental values for set B are from CCCBDB. [c] Mean absolute errors in sets A and B for bond lengths and bond angles. [d] As pointed out in the text, the calculated bond lengths for LiH are not converged with respect to basis set.

comparison of the errors in Tables 3 and 4 shows that scaling yields similar or better agreement with experiment for the true ZPVE as for the harmonic ZPVE. Again the best performer is the PBE model (MAE: 0.043 kcal/mol), followed by TPSSh and TPSS (cf., Table 4). We note that the optimal scaling factor for the B3LYP/6-31G(2df,p) model in Table 4 is in agreement with the scaling factor used in the G3X[10] procedure. The optimal scaling factor for the HF/6-31G(d) model in Table 4 is 0.9167, different from the 0.8929 scaling factor used in G3 theory.[8] Comparison of the B3LYP and TPSSh scaling factors in Tables 3 and 4 shows that the two different methods require similar scaling factors.

The average true ZPVE for these 27 molecules is only 2.52 kcal/mol, so these data have only limited predictive value for larger molecules. The value of the ZPVE can be estimated remarkably accurately (MAE $\approx$ 1 kcal/mol) from the molecular stoichiometry,[30,31] so the value of the ZPVE depends on the size of the molecule.

5.3. Zero-Point Vibrational Energy of Polyatomic Molecules. Accurate fundamental ZPVEs are available for many polyatomic molecules in the CCCBDB.[18] Accurate experimental-quality harmonic and anharmonic ZPVEs are sparingly available for polyatomics. Note that anharmonic second-order perturbation theory (PT2) is not available for linear (e.g., acetylene), and T_d symmetric (e.g., methane) molecules in Gaussian 03,[21] so our tests of it are restricted to nonlinear, non-T_d-symmetric polyatomics. We show in Table 5 the ZPVEs for the eight molecules NH_3, H_2O, H_2S, HCO, SO_2, H_2CO, C_2H_4, and CH_2F_2.[1,7] This set was complemented by eight other molecules from the G3/99 test set studied in ref 7. The molecules and the available experimental ZPVEs are shown in Table 5 together with the errors of the two estimations of the true ZPVE from the harmonic and fundamental ZPVEs (cf., eqs 8 and 13). The results in Table 5 clearly show the superior performance of our eq 13 proposed in this paper.

We have performed about 200 anharmonic PT2 ZPVE calculations for the molecules shown in Table 5. Table 6 shows the statistical results for the B3LYP and B3PW91[4] DFT functionals with various basis sets. The best results for the true ZPVE were obtained with the B3PW91/6-31+G(d,p) model, with average error (AE) about 0.00 kcal/mol and MAE = 0.06 kcal/mol, cf., Table 6, followed closely by the most expensive

TABLE 2: Experimental Harmonic Frequencies ω_e, Anharmonic Constants $\omega_e x_e$, and ZPVEs for 27 Diatomic Molecules[a]

			ZPVE		
molecule	ω_e	$\omega_e x_e$	harmonic	true	fundam.
LiH	1405.7	23.2	2.010	1.993	1.943
BeH	2060.8	36.3	2.946	2.920	2.842
CH	2858.5	63.0	4.086	4.041	3.906
NH	3282.3	78.4	4.692	4.636	4.468
OH	3737.8	84.9	5.343	5.283	5.101
FH	4138.3	89.9	5.916	5.852	5.659
ClH	2990.9	52.8	4.276	4.238	4.125
Li_2	351.4	2.6	0.502	0.500	0.495
LiF	910.3	7.9	1.301	1.296	1.279
CN	2068.6	13.1	2.957	2.948	2.920
CO	2169.8	13.3	3.102	3.092	3.064
N_2	2358.6	14.3	3.372	3.361	3.331
NO	1904.2	14.1	2.722	2.712	2.682
O_2	1580.2	12.0	2.259	2.250	2.225
F_2	916.6	11.2	1.310	1.302	1.278
Na_2	159.1	0.7	0.227	0.227	0.225
Si_2	511.0	2.0	0.731	0.729	0.725
P_2	780.8	2.8	1.116	1.114	1.108
S_2	725.6	2.8	1.037	1.035	1.029
Cl_2	559.7	2.7	0.800	0.798	0.792
SiO	1241.5	6.0	1.775	1.771	1.758
SC	1285.1	6.5	1.837	1.832	1.819
SO	1149.2	5.6	1.643	1.639	1.627
ClO	853.8	5.5	1.221	1.217	1.205
FCl	786.1	6.2	1.124	1.119	1.106
H_2	4401.2	121.3	6.292	6.205	5.945
HS	2711.6	59.9	3.876	3.834	3.705

[a] Note that the ($^3/_4$,$^1/_4$) average of eq 10 gives the true ZPVE for a diatomic molecule. For these molecules, x_e ranges from 0.004 to 0.028, with an average value of 0.011. The mean $\mathrm{ZPVE}^{\mathrm{true}}$ is 2.5 kcal/mol. Harmonic frequencies and anharmonic constants are given in cm^{-1}; harmonic, true, and fundamental ZPVEs are given in kcal/mol. Experimental values from: Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1979.

TABLE 3: Scaling Calculated Harmonic ZPVE for the Estimation of Harmonic ZPVE of the 27 Diatomic Molecules Shown in Table 2, Where for Each Model, the First Scaling Factor Is 1, While the Second Scaling Factor Minimizes the Rms Deviation of the Error Relative to Experiment (Experiment − Calculated)[a]

model	scaling factor	av error	std dev	rms dev	mean absolute error	max error	min error
HF/6	1.0000	−0.227	0.184	0.290	0.240	0.125	−0.594
HF/6	0.9253	−0.021	0.157	0.155	0.117	0.337	−0.381
B3LYP	1.0000	−0.026	0.071	0.075	0.054	0.062	−0.230
B3LYP	0.9947	−0.012	0.073	0.073	0.055	0.090	−0.222
TPSS	1.0000	0.030	0.074	0.078	0.058	0.195	−0.157
TPSS	1.0134	−0.003	0.069	0.067	0.046	0.126	−0.189
TPSSh	1.0000	−0.019	0.067	0.068	0.049	0.100	−0.208
TPSSh	0.9970	−0.011	0.068	0.068	0.049	0.116	−0.204
PBE	1.0000	0.048	0.079	0.092	0.067	0.196	−0.152
PBE	1.0227	−0.008	0.063	0.062	0.044	0.108	−0.186
PBEh	1.0000	−0.074	0.075	0.104	0.078	0.028	−0.286
PBEh	0.9796	−0.021	0.081	0.083	0.063	0.111	−0.254

[a] Here and elsewhere in the tables, we follow a frequently used convention: error = experimental − calculated. Statistical data are given in kcal/mol. The 6-31G(d) basis set was used for HF and the 6-31G(2df,p) basis set was used for DFT calculations.

TABLE 4: Scaling Calculated Harmonic ZPVE for the Estimation of True ZPVE of the 27 Diatomic Molecules Shown in Table 2, Where for Each Model, the First Scaling Factor Is Either a Literature Value or 1, While the Second Scaling Factor Minimizes the Rms Deviation of the Error Relative to Experiment (Experimental − Calculated)[a]

model	scaling factor	av error	std dev	rms dev	mean absolute error	max error	min error
HF/6	0.8929	0.049	0.164	0.168	0.129	0.419	−0.297
HF/6	0.9167	−0.016	0.151	0.149	0.110	0.352	−0.365
B3LYP	0.9854	−0.008	0.069	0.068	0.051	0.079	−0.216
TPSS	1.0000	0.011	0.069	0.068	0.049	0.134	−0.190
TPSS	1.0039	0.001	0.068	0.067	0.046	0.114	−0.216
TPSSh	1.0000	−0.038	0.065	0.075	0.048	0.039	−0.224
TPSSh	0.9877	−0.007	0.065	0.064	0.047	0.104	−0.198
PBE	1.0000	0.029	0.066	0.071	0.054	0.151	−0.160
PBE	1.0132	−0.004	0.060	0.059	0.043	0.100	−0.180
PBEh	1.0000	−0.093	0.074	0.118	0.095	0.014	−0.294
PBEh	0.9706	−0.017	0.075	0.075	0.053	0.103	−0.247

[a] Statistical data are given in kcal/mol. The 6-31G(d) basis set was used for HF and the 6-31G(2df,p) basis set was used for DFT calculations.

TABLE 5: Experimental ZPVEs and Errors of the ($^1/_2$,$^1/_2$) (eq 8) and ($^5/_8$,$^3/_8$) (eq 13) Averages for the True ZPVEs of 16 Polyatomic Molecules[a]

	ZPVE			error	
molecule	harmonic[b]	true[b]	fundam[c]	($^1/_2$,$^1/_2$)[d]	($^5/_8$,$^3/_8$)[d]
NH_3	21.65	21.33	20.63	0.19	0.06
H_2O	13.47	13.25	12.88	0.08	0.00
H_2S	9.54	9.40	9.18	0.04	0.00
HCO	8.34	8.13	7.70	0.11	0.03
SO_2	4.41	4.38	4.33	0.01	0.00
H_2CO	16.83	16.53	16.14	0.05	−0.04
C_2H_4	31.88	31.48	30.83	0.12	−0.01
CH_2F_2	20.67	20.43	20.12	0.03	−0.03
NH_2			11.46		
HOCl			7.97		
F_2O			3.17		
ClNO			3.90		
H_2NNH_2			32.04		
CH_3CHO			33.56		
HCOOH			20.44		
C_6H_5N (pyridine)			54.06		

[a] The mean $\mathrm{ZPVE}^{\mathrm{true}}$ for the first eight molecules is 15.6 kcal/mol; for the next eight it is roughly 21 kcal/mol. The largest $\mathrm{ZPVE}^{\mathrm{true}}$ obtained from scaling HF/6-31G(d) in ref 20 is 147 kcal/mol for C_8H_{18}. ZPVEs are given in kcal/mol. [b] References 1 (SO_2 and NH_3) and 7 (all others). We note that the two references agree well except for C_2H_4 ($\mathrm{ZPVE}^{\mathrm{true}}(C_2H_4)$ = 31.60 kcal/mol in ref 1). [c] Reference 18, calculated from reliable experimental data. [d] Error (experimental − estimated) in kcal/mol. The most reliable experimental data are the fundamental ZPVEs. Experimental true and harmonic ZPVEs are subject to errors around 0.02−0.05 kcal/mol arising from the separation between harmonic and anharmonic contributions.

B3LYP/6-31G(2df,p) model. (For ethylene, the latter model is twice as expensive as the former). The B3PW91/6-31+G(d,p) model shows no systematic bias for the true ZPVE, while the B3LYP/6-31+G(d,p) model systematically underestimates the ZPVE (AE = 0.08 kcal/mol, cf., Table 6). We note that the predictive value of the various statistical data for harmonic and true ZPVEs is somewhat limited due to the small test set (8 molecules). The larger test set (16 molecules) for fundamental ZPVE makes those statistical data probably more reliable. Comparison of the statistical data for the small test set shows that the B3LYP results for the fundamental ZPVEs improve as the basis set increases. However, no comparably large improvement can be seen for the harmonic and the true ZPVEs. Comparison of the statistical data for the fundamental ZPVEs for both test sets shows that the performance of the models is worse for the larger test set containing larger molecules. The largest relative worsening can be observed for the B3LYP/6-31G(2df,p) model. Analysis of the details show that the B3LYP/

TABLE 6: Errors (Experimental − Calculated) of ZPVEs Calculated Directly from the PT2 Anharmonic Perturbation Theory of Reference 7, for the Polyatomic Molecules of Table 5:[a] B3PW91 and B3LYP Models

		ZPVE			
		harmonic[b]	true[b]	fundam[b]	fundam[c]
B3PW91/6-31+G(d,p)	av error	0.01	0.00	0.00	−0.06
	std dev	0.10	0.09	0.07	0.11
	mean abs error	0.07	0.06	0.05	0.09
	max error	0.13	0.11	0.09	0.09
	min error	−0.18	−0.16	−0.14	−0.30
B3LYP/6-31G(d)	av error	0.02	0.02	0.04	0.01
	std dev	0.14	0.13	0.14	0.18
	mean abs error	0.11	0.12	0.12	0.14
	max error	0.18	0.18	0.19	0.40
	min error	−0.26	−0.25	−0.21	−0.23
B3LYP/6-31+G(d,p)[d]	av error	0.08	0.08	0.07	0.03
	std dev	0.10	0.10	0.08	0.11
	mean abs error	0.11	0.11	0.08	0.09
	max error	0.20	0.19	0.17	0.21
	min error	−0.11	−0.10	−0.04	−0.16
B3LYP/6-31G(2df,p)[d]	av error	0.06	0.06	0.02	0.00
	std dev	0.10	0.09	0.05	0.11
	mean abs error	0.10	0.09	0.04	0.08
	max error	0.19	0.18	0.13	0.21
	min error	−0.12	−0.11	−0.03	−0.26

[a] In kcal/mol, deviations for the test set shown in Table 5. [b] Statistics for the first eight molecules in Table 5. [c] Statistics for all 16 molecules of Table 5. [d] Without CH_2F_2.

TABLE 7: Errors (Experimental − Calculated) of ZPVEs Calculated Directly from the PT2 Anharmonic Perturbation Theory of Reference 7, for the Polyatomic Molecules of Table 5:[a] TPSS, TPSSh PBE, and PBEh Models

		ZPVE			
		harmonic[b]	true[b]	fundam[b]	fundam[c]
TPSS/6-31G(d)	av error	0.27	0.24	0.21	0.26
	std dev	0.14	0.18	0.21	0.23
	mean abs error	0.27	0.25	0.24	0.28
	max error	0.47	0.47	0.49	0.67
	min error	0.05	−0.05	−0.15	−0.15
TPSSh/6-31G(d)	av error	0.02	0.01	−0.02	0.00
	std dev	0.19	0.19	0.19	0.19
	mean abs error	0.14	0.14	0.15	0.16
	max error	0.25	0.23	0.23	0.26
	min error	−0.32	−0.34	−0.34	−0.34
TPSSh/6-31+G(d,p)	av error	0.08	0.07	0.06	0.06
	std dev	0.14	0.17	0.19	0.18
	mean abs error	0.13	0.15	0.17	0.16
	max error	0.25	0.23	0.33	0.35
	min error	−0.20	−0.23	−0.19	−0.19
PBE/6-31G(d)	av error	0.47	0.47	0.57	0.54
	std dev	0.12	0.15	0.34	0.38
	mean abs error	0.47	0.47	0.57	0.55
	max error	0.61	0.66	0.71	1.31
	min error	0.25	0.23	0.17	−0.03
PBEh/6-31G(d)	av error	−0.17	−0.18	−0.21	−0.27
	std dev	0.17	0.14	0.16	0.19
	mean abs error	0.17	0.18	0.21	0.27
	max error	0.00	−0.01	−0.04	−0.04
	min error	−0.46	−0.46	−0.48	−0.64
PBEh/6-31+G(d,p)[d]	av error	−0.09	−0.09	−0.10	−0.15
	std dev	0.11	0.10	0.07	0.09
	mean abs error	0.10	0.10	0.10	0.15
	max error	0.05	0.03	0.01	0.01
	min error	−0.31	−0.31	−0.20	−0.34

[a] In kcal/mol; deviations for the test set shown in Table 5. [b] Statistics for the first eight molecules in Table 5. [c] Statistics for all 16 molecules of Table 5, except where noted. [d] Pyridine was not included.

6-31G(2df,p) model yields a very good ZPVE for SO_2 (less than 0.01 kcal/mol deviation, and an improved geometry in Table 1), while the models using the smaller 6-31+G(d,p) basis set do not yield such good results (typically 0.10−0.20 kcal/mol or larger error). For the other molecules in the test set shown in Table 5, using the more expensive B3LYP/6-31G(2df,p) model does not provide clear improvement over the B3LYP/6-31+G(d,p) or especially over the best B3PW91/6-31+G(d,p) model. We have also studied the less expensive B3LYP/6-31+G(d) model (not shown in Table 6): The quality of the results was better than that obtained for the B3LYP/6-31G(d) model, but worse than that obtained for the B3LYP/6-31+G(d,p) model.

Table 7 shows the PT2 statistical results for TPSS, TPSSh PBE, and PBEh DFT functionals with various basis sets for the polyatomic molecules shown in Table 5. The results show that the PBE/6-31G(d) model systematically underestimates (AE = 0.47 kcal/mol) while the PBEh/6-31G(d) model systematically overestimates (AE = −0.18 kcal/mol) the available harmonic and true ZPVEs. The performance of the PBEh/6-31G(d) model is considerably better than the performance of the PBE/6-31G(d) model (cf., Table 7). The best results were given by the PBEh/6-31+G(d,p) and (AE = −0.09 kcal/mol and MAE = 0.10 kcal/mol, cf., Table 7), as the systematic overestimation of the harmonic, true, and fundamental ZPVE by the PBEh/6-31G(d) model was considerably decreased by the larger basis set. We tested the PBEh/6-31G(*2*df,p) model (not shown in Table 7), and obtained slightly improved results.

The TPSS/6-31G(d) model provides considerably improved true ZPVE (i.e., the AE and MAE are almost halved) compared to the PBE/6-31G(d) model, although the ZPVEs remain considerably underestimated. Inclusion of exact exchange via TPSSh balances quite effectively the underestimation tendency of the TPSS functional. Good results were obtained from the TPSSh/6-31+G(d,p) model (AE = 0.07 kcal/mol, MAE = 0.15 kcal/mol), although the small percentage (10%) of exact exchange is not enough to change the underestimating tendency of the TPSS functional. In general it can be observed that an increase of the basis set from 6-31G(d) to 6-31+G(d,p) decreases the calculated ZPVE. (The AE increases by about 0.05−0.10 kcal/mol depending on the ZPVE type, cf., B3LYP, TPSSh and PBEh results in Tables 6 and 7). Consequently, the PBE and TPSS underestimation of the ZPVE worsens with the increase of the basis set. The 25% exact exchange of PBEh is too large and the 10% exact exchange of TPSSh is too small to obtain good ZPVE results for the molecules in this study. It can be observed that the quality of the results for fundamental ZPVE usually slightly worsens with the increase of the test set. Comparison of the best results in Tables 6 and 7 shows that the best MAE for the true ZPVE was given by the B3PW91/6-31+G(d,p) model (0.06 kcal/mol), followed by the B3LYP/6-31G(2df,p), PBEh/6-31+G(d,p), B3LYP/6-31+G(d,p), and TPSSh/6-31+G(d,p) models (MAE = 0.09, 0.10, 0.11, and 0.15 kcal/mol, respectively).

Although our PT2 calculations of the anharmonic constants usually agree with those of ref 7, we have always found very small χ_0s. For pyridine (C_6H_5N), where ref 7 finds $\chi_0 = 0.55$ kcal/mol, we find 0.07 kcal/mol for the same model. We observed that the calculated values of the χ_0s might depend strongly on the model chemistry. The largest χ_0 value (0.24 kcal/mol) was found for H_2NNH_2 with the B3LYP/6-31G(d) model, however, the B3LYP/6-31+G(d) model gave only 0.08 kcal/mol while the TPSS/6-31G(d) model resulted in −0.05 kcal/mol. The most negative χ_0 value (−0.17 kcal/mol) was found for NH_3 with the PBEh/6-31G(d) model, while the PBEh/6-31+G(d,p) model gave −0.04 kcal/mol. These negative χ_0 values help eq 8 to give better agreement with the true ZPVE. For CH_2F_2 the TPSS/6-31+G(d,p) model gave even smaller estimated ZPVE with eq 8 than the calculated true ZPVE, because the value of $-\chi_0$ (0.13 kcal/mol) surprisingly overwhelms the value of $\frac{1}{4}\sum_r \chi_{rr}$ (−0.11 kcal/mol) in eq 9. (This is the only example where we found this in our calculations.)

Although the PT2 anharmonic ZPVE calculations yield the true ZPVE without scaling, it should be noted that the expense of these calculations can be very large for larger molecules. For example, the PT2 anharmonic ZPVE calculation for pyridine is about 55 times more time-consuming than the harmonic ZPVE calculation. Thus, a scaled harmonic ZPVE might be quite a useful alternative for larger molecules. Table 8 shows the scaling factors and the statistical data obtained for the first eight molecules of Table 5. The scaling factors were optimized to fit the experimental true ZPVE in the least squares sense. First, we optimized a scaling factor for the experimental harmonic ZPVE (0.9859 cf., Table 8). This is the ideal scaling factor that would yield the best results from perfect calculated harmonic ZPVEs (AE = −0.007 kcal/mol, MAE = 0.036 kcal/mol). We applied this ideal scaling factor to harmonic ZPVEs calculated by the B3PW91/6-31+G(d,p), TPSSh/6-31+G(d,p), and PBEh/6-31+G(d,p) models, and obtained 0.075, 0.118, and 0.114 kcal/mol MAE (cf., Table 8).

TABLE 8: Scaling Experimental and Calculated Harmonic ZPVEs for the Estimation of the *True* ZPVE of the First Eight Polyatomic Molecules in Table 5, Where the First Four Rows Employ a Scaling Factor That Is Optimal for the Experimental Harmonic ZPVE and the Last Five Rows Employ Scaling Factors that Minimize the rms Deviation for the Given Model[a]

model	scaling factor	av error	std dev	rms dev	mean absolute error	max error	min error
expt harm.	0.9859	−0.007	0.044	0.041	0.036	0.051	−0.064
B3PW91[b]	0.9859	−0.001	0.100	0.093	0.075	0.159	−0.140
TPSSh[b]	0.9859	0.077	0.137	0.149	0.118	0.279	−0.161
PBEh[b]	0.9859	−0.093	0.109	0.138	0.114	0.081	−0.273
HF[c]	0.8929	0.330	0.296	0.430	0.358	0.785	−0.113
HF[c]	0.9142	−0.036	0.129	0.126	0.105	0.102	−0.220
B3LYP[d]	0.9854	0.071	0.065	0.093	0.085	0.155	−0.057
B3PW91[b]	0.9844	0.024	0.092	0.089	0.065	0.166	−0.091
TPSSh[b]	0.9874	0.053	0.146	0.147	0.113	0.272	−0.209
PBEh[b]	0.9793	0.013	0.073	0.069	0.051	0.139	−0.059

[a] (Experimental − calculated) in kcal/mol. [b] 6-31+G(d,p) basis set. [c] 6-31G(d) basis set. [d] 6-31G(2df,p) basis set.

Next we optimized the scaling factors in the least squares sense for each functional. The best results were obtained with the scaled PBEh/6-31+G(d,p) model (0.9793, MAE = 0.051 kcal/mol, cf., Table 8). We note that these results are considerably better than the results obtained from the anharmonic calculations shown in Table 7. However, the optimization of the scaling factor for a small test set is rather uncertain, and the extension of the test set might influence the value of the scaling factor. (For example, if we take out the CH_2F_2 molecule from the test set, the optimal scaling factor changes by 0.0005−0.001.) We added five molecules (C_2H_2, CH_4, CO_2, HCN, and N_2O) with known true ZPVEs[1,5] to the test set of eight polyatomic molecules and obtained 0.9782 scaling factor for PBEh (cf. 0.9793 in Table 8). This shows the dependence of the empirical scaling on the test set.

We also show in Table 8 the performance of the scaled HF/6-31G(d) and B3LYP/6-31G(*2*df,p) models with the usual scaling factors.[10] It can be noticed that the performance of the HF/6-31G(d) model is quite poor even for this small test set (MAE = 0.36 kcal/mol in Table 8). We show a better scaling factor (0.914) for HF/6-31G(d) model for the small test set in Table 8 (MAE = 0.11 kcal/mol). The performance of the scaled (0.9854) B3LYP/6-31G(*2*df,p) model is very good (MAE = 0.09 kcal/mol), similar to the MAE, 0.09 kcal/mol, obtained from the anharmonic PT2 calculations shown in Table 6. This shows that scaling harmonic DFT ZPVEs might provide reasonable results for the true ZPVE at less cost than the anharmonic PT2 analysis does.

We note that applying 0.914 scaling factor to HF/6-31G(d) model ZPVE leads to considerably better agreement between scaled HF/6-31G(d) and B3LYP/6-31G(*2*df,p) true ZPVEs for 76 larger molecules from the G3/99 test set (AE = −0.04 kcal/mol, MAE = 0.26 kcal/mol). For example the difference (B3LYP − HF) of the two scaled ZPVEs changes from 4.2 kcal/mol (cf., introduction) to −0.71 kcal/mol for *n*-octane (C_8H_{18}). Our numerical analysis shows that this 0.914 scaling factor minimizes the MAE of the B3LYP − HF difference for the ZPVEs of the G3/99 test set.

TABLE 9: Estimation of the *True* ZPVE from the Harmonic and Fundamental ZPVEs, Using the ($^1/_2$,$^1/_2$) (eq 8) and ($^5/_8$,$^3/_8$) (eq 13) Averages, for the 16 Polyatomic Molecules of Table 5, Using All 210 PT2-Calculated (Unscaled Harmonic and Unscaled Fundamental) and Experimental ZPVEs[a]

estimate	ave error	std dev	mean abs error	max error	min error
5/8 $ZPVE^{harm}$ + 3/8 $ZPVE^{fund}$	0.00	0.03	0.02	0.11	−0.09
1/2($ZPVE^{harm}$ + $ZPVE^{fund}$)	0.08	0.07	0.08	0.35	−0.02

[a] In this table, the reference or "exact" $ZPVE^{true}$ is correspondingly the calculated or experimental one. (Experimental or calculated − estimated) in kcal/mol.

In Table 9, we show the performance of eq 13 for the estimation of the true ZPVE from the harmonic and the fundamental ZPVEs. For these statistics we used all 235 calculated and experimental ZPVEs for the 16 molecules in Table 5. The results obtained with eq 13 are clearly superior to the results obtained with eq 8. On the basis of the good performance of eq 13, a possibly reliable estimation for $ZPVE^{true}$ might combine the best calculated harmonic ZPVE, preferably $ZPVE^{harm}_{CC/T}$ (where CC/T means CCSD(T)/cc-pVTZ or better) and the reliable $ZPVE^{fund}_{expt}$. In this respect, two sources of error are the error of the calculated $ZPVE^{harm}$ and neglect of χ_0 of eq 1.

Comparison of $^5/_8 ZPVE^{harm}_{CC/T} + {}^3/_8 ZPVE^{fund}_{expt}$ with experimental true ZPVE in Table 5, using CCSD(T)(FC)/cc-pVTZ calculations, resulted in an almost perfect agreement for seven molecules out of eight (MAE = 0.02 kcal/mol). The only outlier is the HCO molecule with a 0.16 kcal/mol deviation. (The predicted true ZPVE is 7.97 kcal/mol vs 8.13 kcal/mol in Table 5.) The origin of this deviation is the relatively small $ZPVE^{harm}_{CC/T}$, 8.13 kcal/mol, that agrees fortuitously well with the $ZPVE^{true}_{expt}$ in Table 5. CCSD(T)(FU)/cc-pVQZ calculations resulted in an 8.23 kcal/mol[32] harmonic ZPVE, leading to a somewhat better estimation of the true ZPVE (8.03 kcal/mol). We note that this approach, which requires the experimental fundamental ZPVE, cannot be applied to transition states or to molecules for which experimental data is unavailable.

For NH_2, HOCl, F_2O, ClNO, using $ZPVE^{harm}_{CC/T}$ 12.00, 8.29, 3.27, 3.99 kcal/mol from ref 7 and the corresponding $ZPVE^{fund}_{expt}$ in Table 5, we obtain the $ZPVE^{true}$ values 11.80, 8.17, 3.24, 3.96 kcal/mol, respectively. The applicability of this method is limited by the extreme computational cost of the CCSD(T)(FC)/pVTZ harmonic ZPVE calculation.

A less expensive alternative, applicable for larger molecules, is to use the best-performing DFT model for harmonic ZPVE instead of CCSD(T). The smallest MAE for harmonic ZPVE was given by B3PW91/6-31+G(d,p) model (cf., Table 6). Comparison of $^5/_8 ZPVE^{harm}_{B3PW91} + {}^3/_8 ZPVE^{fund}_{expt}$ with experimental true ZPVE in Table 5, using B3PW91/6-31+G(d,p) calculations, resulted in a very good agreement for 7 molecules out of 8 (MAE = 0.03 kcal/mol). The only outlier is the HCO molecule with a 0.12 kcal/mol deviation. For NH_2, HOCl, F_2O, ClNO, using $ZPVE^{harm}_{B3PW91}$ 12.00, 8.30, 3.46, 4.15 kcal/mol and the corresponding $ZPVE^{fund}_{expt}$ in Table 5, we obtain the $ZPVE^{true}$ values 11.80, 8.17, 3.35, and 4.05 kcal/mol, respectively. The first two values are in a perfect agreement with the estimations using CCSD(T) harmonic ZPVEs.

TABLE 10: Results from Experimental Correction of the PT2 Harmonic Contribution to $ZPVE^{true}$, Equation 15, and Estimation of $ZPVE^{true}$ from the ($^5/_8$,$^3/_8$) Average, Equation 13, for Acetaldehyde (CH_3CHO), Where $ZPVE^{fund}_{expt}$ = 33.56 kcal/mol (Cf., Table 5)[a]

method	$ZPVE^{harm}$	$ZPVE^{fund}_{PT2}$	$ZPVE^{true}_{PT2.}$	$ZPVE^{true}(^5/_8,{}^3/_8)$	$ZPVE^{true}$ eq 15
B3PW91[b]	34.87	33.66	34.39	34.41	34.30
B3LYP[c]	35.03	33.78	34.54	34.56	34.32
B3LYP[d]	34.74	33.49	34.26	34.27	34.33
B3LYP[b]	34.77	33.59	34.29	34.33	34.26
TPSS[c]	34.58	33.09	34.08	34.02	34.55
TPSSh[c]	35.03	33.79	34.53	34.56	34.31
TPSSh[b]	34.81	33.66	34.35	34.38	34.25
PBE[c]	34.04	32.70	33.53	33.54	34.39
PBEh[c]	35.29	34.16	34.82	34.87	34.22
PBEh[b]	35.03	33.82	34.57	34.58	34.31

[a] In kcal/mol. [b] 6-31+G(d,p) basis set. [c] 6-31G(d) basis set. [d] 6-31G(2df,p) basis set.

TABLE 11: Experimental Correction of the PT2 Harmonic Contribution, Equation 15, for the Estimation of the True ZPVE for the First Eight Polyatomic Molecules in Table 5[a]

model	av error	std dev	mean absolute error	max error	min error
B3PW91[b]	0.01	0.09	0.06	0.16	−0.16
B3LYP[c]	−0.02	0.09	0.06	0.14	−0.15
B3LYP[b]	0.01	0.08	0.05	0.15	−0.08
TPSS[c]	0.05	0.07	0.06	0.17	−0.01
TPSSh[c]	0.04	0.06	0.04	0.17	0.00
TPSSh[b]	0.03	0.08	0.05	0.18	−0.04
PBE[c]	−0.01	0.09	0.06	0.16	−0.12
PBEh[c]	0.03	0.07	0.05	0.17	−0.03
PBEh[b]	0.01	0.09	0.06	0.17	−0.14

[a] (Experimental − calculated) in kcal/mol. The largest positive errors occur for HCO molecule systematically. [b] 6-31+G(d,p) basis set. [c] 6-31G(d) basis set.

Another alternative that is more expensive than the previous one due to the requirement of the PT2 calculation, but less expensive than the CCSD(T)/cc-pVTZ or QZ harmonic calculation for large molecules, is experimental correction of the PT2 harmonic contribution, in which $ZPVE^{true}$ is estimated as

$$ZPVE^{true}_{PT2} + (ZPVE^{fund}_{expt} - ZPVE^{fund}_{PT2}) \qquad (15)$$

The idea behind eq 15 is that the anharmonic contribution to $ZPVE^{true}_{PT2}$ is accurate for any reasonable functional and basis set,[7] and only the harmonic contribution requires correction. The quantity in parentheses in eq 15 is the additive experimental correction to the harmonic contribution. (Equivalently, we can rearrange eq 15 as $ZPVE^{fund}_{expt} + (ZPVE^{true}_{PT2} - ZPVE^{fund}_{PT2})$, and think of it as a PT2 correction to the experimental fundamental ZPVE.) Table 10 for acetaldehyde shows that the results of eq 15 are indeed nearly independent of model. Note that eq 15 is exact in the fully harmonic limit where $ZPVE^{fund}$ approaches $ZPVE^{true}$, and remains well-behaved even in the strongly anharmonic limit where $ZPVE^{fund}$ approaches zero. Equations 13 and 15 both are constructed under the assumption that anharmonic perturbation theory is converged at second order, an assumption that might be questioned for the molecule HCO, where the CH stretch is strongly anharmonic.[33] Table 10 also illustrates the good performance of eq 13.

Comparison of the statistical data in Tables 11 and 7 shows that eq 15 works well for the TPSS, TPSSh, PBE, and PBEh functionals, resulting in a significantly improved performance for these methods. A similar comparison of the data in Tables 11 and 6 shows that a less striking improvement can be observed for B3LYP or B3PW91 functionals. For the HCO molecule, eq 15 produces a true ZPVE in the range of 7.94−7.98 kcal/mol independent of model, in good agreement with the $^5/_8\mathrm{ZPVE}^{\mathrm{harm}}_{\mathrm{CC/T}} + {}^3/_8\mathrm{ZPVE}^{\mathrm{fund}}_{\mathrm{expt}}$ value, 7.97−8.03 kcal/mol as noted earlier.

All the PT2 values $\mathrm{ZPVE}^{\mathrm{harm}}_{\mathrm{PT2}}$, $\mathrm{ZPVE}^{\mathrm{true}}_{\mathrm{PT2}}$, and $\mathrm{ZPVE}^{\mathrm{fund}}_{\mathrm{PT2}}$ by assumption get the same additive correction shown in parentheses in eq 15. Then, if the ($^5/_8$,$^3/_8$) average of eq 13 is exact within PT2, it will remain exact after correction. Note that $\mathrm{ZPVE}^{\mathrm{harm}}_{\mathrm{PT2}}$ is the usual calculated harmonic model ZPVE, which requires no PT2 calculation.

As an alternative to estimate $\mathrm{ZPVE}^{\mathrm{true}}$, start from the ($^5/_8$,$^3/_8$) average of eq 13. Replace $\mathrm{ZPVE}^{\mathrm{fund}}$ by $\mathrm{ZPVE}^{\mathrm{fund}}_{\mathrm{expt}}$, and $\mathrm{ZPVE}^{\mathrm{harm}}$ by $\mathrm{ZPVE}^{\mathrm{harm}}_{\mathrm{PT2}} + (\mathrm{ZPVE}^{\mathrm{fund}}_{\mathrm{expt}} - \mathrm{ZPVE}^{\mathrm{fund}}_{\mathrm{PT2}})$. Rearrange to get

$$\mathrm{ZPVE}^{\mathrm{fund}}_{\mathrm{expt}} + (^5/_8)(\mathrm{ZPVE}^{\mathrm{harm}}_{\mathrm{PT2}} - \mathrm{ZPVE}^{\mathrm{fund}}_{\mathrm{PT2}}) \qquad (16)$$

Because of the remarkable accuracy of eq 13, eq 16 might be accurate. Our results show that eqs 15 and 16 show the same accuracy for the eight polyatomic molecules in our test set. Equation 15 properly includes a contribution from χ_0, while eq 16 (like eq 13) does not.

6. Conclusions

We have examined the performance of various models for molecular geometry of two sets of molecules. Set A contains PF_3, PF_5, P_4, PCl_5, SO_2, SO_3, and SF_6, while set B contains LiH, CH, CH_4, NH_3, H_2O, HF, C_2H_2, C_2H_4, HCN, CO, H_2CO, N_2, N_2H_4, and O_2. The results for set A show that TPSSh/6-31G(2df,p) and B3LYP/6-31G(2df,p) are the best models with the smallest MAE relative to experiment for bond distances (0.015 and 0.011 Å, respectively). These models and the TPSS/6-31G(2df,p) model (MAE = 0.020 Å) are better than the QCISD/6-31G(d), B3LYP/6-31G(d), and MP2(FU)/6-31(d) models (MAE = 0.022, 0.025, and 0.027 Å, respectively) investigated earlier. The TPSSh/6-31G(2df,p) results are almost as good as the MP2/6-31(2df,p) results. The results for set B also indicate improvement of the predictions with increase in basis set size for the B3LYP method, except for LiH, where a triple-ζ-quality basis set is necessary for improved results. The TPSSh and B3LYP/6-31G(2df,p) models yield the smallest MAE relative to experiment for bond distances (0.004 Å), and the B3LYP/6-31G(2df,p) model provides the smallest MAE with experiment for bond angles (1.4°), closely followed by the TPSSh method (1.5°).

The experimental harmonic and true ZPVEs for 27 diatomic molecules were compared to harmonic and true ZPVEs obtained from the scaled HF/6-31G(d), B3LYP/6-31G(2df,p), TPSS/6-31G(2df,p), TPSSh/6-31G(2df,p), PBE/6-31G(2df,p), and PBEh/6-31G(2df,p) models. The best agreement with experimental harmonic ZPVEs was obtained from scaled TPSS and PBE results (MAE = 0.046, and 0.044 kcal/mol obtained with 1.0134 and 1.0227 scaling factors, respectively). For true ZPVEs, the scaled TPSS and PBE results (MAE = 0.046, and 0.043 kcal/mol obtained with 1.0039 and 1.0132 scaling factors, respectively) gave the best agreement with the experiment. The nonscaled TPSSh model shows a particularly good agreement with the experimental harmonic and true ZPVEs (MAE = 0.049, and 0.048 kcal/mol, respectively). It was observed that better results can be obtained by scaling for the true ZPVE than for the harmonic ZPVE. The TPSS and PBE models show a superior performance over the currently used B3LYP and HF models for this test set of 27 diatomic molecules, in agreement with earlier results[14] for harmonic vibrational frequencies of 82 diatomic molecules.

The experimental harmonic, true, and fundamental ZPVEs for eight polyatomic molecules, NH_3, H_2O, H_2S, HCO, SO_2, H_2CO, C_2H_4, and CH_2F_2,were compared to harmonic, true, and fundamental ZPVEs obtained from B3PW91, B3LYP, PBE, TPSS, PBEh, and TPSSh PT2 anharmonic ZPVE calculations. The best MAE for the true ZPVE was given by the B3PW91/6-31+G(d,p) model (0.06 kcal/mol), followed by the B3LYP/6-31G(2df,p), PBEh/6-31+G(d,p), B3LYP/6-31+G(d,p), and TPSSh/6-31+G(d,p) models (MAE = 0.09, 0.10, 0.11, and 0.15 kcal/mol, respectively).

We added eight molecules to the test set (with the largest added molecule being pyridine). However, for these molecules only the experimental fundamental ZPVEs are available. Comparison of the errors of the fundamental ZPVEs shows that the PT2 errors are not stable, and larger errors are obtained for the test set containing 16 molecules. This suggests that probably a larger data set is required for more predictive power, so we shall work on the extension of the data set. However, despite the error differences between the two test sets for fundamental ZPVEs, a similar ranking of the methods was obtained for both sets of molecules. The results for the larger test set show that the best PT2 prediction for fundamental ZPVEs can be obtained from B3LYP/6-31G(2df,p) and B3PW91 or B3LYP/6-31+G(d,p) models (MAE = 0.08 and 0.09 kcal/mol, respectively). However, the latter two models are considerably less expensive. The PBEh/6-31+G(d,p) and TPSSh/6-31+G(d,p) models are less predictive for fundamental ZPVEs (MAE = 0.15 and 0.16 kcal/mol), despite their relatively good performance for harmonic ZPVE (MAE = 0.10 and 0.13 kcal/mol, respectively), equaling the performance of the B3LYP models and slightly worse than the performance of the best B3PW91/6-31+G(d,p) model (MAE = 0.07 kcal/mol).

We have derived an ideal scaling factor (0.9859) to obtain the true ZPVE from the experimental harmonic ZPVE in a least squares sense for the test set of eight molecules in Table 5. This ideal scaling factor gave an MAE of 0.036 kcal/mol. Applying this ideal scaling factor to calculated harmonic ZPVEs, we obtained 0.075 kcal/mol MAE for the B3PW91/6-31+G(d,p) model. The PBEh/6-31+G(d,p) model scales quite well, and the optimized scaling factor (0.9793) yields the best 0.051 kcal/mol MAE. This small test set does not warrant predictive scaling factors, but the poor performance of the scaled (0.8929) HF/6-31G(d) model is quite evident (MAE = 0.358 kcal/mol) for true ZPVE calculations. Very large ZPVE errors can be predicted in this way for larger molecules that are above the required chemical accuracy (1−2 kcal/mol) for standard enthalpies of formation (cf., the 4 kcal/mol differences between scaled true ZPVEs for *n*-octane as mentioned in the Introduction). We derived an optimized scaling factor for the HF/6-31G(d) model (0.9142, MAE = 0.105 kcal/mol) that shows improved performance. This small test set shows the quality of the (more expensive) scaled (0.9854) B3LYP/6-31G(2df,p) model (MAE = 0.085 kcal/mol), and it may be noticed how close the scaling factor is to the ideal 0.9859. These results show that a scaled DFT ZPVE can be as good as the ZPVE calculated from the corresponding very expensive PT2 anharmonic force field.

The scaling factors for ZPVE obtained for diatomic molecules deviate considerably from those obtained for polyatomic molecules. Analysis of the equations shows that for diatomic molecules the ZPVE is three times closer to $\mathrm{ZPVE}^{\mathrm{harm}}$ than to $\mathrm{ZPVE}^{\mathrm{fund}}$. This is certainly not true for the polyatomic molecules, as their ZPVE is shifted toward the simple ($^1/_2$,$^1/_2$) average of $\mathrm{ZPVE}^{\mathrm{harm}}$ and $\mathrm{ZPVE}^{\mathrm{fund}}$. Consequently, mixing diatomic and polyatomic molecules to obtain a single scaling factor for ZPVE is not really helpful. However, the effect of the scaling factor on the very small ZPVE (average 2.5 kcal/mol) of the diatomic molecules is almost negligible, while the ZPVEs of the polyatomic molecules (from 4 to 54 kcal/mol for the present polyatomic molecules) depend more sensitively on the scaling factor.

We have proposed a new formula (eq 13) to estimate the true ZPVE from the harmonic and fundamental ZPVEs of a polyatomic molecule: $^5/_8$ZPVE^{harm} + 3/8 ZPVE^{fund}. The proposed formula yields a good estimation of the true ZPVE for 210 calculated and experimental ZPVEs, with an average error of 0.00 kcal/mol and mean absolute error of 0.02 kcal/mol. We have also proposed an experimental correction of the PT2 harmonic contribution, eqs 15 and 16, which produces improved results for ZPVE^{true} that are almost independent of the choice of model. We note that anharmonic ZPVE calculations are not practical for large molecules. For these molecules, scaling is the most practical solution.

We now summarize our recommendations for estimation of the true ZPVE. (a) The ($^5/_8$,$^3/_8$) average of eq 13, with scaled ZPVE^{harm} from a B3PW91/6-31+G(d,p) calculation and ZPVE^{fund} from experiment, is computationally easy for hundreds of molecules and achieves a mean absolute error of about 0.05 kcal/mol for our test set (the first eight polyatomic molecules in Table 5). (b) Experimental correction of a PT2 calculation, via eq 15, requires a computationally more demanding PT2 calculation but is conceptually more appealing, and achieves about the same small error for this test set. Whenever possible, both estimates a and b could be constructed and compared.

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