

## Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries

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Received June 15, 2010

**Abstract:** Optimized scale factors for calculating vibrational harmonic and fundamental frequencies and zero-point energies have been determined for 145 electronic model chemistries, including 119 based on approximate functionals depending on occupied orbitals, 19 based on single-level wave function theory, three based on the neglect-of-diatomic-differential-overlap, two based on doubly hybrid density functional theory, and two based on multicoefficient correlation methods. Forty of the scale factors are obtained from large databases, which are also used to derive two universal scale factor ratios that can be used to interconvert between scale factors optimized for various properties, enabling the derivation of three key scale factors at the effort of optimizing only one of them. A reduced scale factor optimization model is formulated in order to further reduce the cost of optimizing scale factors, and the reduced model is illustrated by using it to obtain 105 additional scale factors. Using root-mean-square errors from the values in the large databases, we find that scaling reduces errors in zero-point energies by a factor of 2.3 and errors in fundamental vibrational frequencies by a factor of 3.0, but it reduces errors in harmonic vibrational frequencies by only a factor of 1.3. It is shown that, upon scaling, the balanced multicoefficient correlation method based on coupled cluster theory with single and double excitations (BMC–CCSD) can lead to very accurate predictions of vibrational frequencies. With a polarized, minimally augmented basis set, the density functionals with zero-point energy scale factors closest to unity are MPWLYP1M (1.009),  $\tau$ HCTHhyb (0.989), BB95 (1.012), BLYP (1.013), BP86 (1.014), B3LYP (0.986), MPW3LYP (0.986), and VSXC (0.986).

### 1. Introduction

The accurate determination of vibrational frequencies through the use of computational quantum chemistry is essential to many fields of chemistry. For example, computed frequencies can be used to guide spectroscopic measurements by predicting or refining the spectral regions in which transitions of interest might occur, and computed frequencies can also help to identify and characterize transient species, such as molecular radicals, van der Waals complexes, and reactive

intermediates. Furthermore, frequencies are an essential part of computational thermochemistry, and they are used for the calculation of vibrational zero-point energies (ZPEs) and vibrational partition functions, which are also important for thermochemical kinetics.

One goal of computational quantum chemistry is to attain chemical accuracy, which is generally defined for energetic quantities as an accuracy of 1 kcal mol<sup>−1</sup>. The development of increasingly precise electronic model chemistries coupled with improved computational efficiency can now consistently permit the calculation of even more accurate energies (e.g., 1 kJ mol<sup>−1</sup>) for small systems. In fact, Born–Oppenheimer energies can be calculated to such a degree of accuracy by

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some modern electronic model chemistries that the principal source of disagreement between these computations and experiment can shift from unconverged electronic energies to the approximate treatment of ZPEs, thermal vibrational energies, and vibrational free energies. Consequently, the calculation of accurate vibrational frequencies is crucial. For example, the ZPE of 1-pentanol is slightly in excess of 100 kcal mol<sup>-1</sup>, so a 1% error in the ZPE is too large if one is aiming for chemical accuracy.

Electronic model chemistries are usually used to compute vibrational frequencies by invoking the approximation that the potential energy in the vicinity of a minimum varies quadratically with respect to the nuclear coordinates. For ZPEs, this leads to the expression

$$\varepsilon_{\text{vib}}^{\text{G}} \cong \varepsilon_{\text{vib}}^{\text{GH}} = \frac{\hbar c}{2} \sum_m \omega_m \quad (1)$$

where  $\varepsilon_{\text{vib}}^{\text{G}}$  is the ZPE (difference between ground vibrational-state energy and the potential energy at the classical equilibrium position),  $\varepsilon_{\text{vib}}^{\text{GH}}$  is the harmonic approximation to it,  $\omega_m$  is the computed harmonic vibrational frequency of mode  $m$  in wave numbers (this is computed from the Hessian, that is, the matrix of quadratic force constants),  $\hbar$  is Planck's constant, and  $c$  is the speed of light. The neglect of anharmonicity tends to overestimate the ZPE.<sup>1</sup> Therefore, in order to obtain accurate zero-point energies, one must either calculate the anharmonic corrections or scale the frequencies. Calculating the anharmonicity requires higher-order (e.g., cubic and quartic) force constants and information about torsional barriers or full potential energy surfaces, and this additional data is often unavailable or even unaffordable. For small molecules, perturbative approaches may be affordable and can yield accurate anharmonic vibrational frequencies provided that these approaches are not significantly affected by the problem of Fermi resonances.<sup>2–6</sup> However, linear species cannot be treated with this formalism, and for large systems, the associated computational cost may not be affordable since analytic second derivatives are required for such calculations. Therefore, in order to obtain more accurate ZPEs directly from the computed quadratic force constants for complex systems, it is customary to use scaling, and this is the subject of the present article.

We will scale the harmonic frequencies by a constant:

$$\varepsilon_{\text{vib}}^{\text{G}} \cong \frac{\hbar c}{2} \sum_m (\lambda \omega_m) \quad (2)$$

Alternatively, it might be of interest to obtain the true harmonic or fundamental frequencies from the set of computed harmonic frequencies:

$$\omega_m^{\text{true}} \cong \lambda \omega_m \quad (3)$$

$$v_m \cong \lambda \omega_m \quad (4)$$

where  $\omega_m^{\text{true}}$  are the true harmonic frequencies, and  $v_m$  are the observable fundamental frequencies. The constant  $\lambda$  is commonly referred to as a “scale factor,” and its specific value depends on the molecule and the electronic model chemistry used to compute the frequencies. We will use the

language of Pople,<sup>7</sup> by which an electronic structure method is called a theoretical model chemistry or—in the present context—an electronic model chemistry, and for single-level methods, it denotes a choice of one-electron basis set and either a level of correlation of the electronic wave function or a choice of approximate density functional. An electronic model chemistry can also be a multilevel method, such as BMC–CCSD<sup>8</sup> or MC3BB.<sup>9</sup>

For highest accuracy, the values of the scale factors  $\lambda$  will be different in each of eqs 2–4, i.e., they will depend not only on the electronic model chemistry but also on the property for which they are optimized.<sup>10,11</sup> In the present work, we optimize general scale factors that can be used to obtain accurate fundamental ( $\lambda^{\text{F}}$ ) and true harmonic frequencies ( $\lambda^{\text{H}}$ ) and ZPEs ( $\lambda^{\text{ZPE}}$ ). These optimized values are obtained, for a given electronic model chemistry, by correlating computed harmonic frequencies with specially constructed experimental databases. In addition, we also test the assumption that the scale factors  $\lambda^{\text{F}}$ ,  $\lambda^{\text{H}}$ , and  $\lambda^{\text{ZPE}}$  can be related to one another through simple proportionality constants. Accepting these proportionalities allows us to derive a set of universal scale factor ratios that can be used to interconvert between scale factors optimized for different purposes, making it possible to obtain all three scale factors at the expense of explicitly calculating just one, for any given electronic model chemistry. Finally, we construct a representative database of accurate zero-point energies that is smaller than the original one but statistically representative, so that additional scale factor optimizations can be carried out with minimal effort, allowing—in the future—the convenient derivation of scale factors for new density functionals, new wave function approximations, and new basis sets.

## 2. Methodology

**2.1. Accurate Vibrational Frequencies and Zero-Point Energies.** In order to determine the optimal values for the scale factors of interest, it is essential to first establish reliable databases of accurate experimental quantities to which the computed analogs can be compared. We recall that although fundamental frequencies can be observed directly, the corresponding harmonic analogs are just conceptual, and in practice, these are obtained from experiment by extrapolating a vibrational progression to the experimentally inaccessible vibrationless state.<sup>12</sup> For harmonic frequencies, we employ the recently compiled F38/06 database,<sup>13</sup> which consists of the 38 experimental harmonic frequencies of the 15 molecules used in this study, originally taken from Martin et al.<sup>14</sup> (Note that F in the name of the database denotes frequencies, although elsewhere in the article it denotes fundamentals.) In Table 1 we supplement the F38/06 database with an additional column containing the 38 experimentally observed fundamental frequencies for the 15 molecules in question, taken from the Computational Chemistry Comparison and Benchmark Database and the NIST Chemistry Web book.<sup>15,16</sup> This compilation of the harmonic and fundamental frequencies will be denoted as the F38/10 database.

**Table 1.** F38/10 Database: Experimental Harmonic and Fundamental Vibrational Frequencies

molecule	mode	symmetry	harmonic frequency <sup>a</sup> (cm <sup>-1</sup> )	fundamental frequency <sup>b</sup> (cm <sup>-1</sup> )
HF	1	$\sigma$	4138	3959
H <sub>2</sub>	1	$\sigma_g$	4401	4159
N <sub>2</sub>	1	$\sigma_g$	2359	2330
F <sub>2</sub>	1	$\sigma_g$	917	894
CO	1	$\sigma$	2170	2143
OH	1	$\sigma$	3738 <sup>b</sup>	3568
Cl <sub>2</sub>	1	$\sigma_g$	560 <sup>b</sup>	554
CO <sub>2</sub>	1	$\sigma_g$	1354	1333
	2	$\sigma_u$	2397	2349
	3	$\pi_u$	673	667
H <sub>2</sub> O	1	$a_1$	3832	3657
	2	$a_1$	1648	1595
	3	$b_1$	3942	3756
N <sub>2</sub> O	1	$\sigma$	2282	2224
	2	$\sigma$	1298	1285
	3	$\pi$	596	589
HCN	1	$\sigma$	3443	3312
	2	$\sigma$	2127	2089
	3	$\pi$	727	712
C <sub>2</sub> H <sub>2</sub>	1	$\sigma_g$	3495	3374
	2	$\sigma_g$	2008	1974
	3	$\sigma_u$	3415	3289
	4	$\pi_g$	624	612
	5	$\pi_u$	747	730
H <sub>2</sub> CO	1	$a_1$	2937	2782
	2	$a_1$	1778	1746
	3	$a_1$	1544	1500
	4	$b_1$	1188	1167
	5	$b_2$	3012	2843
	6	$b_2$	1269	1249
NH <sub>3</sub>	1	$a_1$	3478	3337
	2	$a_1$	1084	950
	3	$e$	3597	3444
	4	$e$	1684	1627
CH <sub>4</sub>	1	$a_1$	3026	2917
	2	$e$	1583	1534
	3	$t_2$	3157	3019
	4	$t_2$	1367	1306

<sup>a</sup> Martin et al.<sup>14</sup> <sup>b</sup> NIST Web book and Computational Chemistry Comparison and Benchmark Database.<sup>15,16</sup>

Because real molecules cannot have stationary energies lower than those of their ground states, the ZPE, which in quantum chemistry is defined as the difference between the energy of the vibrational ground state and the energy minimum on the Born–Oppenheimer<sup>17</sup> or Born–Huang<sup>18</sup> potential energy surface, is not a measurable quantity. However, ZPEs have been estimated from experiment by a two-step process in which first the spectroscopic data are used to infer a potential energy surface or a set of spectroscopic constants, and then the ZPE is inferred from the surface or constants. In previous work<sup>13</sup> on the optimization of scale factors for ZPEs, we have used the ZPVE15/06 database, which is composed of such “experimental” ZPEs, originally taken from the compilations of Martin<sup>19</sup> and Grev et al.,<sup>10</sup> for the 15 molecules investigated here. Recently, however, Irikura and co-workers have meticulously reanalyzed the available spectroscopic parameters for many important molecules, including 12 of the 15 used in this study and arrived at somewhat different values for their respective ZPEs.<sup>20,21</sup> In addition, Irikura and co-workers have also carefully taken into account the propagation of the statistical

uncertainties associated with the spectroscopic constants reported in literature as well as those resulting from bias, to arrive at an estimate of the standard uncertainty for the ZPEs derived in their work.<sup>20,21</sup>

Aside from the aim of compiling a list of precise ZPEs against which computational methods can be validated, Irikura’s reanalysis of these quantities was further motivated by the fact that the formulas commonly used to extract “experimental” ZPEs from spectroscopic constants were often inadequate due to the inclusion of only a subset of terms in the power series of vibrational energy as a function of vibrational quantum numbers.<sup>2,4,20–26</sup> For example, in the case of a diatomic molecule, the most commonly used formula for obtaining the vibrational energy levels relative to the energetic minimum on the potential energy curve is

$$G(v) \cong \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \omega_e y_e \left( v + \frac{1}{2} \right)^3 + \dots \quad (5)$$

where  $\omega_e$ ,  $\omega_e x_e$ , and  $\omega_e y_e$  denote parameters corresponding to the harmonic frequency and the first and second anharmonicity constants, respectively, and  $v$  is the vibrational quantum number.<sup>27</sup> This leads to the expression:

$$\frac{\epsilon_{\text{vib}}^G}{hc} \equiv G(0) \cong \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + \frac{1}{8}\omega_e y_e \quad (6)$$

for the ZPE. In contrast, Dunham has shown<sup>28</sup> that the ZPE of a diatomic species can be expressed more accurately through the power series:

$$G(v) \cong Y_{00} + Y_{10} \left( v + \frac{1}{2} \right) - Y_{20} \left( v + \frac{1}{2} \right)^2 + Y_{30} \left( v + \frac{1}{2} \right)^3 + \dots \quad (7)$$

where  $Y_{10}$ ,  $Y_{20}$ , and  $Y_{30}$  approximately correspond to  $\omega_e$ ,  $\omega_e x_e$ , and  $\omega_e y_e$ , and  $Y_{00}$  is a constant that is commonly neglected. The values of the constant term  $Y_{00}$  and the higher-order anharmonicity  $\omega_e y_e$  are often unknown and even more often neglected; however, although they are usually small (often no more than a few cm<sup>-1</sup>), they are not completely negligible and taking them into account leads to more accurate estimations of the diatomic ZPEs.<sup>20</sup> The inclusion of all of these constants into eq 6 leads to

$$\frac{\epsilon_{\text{vib}}^G}{hc} \equiv G(0) \cong Y_{00} + \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e + \frac{1}{8}\omega_e y_e \quad (8)$$

which is the formula used by Irikura to derive the ZPEs for the diatomics in his work.<sup>20</sup>

A constant term called  $E_0$ ,<sup>2,22</sup> analogous to  $Y_{00}$ , has often been neglected in analyzing polyatomic spectra. Irikura et al. have estimated this term and higher-order anharmonic terms for polyatomics and thereby also derived refined values for polyatomic ZPEs.<sup>21</sup> Therefore, in the present work, we update the original ZPVE15/06 database by replacing the old ZPE values from this database with the recently refined values from Irikura and co-workers, with the exception of N<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub>, whose ZPE values have not been reanalyzed by Irikura et al.<sup>20,21</sup> We denote this new compila-

**Table 2.** ZPVE15/10 Database: Experimental ZPEs for the 15 Molecules Used in This Work

molecule	ZPE <sup>a</sup> (kcal mol <sup>-1</sup> )
HF	5.86353 <sup>a</sup>
H <sub>2</sub>	6.2310 <sup>a</sup>
N <sub>2</sub>	3.3618 <sup>a</sup>
F <sub>2</sub>	1.3021 <sup>a</sup>
CO	3.0929144 <sup>a</sup>
OH	5.2915 <sup>a</sup>
Cl <sub>2</sub>	0.7983 <sup>a</sup>
CO <sub>2</sub>	7.3 <sup>a</sup>
H <sub>2</sub> O	13.26 <sup>a</sup>
N <sub>2</sub> O	6.770 <sup>b</sup>
HCN	10.0 <sup>a</sup>
C <sub>2</sub> H <sub>2</sub>	16.49 <sup>a</sup>
H <sub>2</sub> CO	16.1 <sup>a</sup>
NH <sub>3</sub>	21.200 <sup>c</sup>
CH <sub>4</sub>	27.710 <sup>b</sup>

<sup>a</sup> Irikura et al.<sup>20,21</sup> <sup>b</sup> Grev et al.<sup>10</sup> <sup>c</sup> Martin.<sup>19</sup>

tion of 15 ZPEs as the ZPVE15/10 database, and we present it in Table 2.

**2.2. Computational Methods.** In the first stage of this work, the harmonic frequencies of the 15 molecules comprising the F38/10 database have been computed using 22 combinations of approximate density functionals with one-electron basis sets and also using the BMC–CCSD<sup>8</sup> multicoefficient correlation method. The density functionals used in this first stage are B1LYP,<sup>29–31</sup> M05-2X,<sup>32</sup> M06-L,<sup>33</sup> M06-HF,<sup>34</sup> M06,<sup>13</sup> M06-2X,<sup>13</sup> M08-SO,<sup>35</sup> and M08-HX.<sup>35</sup> Each of these functionals was paired with both the 6-31+G(d,p)<sup>1,36</sup> double- $\zeta$  basis sets and several triple- $\zeta$  basis sets: MG3S,<sup>37</sup> def2-TZVPP,<sup>38,39</sup> MG3SXP,<sup>35</sup> cc-pVTZ+,<sup>40–43</sup> aug-cc-pVTZ,<sup>40,42,44</sup> and maug-cc-pV(T+d)Z.<sup>40,42–45</sup> In this stage, we also reoptimized the ZPE scale factors obtained with HF/MG3S theory, where HF denotes Hartree–Fock, and 16 important functional/MG3S combinations that have recently been published,<sup>13</sup> and we supplemented these with newly derived scale factors for frequencies. The 16 functionals involved in this step are BLYP,<sup>29,30</sup> B3LYP,<sup>29,30,46,47</sup> PBE,<sup>48</sup> B98,<sup>49</sup> VSXC,<sup>50</sup> PBE0,<sup>51–53</sup> HFLYP,<sup>54,55</sup> TPSSH,<sup>56</sup> BMK,<sup>57</sup> B97-3,<sup>58</sup> M05,<sup>59</sup> M05-2X,<sup>32</sup> M06-L,<sup>33</sup> M06-HF,<sup>34</sup> M06,<sup>13</sup> and M06-2X.<sup>13</sup> In all, the set of three scale factors were optimized for 40 electronic model chemistries using the full databases in stage one.

In the second stage of this study, we obtain and employ a representative database (which is a key component of what will be called a reduced optimization model) or, in some cases, make use of approximate systematic corrections to efficiently derive and/or update scale factors for 105 additional electronic model chemistries. The electronic model chemistries used in stage two are some of the density functionals listed above, plus single-level wave function approximations: HF, MP2,<sup>1</sup> MP4(SDQ),<sup>1</sup> QCISD,<sup>60</sup> CCSD,<sup>61</sup> CCSD(T),<sup>62</sup> CCSD-F12,<sup>63,64</sup> CCSD(T)-F12,<sup>63,64</sup> other density functionals that depend on occupied orbitals: B1B95,<sup>30,65</sup> B3P86,<sup>46,66</sup> B3PW91,<sup>46,67–71</sup> BB1K,<sup>30,65,72</sup> BB95,<sup>30,65</sup> BP86,<sup>30,66</sup> CAM-B3LYP,<sup>73</sup> HSEh1PBE,<sup>74–80</sup> MOHLYP,<sup>29,81</sup> MPW1B95,<sup>65,82,83</sup> MPW1K,<sup>83–85</sup> MPW3LYP,<sup>29,82,83,86</sup> MPWB1K,<sup>65,82,83</sup> MPWL1P1M,<sup>29,81</sup> PBE1K CIS,<sup>48,87,88</sup> PW6B95,<sup>89</sup> SOGGA,<sup>90</sup>  $\tau$ -HCTHhyb,<sup>84</sup> TPSS1K CIS,<sup>87,91,92</sup>

$\omega$ B97,<sup>93</sup>  $\omega$ B97X,<sup>93</sup> XB1K,<sup>29,30,65,67,82,86</sup> X1B95,<sup>29,30,65,67,82,86</sup> one of these reoptimized with molecular mechanics dispersion terms:  $\omega$ B97X-D,<sup>94</sup> three methods based on the neglect of diatomic differential overlap: AM1,<sup>95</sup> PM3,<sup>96,97</sup> PM6,<sup>98</sup> two doubly hybrid density functional methods: MC3BB,<sup>9</sup> MC3MPW,<sup>9</sup> and one more multicoefficient correlation method: MC-QCISD/3.<sup>99</sup> The density functionals and single-level wave function approximations are paired with various basis sets, many of which have also been used in stage one, plus def2-TZVP,<sup>38,39</sup> ma-TZVP,<sup>38,39,100</sup> jul-cc-pVTZ,<sup>40,42–45,101</sup> MIDI! (also called MIDIX),<sup>102,103</sup> MIDIY,<sup>102–104</sup> and a host of Pople-type basis sets.

The selection of these electronic model chemistries was made to strategically complement and extend our pre-existing database<sup>105</sup> of available scale factors for electronic model chemistries, a copy of which is provided in the form of Table S1 in the Supporting Information. All of the density functional calculations employed “ultrafine” integration grids, and, unless otherwise indicated, were carried out with a locally modified version of the Gaussian 03 program suite.<sup>106,107</sup> The BMC–CCSD, MC3BB, MC3MPW, and MC-QCISD/3 calculations were performed using the ML-GAUSS program.<sup>108</sup>

A comment on basis sets may be helpful here. We have shown<sup>100,101</sup> that a very suitable basis set of for many density functional applications is a polarized valence-triple- $\zeta$  basis set minimally augmented with diffuse functions, where minimal augmentation is defined as adding diffuse s and p subshells to atoms heavier than hydrogen or helium. Several of the basis sets used here correspond to this “minimally augmented polarized triple- $\zeta$ ” class, in particular, MG3S,<sup>37</sup> MG3SXP,<sup>35</sup> cc-pVTZ+,<sup>40–43</sup> maug-cc-pV(T+d)Z,<sup>40,42–45</sup> and ma-TZVP;<sup>38,39,100</sup> full details of these basis sets and all the other basis sets used here are given in the references cited.

**2.3. Scale Factors for Vibrational Frequencies and Zero-Point Energies.** To determine the optimal scale factors for the true harmonic and fundamental frequencies, the computed harmonic frequencies were fit against the experimental values available for these quantities, found in the F38/10 database (Table 1). The scale factors  $\lambda^F$  and  $\lambda^H$  were optimized by minimizing the respective root-mean-square (rms) deviations for the entire set of 38 frequencies. Specifically, the rms deviations for the two properties are defined as

$$\text{RMS(harmonic frequencies)} = \left\{ \left[ \sum_{m=1}^{38} (\lambda^H \omega_m - \omega_m^{\text{true}})^2 \right] / 38 \right\}^{1/2} \quad (9)$$

$$\text{RMS(fundamentals)} = \left\{ \left[ \sum_{m=1}^{38} (\lambda^F \omega_m - v_m)^2 \right] / 38 \right\}^{1/2} \quad (10)$$

where  $\omega_m$  is the computed harmonic frequency,  $\omega_m^{\text{true}}$  is the harmonic frequency derived from extrapolations of the observed vibrational progressions, and  $v_m$  is the experimental fundamental frequency, all found in Table 1.



**Table 3.** Compilation of Optimal Scale Factors

model chemistry	$\lambda^{\text{ZPE}}$	rms deviation <sup>a</sup>		$\lambda^{\text{H}}$	rms deviation <sup>b</sup>		$\lambda^{\text{F}}$	rms deviation <sup>b</sup>	
		scaling	no scaling		scaling	no scaling		scaling	no scaling
B1LYP/MG3S	0.978	0.13	0.31	0.994	42	44	0.955	31	117
B3LYP/MG3S	0.983	0.12	0.25	0.998	41	41	0.960	30	104
B97-3/MG3S	0.972	0.14	0.38	0.986	44	57	0.947	35	138
B98/MG3S	0.982	0.12	0.25	0.995	41	42	0.956	34	114
BLYP/MG3S	1.013	0.11	0.19	1.031	38	85	0.991	38	43
BMC-CCSD	0.985	0.14	0.23	1.001	16	16	0.962	34	101
BMK/MG3S	0.971	0.16	0.40	0.984	54	69	0.945	46	147
HF/MG3S	0.919	0.28	1.12	0.932	86	201	0.895	70	288
HFLYP/MG3S	0.899	0.30	1.40	0.912	92	259	0.876	75	347
M05-2X/6-31+G(d,p)	0.961	0.19	0.54	0.974	61	90	0.936	50	171
M05-2X/def2-TZVPP	0.962	0.22	0.52	0.976	63	87	0.938	51	166
M05-2X/MG3S	0.962	0.21	0.53	0.975	60	87	0.937	50	168
M05/MG3S	0.977	0.16	0.33	0.989	56	63	0.951	46	132
M06-2X/6-31+G(d,p)	0.967	0.18	0.45	0.979	60	81	0.940	51	159
M06-2X/aug-cc-pVTZ	0.971	0.20	0.41	0.985	61	72	0.946	48	144
M06-2X/def2-TZVPP	0.970	0.20	0.43	0.983	61	75	0.945	48	148
M06-2X/maug-cc-pV(T+d)Z	0.971	0.20	0.42	0.984	60	73	0.945	48	146
M06-2X/MG3S	0.970	0.19	0.43	0.982	60	74	0.944	47	149
M06-HF/6-31+G(d,p)	0.954	0.29	0.65	0.969	88	119	0.931	77	193
M06-HF/def2-TZVPP	0.958	0.29	0.61	0.970	87	117	0.932	76	191
M06-HF/MG3S	0.955	0.30	0.65	0.967	86	119	0.930	77	194
M06-L/6-31+G(d,p)	0.978	0.10	0.30	0.992	42	46	0.953	35	123
M06-L/def2-TZVPP	0.976	0.11	0.32	0.995	46	48	0.956	33	114
M06-L/MG3S	0.978	0.10	0.30	0.996	45	46	0.958	33	111
M06/6-31+G(d,p)	0.980	0.15	0.29	0.989	56	62	0.950	46	133
M06/def2-TZVPP	0.979	0.19	0.33	0.992	65	68	0.953	48	127
M06/MG3S	0.981	0.18	0.30	0.994	60	68	0.955	49	123
M08-HX/6-31+G(d,p)	0.972	0.18	0.40	0.983	64	78	0.944	51	150
M08-HX/cc-pVTZ+	0.974	0.20	0.39	0.985	66	76	0.946	51	144
M08-HX/def2-TZVPP	0.973	0.20	0.40	0.984	67	78	0.945	52	147
M08-HX/MG3S	0.973	0.19	0.39	0.984	65	76	0.946	50	145
M08-SO/6-31+G(d,p)	0.979	0.18	0.32	0.989	60	66	0.951	49	134
M08-SO/cc-pVTZ+	0.982	0.20	0.30	0.995	64	65	0.956	47	120
M08-SO/def2-TZVPP	0.980	0.21	0.32	0.993	65	68	0.954	48	125
M08-SO/MG3S	0.983	0.20	0.29	0.995	64	66	0.956	48	119
M08-SO/MG3SXP	0.984	0.21	0.29	0.996	66	67	0.957	49	119
PBE/MG3S	1.010	0.09	0.15	1.025	37	72	0.985	33	48
PBE0/MG3S	0.975	0.15	0.34	0.989	50	57	0.950	37	131
TPSSH/MG3S	0.984	0.12	0.23	1.002	37	38	0.963	33	97
VSXC/MG3S	0.986	0.08	0.19	1.001	32	33	0.962	32	98
average <sup>c</sup>		0.18	0.41		58	76		47	142

<sup>a</sup> In units of kcal mol<sup>-1</sup>. <sup>b</sup> In units of cm<sup>-1</sup>. <sup>c</sup> The average absolute deviation for ZPE is 0.14 kcal mol<sup>-1</sup>, and the absolute percent deviation is 2.8% (see Supporting Information).

Optimal scale factors for ZPEs ( $\lambda^{\text{ZPE}}$ ) can be obtained in an analogous manner, by minimizing the rms deviations between the set of the computed harmonic ZPEs for the 15 species and their “experimental” ZPEs:

$$\text{RMS}(\text{ZPE}) = \left\{ \left[ \sum_{m=1}^{15} (\lambda^{\text{ZPE}} \varepsilon_{\text{vib}_m}^{\text{GH}} - \varepsilon_{\text{vib}_m}^{\text{G}})^2 / 15 \right] \right\}^{1/2} \quad (11)$$

The best estimates for the “experimental” ZPEs of the 15 species of interest,  $\varepsilon_{\text{vib}_m}^{\text{G}}$ , are taken from the ZPVE15/10 database (Table 2).

This procedure yields

$$\lambda^{\text{ZPE}} = \frac{\sum_{m=1}^M (\varepsilon_{\text{vib}_m}^{\text{GH}} \varepsilon_{\text{vib}_m}^{\text{G}})}{\sum_{m=1}^M (\varepsilon_{\text{vib}_m}^{\text{GH}})^2} \quad (12)$$

where  $M$  is the number of ZPEs. Analogous expressions can be obtained for  $\lambda^{\text{H}}$  and  $\lambda^{\text{F}}$  by substituting the corresponding experimental and calculated quantities in the above equation and performing the two summations over the number of frequencies with  $M = 38$ .

### 3. Results and Discussion

#### 3.1. Stage One: Scale Factors Obtained from Large Databases. 3.1.1. Scale Factors for Vibrational Frequencies.

The optimal scale factors for reproducing the set of vibrational frequencies of interest from the harmonic vibrational frequencies computed with the electronic model chemistries used in stage one of this work are presented in Table 3. As can be seen in Table 3, the rms deviations for the prediction of vibrational frequencies using the optimal scale factors are fairly reasonable, averaging 58 and 47 cm<sup>-1</sup> in the case of harmonic and fundamental frequencies, respectively, which mark substantial improvements over the 76 and 142 cm<sup>-1</sup> rms deviations that are obtained for the same quantities in the absence of scaling. Overall, upon scaling, the most reliable results are obtained with the BMC-CCSD multilevel method, which has an average rms deviation (average of eqs 9 and 10) of only 20 cm<sup>-1</sup>. The best performance of any density functional tested is for VSXC, which has an average rms deviation of 32 cm<sup>-1</sup>, and the best performance of any Minnesota functional is for M06-L, which has an average rms deviation of 39–40 cm<sup>-1</sup>, depending on the basis set used.

Most of the electronic model chemistries, however, used in conjunction with the appropriate scale factors, yield

frequencies that are usually in reasonable agreement with experiment, with average absolute deviations of  $44 \pm 13 \text{ cm}^{-1}$  ( $2.9 \pm 0.9\%$ ) and  $35 \pm 10 \text{ cm}^{-1}$  ( $2.4 \pm 0.6\%$ ) for harmonic and fundamental frequencies, respectively; although HF, HFLYP, and M06-HF (all with 100% Hartree–Fock exchange) are much less reliable than the other electronic model chemistries tested (Table 4). However, because the rms deviations can be misleading when trying to select an appropriate method for a specific problem, we have tabulated in Table 4 the number  $N$  of “outlier” frequencies for each of the electronic model chemistries tested. We have arbitrarily defined outliers as scaled frequencies that differ from their corresponding experimental values by more than 5%. In addition, Table 4 also contains a list of the outlying frequencies. In an earlier study of computational harmonic frequencies and equilibrium geometries, Martin noted that “the  $\text{F}_2$  molecule proves troublesome for all functionals with regard to bond length and harmonic frequencies (this is less the case for HF).”<sup>14</sup> It is interesting to note that even upon scaling, almost all of the electronic model chemistries tested severely overestimated the harmonic and fundamental stretching frequency in  $\text{F}_2$ . In fact, only the BMC–CCSD and M06-L/6-31+G(d,p) electronic model chemistries were successful in predicting both the  $\text{F}_2$  harmonic and fundamental frequencies with deviations of less than 5%.

Increasing the size of the one-electron basis set for a given density functional did not significantly alter the ensuing values for  $\lambda^{\text{F}}$  and  $\lambda^{\text{H}}$  nor lead to more accurate results. In fact, increasing the basis set generally resulted in a slight loss of accuracy with regard to the prediction of both the harmonic and fundamental frequencies. We also note that while  $\lambda^{\text{F}}$  and  $\lambda^{\text{H}}$  change somewhat in going from a double- to a triple- $\zeta$  basis set, these parameters do not show much sensitivity toward the nature of the triple- $\zeta$  basis set used, with all differences in optimum scale factors being 0.004 or less. These results are consistent with the observations of Andersson and Uvdal,<sup>109</sup> who, in their study of the basis set dependence of vibrational frequencies computed with the B3LYP density functional, found that “convergence of the vibrational frequencies with respect to the addition of diffuse and polarization functions is generally met already at the 6-311G(d,p) level,” based on the fact that the vibrational frequencies calculated with B3LYP/6-311G(d,p) typically agreed to within  $10 \text{ cm}^{-1}$  with those obtained from B3LYP/6-311++G(3df,3pd). All of the triple- $\zeta$  basis sets examined in the present study are larger than 6-311G(d,p), and the observed scale factor invariance, with respect to the triple- $\zeta$  basis sets used in conjunction with the various density functionals tested in this work, suggests that the convergence criteria proposed by Andersson and Uvdal in the case of B3LYP is applicable to density functionals in general.

The above observation about basis set convergence of vibrational frequencies enables us to deduce whether or not the scale factors obtained in this study, optimized based on a limited set of frequencies, reasonably represents those that would be obtained from a more extensive set because it legitimizes direct comparison with the results of other existing studies in which basis sets of at least a 6-311G(d,p) caliber were used. Andersson and Uvdal<sup>109</sup> employed 950

vibrational frequencies (belonging to 125 molecules) in their database, which led to a value for  $\lambda^{\text{F}}$  of 0.968 in the case of B3LYP/6-311+G(d,p). This value compares reasonably well with the  $\lambda^{\text{F}}$  we obtained for B3LYP/MG3S, 0.960. Another comprehensive study of scale factors has been performed by Scott and Radom<sup>11</sup> and incorporates 1066 frequencies (including degeneracies), belonging to 122 molecules, in the optimization of  $\lambda^{\text{F}}$ . In the tests conducted here and in the study of Scott and Radom, HF and the BLYP and B3LYP density functionals form a common subset, although different basis sets were used in the two studies. In our study, we used the MG3S basis set, while in Scott and Radom’s study, HF was paired with six different basis sets ranging from 3 to 21G to 6-311G(df,p), BLYP is included in conjunction with 6-31G(d) and 6-311G(df,p), and B3LYP is included with just the 6-31G(d) basis set. In the case of HF, we find that the values for  $\lambda^{\text{F}}$  of 0.9051 and 0.9054 obtained by Scott and Radom with 6-311G(d,p) and 6-311G(df,p), respectively, the only two basis sets which meet the convergence criteria set forth by Andersson and Uvdal, compare reasonably well with the value of 0.895 we obtained with the MG3S basis set. For BLYP/6-311G(df,p), Scott and Radom obtained  $\lambda^{\text{F}} = 0.9986$ , which is in relatively good accord with our value of 0.991. Although the 6-31G(d) basis set used with B3LYP by Scott and Radom is likely too small to have reached convergence with respect to vibrational frequencies, we note that the value of  $\lambda^{\text{F}} = 0.9614$  they reported agrees well with 0.960, the value we obtained for B3LYP/MG3S. Finally, although not directly comparable, we note the similarity of our values for  $\lambda^{\text{F}}$  with those derived by Rauhut and Pulay for BLYP/6-31G(d) and B3LYP/6-31G(d), namely 0.995 and 0.963, respectively, for a different test set comprised of the 347 fundamental frequencies of 20 molecules.<sup>110</sup> The results of these analyses indicate that the fundamental frequencies in the F38/10 database constitute a fair representative subset of a more comprehensive set, provided that one recognizes that optimal general scale factors are intrinsically uncertain by  $\sim 0.01$  (we say “at least” because actual estimates of uncertainties (cited below) are larger). Values for  $\lambda^{\text{H}}$  were not derived in the studies of Andersson and Uvdal, Scott and Radom, or Rauhut and Pulay. We also note that although various integration grids have been employed in these studies, it has been shown that the effect of increasing the integration grid is usually negligible for vibrational frequencies.<sup>11</sup>

Rauhut and Pulay also explored a more sophisticated scaling approach, based on the scaled quantum mechanical (SQM) force field procedure,<sup>111</sup> in which separate scale factors are optimized for 11 different types of internal coordinates in an effort to more closely reproduce the observed fundamentals.<sup>110</sup> Although that procedure led to modest improvements, it is more complicated. To make the method more general, Rauhut and Pulay also investigated the degree of transferability of the set of internal-coordinate specific scale factors by optimizing the 11 parameters for an extended test set composed of 31 molecules, and they found that while most of these scale factors were not changed significantly, “the scaling factors for the out-of-plane modes, the torsion of conjugated systems, and the torsions of single-bonded systems show bigger deviations.”<sup>110</sup> Therefore, while

**Table 4.** Scaled Harmonic and Fundamental Frequencies: Absolute Deviations and Outliers

model chemistry	harmonic frequencies			fundamental frequencies		
	dev <sup>a</sup>	N <sup>b</sup>	outlier frequencies <sup>c</sup>	dev <sup>a</sup>	N <sup>b</sup>	outlier frequencies <sup>c</sup>
B1LYP/MG3S	31 (2.2)	3	F <sub>2</sub> (15), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (8), <sup>2</sup> NH <sub>3</sub> (-6)	22 (1.6)	2	F <sub>2</sub> (13), Cl <sub>2</sub> (-7)
B3LYP/MG3S	31 (2.1)	3	F <sub>2</sub> (13), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (7), <sup>2</sup> NH <sub>3</sub> (-6)	22 (1.6)	2	F <sub>2</sub> (12), Cl <sub>2</sub> (-7)
B97-3/MG3S	32 (2.2)	3	F <sub>2</sub> (17), <sup>3</sup> HCN(5), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (7)	26 (1.8)	1	F <sub>2</sub> (15)
B98/MG3S	29 (1.9)	1	F <sub>2</sub> (16)	25 (1.6)	1	F <sub>2</sub> (15)
BLYP/MG3S	27 (1.4)	2	F <sub>2</sub> (8), Cl <sub>2</sub> (-8)	28 (1.8)	3	F <sub>2</sub> (6), Cl <sub>2</sub> (-11), <sup>2</sup> NH <sub>3</sub> (6)
BMC-CCSD	13 (0.8)	0		28 (1.6)	1	<sup>2</sup> NH <sub>3</sub> (6)
BMK/MG3S	41 (2.7)	4	F <sub>2</sub> (20), Cl <sub>2</sub> (7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (8), <sup>2</sup> NH <sub>3</sub> (-7)	36 (2.2)	2	F <sub>2</sub> (19), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (6)
HF/MG3S	67 (4.5)	10	<sup>1,3</sup> N <sub>2</sub> O(6.13), F <sub>2</sub> (29), N <sub>2</sub> (8), <sup>3</sup> CO <sub>2</sub> (8), <sup>2,3</sup> HCN(5.13), <sup>4,5</sup> C <sub>2</sub> H <sub>2</sub> (22.8), <sup>2</sup> NH <sub>3</sub> (-6)	54 (3.7)	5	F <sub>2</sub> (27), <sup>3</sup> N <sub>2</sub> O(9), <sup>3</sup> HCN(11), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (19), <sup>5</sup> C <sub>2</sub> H <sub>2</sub> (6)
HFLYP/MG3S	72 (5.0)	11	<sup>4,5</sup> C <sub>2</sub> H <sub>2</sub> (23.7), F <sub>2</sub> (31), N <sub>2</sub> (8), <sup>1,3</sup> N <sub>2</sub> O(7.13), <sup>2,3</sup> HCN(6.13), <sup>3</sup> CO <sub>2</sub> (8), <sup>2</sup> NH <sub>3</sub> (-10), <sup>2</sup> H <sub>2</sub> CO(5)	56 (3.9)	6	F <sub>2</sub> (30), <sup>1</sup> N <sub>2</sub> O(6), <sup>3</sup> N <sub>2</sub> O(10), <sup>3</sup> HCN(11), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (21), <sup>5</sup> C <sub>2</sub> H <sub>2</sub> (6)
M05-2X/6-31+G(d,p)	42 (2.8)	5	N <sub>2</sub> (6), F <sub>2</sub> (24), Cl <sub>2</sub> (-7), <sup>2</sup> H <sub>2</sub> O(-6), <sup>2</sup> NH <sub>3</sub> (-10)	35 (2.5)	3	F <sub>2</sub> (22), Cl <sub>2</sub> (-9), <sup>2</sup> H <sub>2</sub> O(-7)
M05-2X/def2-TZVPP	45 (3.1)	6	<sup>2</sup> NH <sub>3</sub> (-8), F <sub>2</sub> (26), <sup>3</sup> N <sub>2</sub> O(7), <sup>3</sup> HCN(6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (12), N <sub>2</sub> (6)	34 (2.4)	2	F <sub>2</sub> (24), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (10)
M05-2X/def2-TZVPP	43 (3.0)	6	<sup>2</sup> NH <sub>3</sub> (-9), F <sub>2</sub> (25), <sup>3</sup> N <sub>2</sub> O(7), <sup>3</sup> HCN(6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (11), N <sub>2</sub> (5)	33 (2.3)	2	F <sub>2</sub> (24), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (9)
M05-2X/MG3S	47 (3.2)	7	F <sub>2</sub> (17), Cl <sub>2</sub> (6), <sup>2,3</sup> N <sub>2</sub> O(6.9), <sup>3</sup> HCN(8), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (6), <sup>2</sup> NH <sub>3</sub> (-9)	38 (2.4)	3	F <sub>2</sub> (16), <sup>3</sup> N <sub>2</sub> O(6), <sup>3</sup> HCN(6)
M06-2X/MG3S	46 (3.0)	3	F <sub>2</sub> (22), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (6), <sup>2</sup> NH <sub>3</sub> (-8)	36 (2.5)	4	F <sub>2</sub> (21), Cl <sub>2</sub> (-6), <sup>3</sup> CO <sub>2</sub> (-6), <sup>2</sup> H <sub>2</sub> O(-6)
M06-2X/6-31+G(d,p)	45 (3.2)	5	F <sub>2</sub> (25), <sup>3</sup> N <sub>2</sub> O(8), <sup>3</sup> HCN(6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (12), <sup>2</sup> NH <sub>3</sub> (-6)	33 (2.4)	2	F <sub>2</sub> (23), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (9)
M06-2X/def2-TZVPP	46 (3.3)	5	F <sub>2</sub> (25), <sup>3</sup> N <sub>2</sub> O(8), <sup>3</sup> HCN(7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (13), <sup>2</sup> NH <sub>3</sub> (-6)	32 (2.5)	2	F <sub>2</sub> (23), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (10)
M06-2X/def2-TZVPP	45 (3.2)	6	F <sub>2</sub> (25), <sup>3</sup> N <sub>2</sub> O(7), <sup>3</sup> HCN(6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (12), <sup>2</sup> NH <sub>3</sub> (-7)	33 (2.4)	2	F <sub>2</sub> (23), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (10)
M06-2X/maug-cc-pV(T+d)Z	45 (3.2)	7	<sup>2</sup> NH <sub>3</sub> (-7), F <sub>2</sub> (24), <sup>3</sup> N <sub>2</sub> O(8), <sup>3</sup> HCN(7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (13), N <sub>2</sub> (5)	58 (3.8)	7	N <sub>2</sub> (6), F <sub>2</sub> (29), Cl <sub>2</sub> (-11), <sup>3</sup> CO <sub>2</sub> (-7), <sup>2</sup> H <sub>2</sub> O(-8), <sup>2</sup> N <sub>2</sub> O(-8), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (14)
M06-2X/MG3S	66 (4.2)	9	<sup>2</sup> NH <sub>3</sub> (-11), F <sub>2</sub> (31), <sup>1</sup> N <sub>2</sub> O(6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (16), <sup>2</sup> H <sub>2</sub> O(-8), N <sub>2</sub> (9), <sup>2</sup> HCN(7), <sup>3</sup> HCN(7), Cl <sub>2</sub> (-8),	56 (3.5)	4	F <sub>2</sub> (31), <sup>2</sup> H <sub>2</sub> O(-7), <sup>2</sup> N <sub>2</sub> O(-6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (17)
M06-HF/6-31+G(d,p)	65 (4.1)	8	<sup>2</sup> NH <sub>3</sub> (-9), F <sub>2</sub> (33), <sup>1</sup> N <sub>2</sub> O(6), <sup>3</sup> N <sub>2</sub> O(8), <sup>2</sup> H <sub>2</sub> O(-6), N <sub>2</sub> (8), <sup>2</sup> HCN(6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (19)	56 (3.5)	5	F <sub>2</sub> (30), Cl <sub>2</sub> (-7), <sup>2</sup> H <sub>2</sub> O(-6), <sup>2</sup> N <sub>2</sub> O(-6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (16)
M06-HF/def2-TZVPP	65 (4.1)	9	<sup>2</sup> NH <sub>3</sub> (-10), F <sub>2</sub> (32), N <sub>2</sub> (8), <sup>1,3</sup> N <sub>2</sub> O(6.8), <sup>2,3</sup> HCN(6.6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (18), <sup>2</sup> H <sub>2</sub> O(-6)	31 (2.0)	2	Cl <sub>2</sub> (-6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (-9)
M06-HF/MG3S	33 (2.1)	1	<sup>4</sup> C <sub>2</sub> H <sub>2</sub> (-7)	27 (1.8)	2	<sup>3</sup> HCN(6), <sup>2</sup> NH <sub>3</sub> (9)
M06-L/6-31+G(d,p)	35 (2.2)	5	F <sub>2</sub> (7), <sup>3</sup> N <sub>2</sub> O(7), <sup>3</sup> HCN(8), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (6), <sup>5</sup> C <sub>2</sub> H <sub>2</sub> (6)	28 (1.8)	2	<sup>3</sup> HCN(6), <sup>2</sup> NH <sub>3</sub> (8)
M06-L/def2-TZVPP	35 (2.2)	5	F <sub>2</sub> (6), <sup>3</sup> N <sub>2</sub> O(7), <sup>3</sup> HCN(8), <sup>4,5</sup> C <sub>2</sub> H <sub>2</sub> (5.6)	38 (2.3)	1	F <sub>2</sub> (12)
M06/6-31+G(d,p)	45 (2.8)	3	F <sub>2</sub> (13), <sup>3</sup> HCN(6), <sup>2</sup> NH <sub>3</sub> (-13)	40 (2.6)	4	F <sub>2</sub> (14), <sup>3</sup> N <sub>2</sub> O(6), <sup>3</sup> HCN(8), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (9)
M06/def2-TZVPP	55 (3.6)	7	F <sub>2</sub> (16), <sup>3</sup> N <sub>2</sub> O(6), <sup>3</sup> N <sub>2</sub> O(9), <sup>3</sup> HCN(10), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (11), <sup>5</sup> C <sub>2</sub> H <sub>2</sub> (6), <sup>2</sup> NH <sub>3</sub> (-8)	41 (2.6)	4	F <sub>2</sub> (14), <sup>3</sup> N <sub>2</sub> O(6), <sup>3</sup> HCN(7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (9)
M06/MG3S	57 (3.6)	6	<sup>2</sup> NH <sub>3</sub> (-9), F <sub>2</sub> (16), <sup>3</sup> HCN(9), <sup>2,3</sup> N <sub>2</sub> O(6.9), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (12)	40 (2.6)	3	F <sub>2</sub> (21), Cl <sub>2</sub> (-7), <sup>3</sup> CO <sub>2</sub> (-6)
M08-HX/6-31+G(d,p)	48 (3.0)	4	N <sub>2</sub> (6), F <sub>2</sub> (22), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (6), <sup>2</sup> NH <sub>3</sub> (-7)	38 (2.6)	2	F <sub>2</sub> (23), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (9)
M08-HX/cc-pVTZ+	49 (3.3)	6	N <sub>2</sub> (6), F <sub>2</sub> (25), <sup>1</sup> N <sub>2</sub> O(5), <sup>3</sup> N <sub>2</sub> O(7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (11), <sup>2</sup> NH <sub>3</sub> (-6)	39 (2.6)	3	F <sub>2</sub> (22), <sup>3</sup> N <sub>2</sub> O(5), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (8)
M08-HX/def2-TZVPP	50 (3.3)	7	N <sub>2</sub> (6), F <sub>2</sub> (24), <sup>1</sup> N <sub>2</sub> O(5), <sup>3</sup> N <sub>2</sub> O(8), <sup>2</sup> HCN(5), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (10), <sup>2</sup> NH <sub>3</sub> (-5)	39 (2.6)	2	F <sub>2</sub> (22), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (9)
M08-HX/MG3S	49 (3.3)	5	N <sub>2</sub> (6), F <sub>2</sub> (23), <sup>3</sup> N <sub>2</sub> O(8), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (12), <sup>2</sup> NH <sub>3</sub> (-6)	37 (2.5)	3	F <sub>2</sub> (18), <sup>2</sup> H <sub>2</sub> O(-7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (6)
M08-SO/6-31+G(d,p)	46 (3.0)	5	F <sub>2</sub> (20), <sup>2</sup> H <sub>2</sub> O(-6), <sup>3</sup> HCN(6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (8), <sup>2</sup> NH <sub>3</sub> (-11)	34 (2.4)	2	F <sub>2</sub> (21), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (11)
M08-SO/cc-pVTZ+	49 (3.4)	6	<sup>2</sup> NH <sub>3</sub> (-8), F <sub>2</sub> (23), <sup>3</sup> N <sub>2</sub> O(7), <sup>3</sup> HCN(6), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (13), N <sub>2</sub> (6)	35 (2.5)	4	F <sub>2</sub> (21), <sup>3</sup> N <sub>2</sub> O(5), <sup>3</sup> HCN(5), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (12)
M08-SO/def2-TZVPP	51 (3.5)	7	<sup>2</sup> NH <sub>3</sub> (-8), F <sub>2</sub> (22), <sup>1</sup> N <sub>2</sub> O(5), <sup>3</sup> HCN(7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (14), N <sub>2</sub> (6), <sup>3</sup> N <sub>2</sub> O(8)	36 (2.5)	2	F <sub>2</sub> (20), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (12)
M08-SO/MG3S	51 (3.5)	5	<sup>2</sup> NH <sub>3</sub> (-9), F <sub>2</sub> (22), <sup>3</sup> N <sub>2</sub> O(8), <sup>3</sup> HCN(7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (14)	38 (2.5)	2	F <sub>2</sub> (20), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (11)
M08-SO/MG3SXP	53 (3.6)	6	<sup>2</sup> NH <sub>3</sub> (-8), F <sub>2</sub> (22), <sup>3</sup> N <sub>2</sub> O(8), <sup>3</sup> HCN(7), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (13), N <sub>2</sub> (6)	25 (1.7)	2	F <sub>2</sub> (9), Cl <sub>2</sub> (-5)
PBE/MG3S	29 (1.7)	1	F <sub>2</sub> (11)	28 (2.0)	2	F <sub>2</sub> (16), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (5)
PBE0/MG3S	38 (2.6)	5	<sup>2</sup> NH <sub>3</sub> (-6), F <sub>2</sub> (18), <sup>3</sup> N <sub>2</sub> O(7), <sup>3</sup> HCN(5), <sup>4</sup> C <sub>2</sub> H <sub>2</sub> (7)	26 (1.5)	3	F <sub>2</sub> (12), Cl <sub>2</sub> (-5), <sup>2</sup> NH <sub>3</sub> (6)
TPSSH/MG3S	28 (1.7)	3	F <sub>2</sub> (13), <sup>3</sup> HCN(5)	35 (2.4)	3	Cl <sub>2</sub> (-10)
V5XC/MG3S	24 (1.6)	3	<sup>2</sup> NH <sub>3</sub> (-5), F <sub>2</sub> (6), Cl <sub>2</sub> (-7)			
average	44 (2.9)	5				

<sup>a</sup> Mean absolute deviations (cm<sup>-1</sup>) and, in parentheses, mean absolute % deviations after scaling. <sup>b</sup> N corresponds to the number of outlier frequencies, which we define as differing from experiment by more than 5%, after scaling. <sup>c</sup> Numbers in parentheses are the % deviations between the scaled and experimental frequencies. Superscripts are the mode numbers given in Table 1.

the SQM procedure can lead to improved accuracy, it does not do so uniformly and involves a trade-off of accuracy and simplicity.

**3.1.2. Scale Factors for Zero-Point Energies.** The optimal scale factors for the prediction of ZPEs from the computed harmonic vibrational frequencies obtained with the 40 electronic model chemistries tested in this study are summarized in Table 3. The rms deviation for the set is 0.41 kcal mol<sup>-1</sup>, and upon scaling, this quantity is reduced to 0.18 kcal mol<sup>-1</sup>. After scaling, the best electronic model chemistry tested is VSXC/MG3S, with an rms deviation of 0.08 kcal mol<sup>-1</sup>. The BLYP, M06-L, and Perdew–Burke–Ernzerhof (PBE) functionals also yielded high-quality ZPEs upon scaling, with rms deviations ranging from 0.09 to 0.11 kcal mol<sup>-1</sup>. The other electronic model chemistries tested also performed reasonably well on this front, with rms deviations of no more than 0.22 kcal mol<sup>-1</sup> and with the exception of those with 100% Hartree–Fock exchange (HF theory and the HFLYP and M06-HF density functionals), which yielded rms deviations that are slightly larger (0.28 – 0.30 kcal mol<sup>-1</sup>). In addition, in the Supporting Information, we also report the absolute and absolute percent deviations between the experimental ZPEs and those computed with each of the 40 electronic model chemistries for all of the species studied. This analysis shows that on average these deviations amount to 0.14 ± 0.05 kcal mol<sup>-1</sup> and 2.8 ± 1.0%. Twelve of the electronic model chemistries tested yield ZPEs that, when appropriately scaled, agree with experiment to within 0.1 kcal mol<sup>-1</sup> on average. Out of these, the smallest mean absolute percent deviations result from the use of BMC–CCSD and M06-L and have a value of 1.1% in the case of the former and 1.2% in the case of the latter (when averaged over the results obtained with the three different basis sets). In particular, we identify BMC–CCSD as the most universally reliable method (of those examined here; we note that we intentionally did not examine the expensive methods that are usually affordable only for the smallest systems) for obtaining ZPEs, as evidenced by the fact that this is the only electronic model chemistry that can reproduce all of the ZPEs investigated to within 2.9%, even that of F<sub>2</sub>, which is overestimated by the other 39 electronic model chemistries by 19.0% on average.

The  $\lambda^{\text{ZPE}}$  values for 17 of the 40 electronic model chemistries involved in the calculations described were also previously determined in a separate study.<sup>13</sup> However, as noted earlier, these previous determinations relied on the ZPEs contained in the ZPVE15/06 database, many of which have since been revised by Irikura and co-workers.<sup>20,21</sup> It is interesting to note that the previously determined values for  $\lambda^{\text{ZPE}}$  are only slightly different from those determined here. In fact, these differences are not just small but also systematic, with the new values being less than the old by 0.0024–0.0026 for any given electronic model chemistry, which only amounts to about a quarter of a percent difference. We further note that these two sets of scale factors are not statistically different, since the uncertainty associated with scale factors for ZPEs has been shown to be of at least ±0.02.<sup>21</sup>

As was the case for  $\lambda^{\text{F}}$  and  $\lambda^{\text{H}}$ , it can be seen that the values of  $\lambda^{\text{ZPE}}$  obtained in this study also appear to be relatively invariant with respect to the one-electron basis set used. Because of this, we can compare our scale factors to those of Scott and Radom,<sup>11</sup> as in the previous section, in order to assess if our subset of ZPEs represents a bigger data set well. In doing so, we find that the HF/MG3S  $\lambda^{\text{ZPE}}$  value of 0.919 obtained here agrees well with those obtained by Scott and Radom for HF/6-311G(d,p) and HF/6-311G(df,p), 0.9248 and 0.9247, respectively, and the  $\lambda^{\text{ZPE}}$  value of 1.013 we obtained for BLYP/MG3S is in good accord with the value of 1.0167 Scott and Radom obtained for BLYP/6-311G(df,p). In addition, we note that our  $\lambda^{\text{ZPE}}$  value and that of Scott and Radom for B3LYP are also in very close agreement, 0.983 and 0.9806, respectively, although Scott and Radom used a double- $\zeta$  basis set, 6-31G(d), while we employed the much larger triple- $\zeta$  basis set, MG3S. These close agreements between the  $\lambda^{\text{ZPE}}$  values we obtain with the 15 ZPEs in the ZPVE15/10 database and those obtained by Scott and Radom based on the larger test set of 122 molecules indicate that, in the case of ZPEs, the ZPVE15/10 database is a reasonable representative of the bigger data set.

**3.1.3. Universal Scale Factor Ratios.** Careful analysis of the scale factors obtained in this study lead to the realization that, for any given electronic model chemistry, knowledge of any of the three scale factors  $\lambda^{\text{H}}$ ,  $\lambda^{\text{F}}$ , or  $\lambda^{\text{ZPE}}$  permits the accurate estimation of the other two scale factors directly, without the usual rigorous analysis of minimizing the rms deviation. Specifically, it can be seen that regardless of the electronic model chemistry used, the ratios  $\lambda^{\text{H}}/\lambda^{\text{ZPE}}$  and  $\lambda^{\text{F}}/\lambda^{\text{ZPE}}$  are, to a good approximation, constant, such that:

$$\lambda^{\text{H}} = \alpha^{\text{H/ZPE}} \lambda^{\text{ZPE}} \quad (13)$$

$$\lambda^{\text{F}} = \alpha^{\text{F/ZPE}} \lambda^{\text{ZPE}} \quad (14)$$

where the proportionality constants  $\alpha^{\text{H/ZPE}}$  and  $\alpha^{\text{F/ZPE}}$  are almost independent of the electronic model chemistry. For the set of the 40 electronic model chemistries considered in Table 3, we obtain, as shown in Table 5, the average values of 1.014 ± 0.002 and 0.974 ± 0.002 for  $\alpha^{\text{H/ZPE}}$  and  $\alpha^{\text{F/ZPE}}$ , respectively, where the uncertainties represent 1 standard deviation (SD).

It should be emphasized that the standard deviations we attribute to these quantities only reflect the statistical scatter within a given data set, thereby neglecting any contributions from the propagation of the uncertainties in the scale factors. Irikura's statistical analyses suggest that the typical uncertainties associated with  $\lambda^{\text{F}}$  and  $\lambda^{\text{ZPE}}$  for electronic model chemistries comparable to those in this study are in the range of 0.02–0.06.<sup>21,112</sup> Propagating these uncertainties indicates that our estimate of  $\alpha^{\text{F/ZPE}}$  is realistically only reliable to about 3–8%. A similar measure of reliability is expected for  $\alpha^{\text{H/ZPE}}$ .

The value for  $\alpha^{\text{F/ZPE}}$  obtained here can also be compared with those that can be derived from the studies of Pople et al.<sup>113</sup> and Scott and Radom.<sup>11</sup> From the  $\lambda^{\text{F}}$  and  $\lambda^{\text{ZPE}}$  values obtained in the study of Pople et al., which focused on just two electronic model chemistries, and the work of Scott and



**Table 5.** Universal Scale Factor Ratios for Interrelating the Three Properties of Interest

model chemistry	scale factor ratios	
	$\alpha^{H/ZPE}$	$\alpha^{F/ZPE}$
B1LYP/MG3S	1.016	0.977
B3LYP/MG3S	1.016	0.977
B97-3/MG3S	1.014	0.974
B98/MG3S	1.014	0.974
BLYP/MG3S	1.017	0.979
BMC-CCSD	1.017	0.977
BMK/MG3S	1.013	0.973
HF/MG3S	1.015	0.975
HFLYP/MG3S	1.014	0.974
M05-2X/6-31+G(d,p)	1.014	0.974
M05-2X/def2-TZVPP	1.014	0.975
M05-2X/MG3S	1.013	0.974
M05/MG3S	1.013	0.973
M06-2X/6-31+G(d,p)	1.012	0.972
M06-2X/aug-cc-pVTZ	1.014	0.974
M06-2X/def2-TZVPP	1.014	0.974
M06-2X/maug-cc-pV(T+d)Z	1.013	0.974
M06-2X/MG3S	1.013	0.974
M06-HF/6-31+G(d,p)	1.015	0.976
M06-HF/def2-TZVPP	1.012	0.973
M06-HF/MG3S	1.013	0.975
M06-L/6-31+G(d,p)	1.015	0.975
M06-L/def2-TZVPP	1.020	0.980
M06-L/MG3S	1.019	0.980
M06/6-31+G(d,p)	1.009	0.970
M06/def2-TZVPP	1.014	0.974
M06/MG3S	1.014	0.974
M08-HX/6-31+G(d,p)	1.011	0.972
M08-HX/cc-pVTZ+	1.012	0.972
M08-HX/def2-TZVPP	1.011	0.972
M08-HX/MG3S	1.012	0.972
M08-SO/6-31+G(d,p)	1.010	0.971
M08-SO/cc-pVTZ+	1.013	0.973
M08-SO/def2-TZVPP	1.013	0.973
M08-SO/MG3S	1.013	0.973
M08-SO/MG3SXP	1.012	0.972
PBE/MG3S	1.015	0.976
PBE0/MG3S	1.014	0.974
TPSSH/MG3S	1.018	0.979
VSXC/MG3S	1.016	0.976
average ( $\pm\sigma$ ) <sup>a</sup>	1.014(2)	0.974(2)

<sup>a</sup> Numbers in parentheses represent the statistical uncertainties of the last significant figure.

Radom, which extended the study of Pople et al. to 17 electronic model chemistries, we derive  $\alpha^{F/ZPE}$  values of 0.977 and 0.979 for their respective data sets. These values compare well with the average value of 0.974 for  $\alpha^{F/ZPE}$  obtained in the present work. Values for  $\lambda^H$  were not reported in these<sup>11,113</sup> studies, precluding the comparison of  $\alpha^{H/ZPE}$  values.

It is interesting to note that our study and that of Scott and Radom differ greatly in the relative attention paid to wave function (WFT) and density functional (DFT) theories. In our study only 2 of the 40 electronic model chemistries tested were based on WFT, in particular HF and BMC-CCSD, while 11 of the 17 electronic model chemistries tested by Scott and Radom were based on WFT. Therefore, the work of Scott and Radom can be used to check whether the ratio  $\alpha^{F/ZPE}$  is indeed universal or depends on whether DFT or WFT is used. We find that this ratio is virtually the same regardless of whether DFT or WFT is used, as the average

values for  $\alpha^{F/ZPE}$  are  $0.981 \pm 0.001$  and  $0.978 \pm 0.004$  for the two respective subgroups.

### 3.2. Stage Two: Reduced Scale Factor Optimization

**Model.** As demonstrated by Irikura et al., careful consideration of the uncertainty associated with scale factors can lead to overall error margins in these quantities in the range of 0.02–0.06 for electronic model chemistries similar to the ones employed here.<sup>21,112</sup> This highlights the intrinsically approximate nature of scale factors and of the resultant scaled properties, as with these kinds of error margins, many of the scale factors reported for various electronic model chemistries are in fact not statistically different. Nonetheless, it is not only customary but also very useful to have method specific scale factors optimized for the properties of interest, especially if these can be obtained at a modest computational cost.

In the preceding sections, we have shown that all three property specific scale factors can be obtained from the knowledge of just one of these by conveniently using the universal scale factor ratios established in this work. We have also shown that  $\lambda^F$ ,  $\lambda^H$ , and  $\lambda^{ZPE}$  do not depend on the size of the test set of frequencies used in deriving them. This observation leads one to question whether the original sets of frequencies and the ZPEs can be further reduced without significantly affecting the ensuing scale factors, just as small, representative databases have been introduced in previous work<sup>81,114–117</sup> for other properties.

Specifically, since  $\lambda^{ZPE}$  is the scale factor most commonly utilized in the literature, we investigate whether a smaller representative subset of just 6 of the 15 original ZPEs can be used to obtain values for  $\lambda^{ZPE}$  that agree to within 0.001 with those originally obtained for the full set of ZPEs. Out of the 5005 such possible subsets, we find that the best representative subset is that which includes the ZPEs of CH<sub>4</sub>, NH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>CO, H<sub>2</sub>O, and N<sub>2</sub>O, with a mean absolute deviation between  $\lambda^{ZPE}$  for the subset and  $\lambda^{ZPE}$  for the full set of 0.0007 for the 40 electronic model chemistries tested in this study. The subset of six ZPEs is called the ZPE6 database.

The finding that this subset is entirely composed of polyatomics is reasonable as one might expect that the largest ZPEs would more significantly influence the value of the scale factor by receiving the most weight in a procedure aimed at minimizing the rms deviation. However, it is interesting that the representative subset is not composed of the six molecules with the largest ZPEs but rather of five of these molecules and N<sub>2</sub>O, which has the eighth largest ZPE. This suggests that, in general, the deviation between the computed and experimental ZPE of N<sub>2</sub>O is larger than those for the molecules with the sixth and seventh largest ZPEs, HCN and CO<sub>2</sub>, respectively. This hypothesis can be verified by inspecting Table S3 of the Supporting Information, from which it can be seen that the absolute deviation for the ZPE of N<sub>2</sub>O is larger than those for the ZPEs of HCN and CO<sub>2</sub> for 34 of the 40 electronic model chemistries tested.

This discrepancy between the computed and experimental ZPE of N<sub>2</sub>O might be partly due to the significant multireference character of this molecule. As has been previously noted,<sup>32,81</sup> “the Hartree–Fock exchange approximation fails

**Table 6.** Absolute Differences between the ZPEs of Polyatomic Species Computed with BLYP/MG3S and B1LYP/MG3S<sup>a</sup>

molecule	ZPE <sub>B</sub> (kcal mol <sup>-1</sup> )	ZPE <sub>B1</sub> (kcal mol <sup>-1</sup> )	ZPE <sub>B1</sub> - ZPE <sub>B</sub>   (kcal mol <sup>-1</sup> )	100 ×  ZPE <sub>B1</sub> - ZPE <sub>B</sub>   / ZPE <sub>B</sub> (%)
CH <sub>4</sub>	27.367	28.128	0.762	2.8
NH <sub>3</sub>	20.918	21.607	0.689	3.3
H <sub>2</sub> O	12.944	13.470	0.526	4.1
C <sub>2</sub> H <sub>2</sub>	16.368	17.034	0.667	4.1
HCN	9.885	10.305	0.419	4.2
H <sub>2</sub> CO	16.059	16.750	0.691	4.3
CO <sub>2</sub>	7.012	7.387	0.375	5.3
N <sub>2</sub> O	6.625	7.053	0.428	6.5

<sup>a</sup> Expressed in kcal mol<sup>-1</sup> and as a percentage.

badly for multireference systems, whereas generalized gradient approximations (GGAs) can usually handle these systems almost as well as they handle single-reference systems.” An inexpensive and useful indicator of multireference character is the B1 diagnostic,<sup>32,81</sup> which relies on the comparison of the results obtained with the BLYP<sup>29,30</sup> and B1LYP<sup>51–53</sup> functionals, where the former is a local functional, and the latter is a hybrid functional, and the two functionals differ only in that the latter incorporates 25% of HF exchange in its design. Though the B1 diagnostic was originally defined so as to offer a semiquantitative measure of the multireference character of bond energies,<sup>32,81</sup> it was later generalized to gauge the approximate extent of multireference character “for any quantity with units of energy.”<sup>118</sup> Its recommended threshold of an energetic discrepancy of 10 kcal mol<sup>-1</sup> between the results of BLYP and those of B1LYP as the indicator of multireference character was, however, designed for bond energies and exceeds the values of most of the ZPEs in this study. Consequently, here we only use the concept underlying this diagnostic to qualitatively assess the degree of multireference character in the polyatomic molecules presently studied, as reflected by their ZPEs. In this analysis, we simply calculate the absolute differences between the unscaled ZPEs of the eight polyatomic species computed with BLYP/MG3S and B1LYP/MG3S. The results, presented in Table 6, show that the largest such difference between computed ZPEs does in fact occur in the case of N<sub>2</sub>O, suggesting that out of the eight polyatomic species studied, this molecule may possess the most multireference character. The fact that CH<sub>4</sub> and NH<sub>3</sub> are at the other end of the spectrum, as might be expected, is reassuring.

Based on the generalization that the inclusion of HF exchange into electronic model chemistries can lead to bad performance when dealing with multireference systems, one would expect that HF and hybrid density functionals which incorporate the most HF exchange within their scheme will be affected the most in cases involving multireference systems. As can be seen in Table S3 of the Supporting Information, HF and HFLYP do exhibit some of the largest deviations when computing the ZPE of N<sub>2</sub>O; however, M06-HF does not, which is consistent with the previous experience<sup>34</sup> that M06-HF is the first functional with 100% Hartree–Fock exchange that competes well with popular functionals that typically have 20–25% Hartree–Fock exchange. Furthermore, if this inability of HF exchange-based electronic model chemistries to adequately characterize multireference systems was the dominant reason for the magnitude of the deviations in the ZPE of N<sub>2</sub>O, one would

expect M05 and M06 to outperform their 2X counterparts on this front, since 2X refers to the fact that twice the amount of HF exchange has been added in going from M0*n* to M0*n*-2X (where *n* = 5 or 6), however, this is not the case for the Minnesota functionals. Therefore, the observed deviations associated with computing the ZPE of N<sub>2</sub>O are likely due to a combination of several factors.

Regardless of the nature of the optimal subset, the level of agreement between  $\lambda^{\text{ZPE}}$  for the subset and  $\lambda^{\text{ZPE}}$  for the full set indicates that they are often identical to the precision that we report these quantities, to the thousandths place. In addition, this signifies that no accuracy would be lost in the subsequent determinations of  $\lambda^{\text{H}}$  and  $\lambda^{\text{F}}$  through the use of universal scale factor ratios. This procedure, which we call the reduced scale factor optimization model, greatly reduces the computational cost of determining the three most important scale factors. For clarity, we summarize this reduced model as follows: (i) calculate the harmonic frequencies of CH<sub>4</sub>, NH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>CO, H<sub>2</sub>O, and N<sub>2</sub>O; (ii) find  $\lambda^{\text{ZPE}}$  by minimizing the rms deviation of eq 11 but with these 6 molecules rather than 15 (the required data are in rows 9, 10, and 12–15 of Table 2); (iii) multiply  $\lambda^{\text{ZPE}}$  by 1.014 and 0.974 to obtain  $\lambda^{\text{H}}$  and  $\lambda^{\text{F}}$ , respectively.

By the time this work is published, we expect to have an automated scale factor generator utility available on the Truhlar group Web site (<http://comp.chem.umn.edu/truhlar/index.htm>), which will efficiently optimize these three scale factors for any user specified electronic model chemistry through the implementation of the reduced scale factor optimization model.

**3.3. Scale Factors for Additional Methods.** The above analysis allows us to update Table S1 (Supporting Information) of previously computed scale factors. For any electronic model chemistry in Table S1 (Supporting Information) for which  $\lambda^{\text{ZPE}}$  was obtained from ZPVE15/06,<sup>13</sup> we decrease  $\lambda^{\text{ZPE}}$  by 0.0025 (see Section 3.1.2). In addition, we have found that the scale factors obtained from the ZPVE13/99 database,<sup>82,119</sup> which differs from ZPVE15/06 only in that it excludes the ZPEs of Cl<sub>2</sub> and OH, typically agree with those obtained from ZPVE15/06 to within 0.00001, which is well within the precision of 0.001 reported in this work. Therefore, for any electronic model chemistry in Table S1 (Supporting Information) for which  $\lambda^{\text{ZPE}}$  was obtained from ZPVE13/99, we also simply decrease  $\lambda^{\text{ZPE}}$  by 0.0025 to obtain updated quantities. For any electronic model chemistry in Table S1 (Supporting Information) for which the scale factor was not obtained from ZPVE15/06 or ZPVE13/99,

**Table 7.** Updated  $\lambda^{\text{ZPE}}$  Values to Be Used Instead of the Previous Ones Listed in Table S1 (Supporting Information)<sup>a</sup>

model chemistry	$\lambda^{\text{ZPE}}$	% dev <sup>e</sup>
AM1 <sup>b</sup>	0.948	0.58 <sup>f</sup>
B1B95/6-31+G(d,p) <sup>c</sup>	0.971	0.26
B1B95/MG3S <sup>c</sup>	0.973	0.29
B3LYP/6-31(2df,2p) <sup>c</sup>	0.981	0.20
B3LYP/6-31G(d) <sup>b</sup>	0.977	0.37
B3P86/6-31G(d) <sup>b</sup>	0.971	0.50
B3PW91/6-31G(d) <sup>b</sup>	0.972	0.53
BB1K/6-31+G(d,p) <sup>c</sup>	0.954	0.22
BB1K/MG3S <sup>c</sup>	0.957	0.21
BB95/6-31+G(d,p) <sup>c</sup>	1.011	0.29
BB95/MG3S <sup>c</sup>	1.012	0.24
BLYP/6-311G(df,p) <sup>b</sup>	1.013	0.36
BLYP/6-31G(d) <sup>b</sup>	1.009	0.36
BP86/6-31G(d) <sup>b</sup>	1.007	0.38
HF/3-21G <sup>b</sup>	0.919	0.18
HF/6-31+G(d) <sup>b</sup>	0.911	0.58
HF/6-31+G(d,p) <sup>c</sup>	0.915	0.25
HF/6-311G(d,p) <sup>b</sup>	0.920	0.52
HF/6-311G(df,p) <sup>b</sup>	0.920	0.51
HF/6-31G(d) <sup>b</sup>	0.909	0.49
HF/6-31G(d,p) <sup>b</sup>	0.913	0.56
MC3BB <sup>c</sup>	0.965	0.26
MC3MPW <sup>c</sup>	0.964	0.30
MC-QCISD/3 <sup>c</sup>	0.992	0.20
MP2(FC)/6-31+G(d,p) <sup>c</sup>	0.968	0.21
MP2(FC)/6-311G(d,p) <sup>b</sup>	0.970	0.49
MP2(FC)/6-31G(d) <sup>b</sup>	0.964	0.31
MP2(FC)/6-31G(d,p) <sup>b</sup>	0.958	0.29
MP2(FC)/cc-pVDZ <sup>c</sup>	0.977	0.20
MP2(FULL)/6-31G(d) <sup>b</sup>	0.963	0.17
MPW1B95/6-31+G(d,p) <sup>c</sup>	0.970	0.22
MPW1B95/MG3S <sup>c</sup>	0.970	0.23
MPW1B95/MG3S <sup>c</sup>	0.972	0.27
MPW1K/MG3S <sup>c</sup>	0.953	0.23
MPW1K/MG3S <sup>c</sup>	0.956	0.22
MPW3LYP/6-31+G(d,p) <sup>c</sup>	0.980	0.25
MPW3LYP/MG3S <sup>c</sup>	0.982	0.26
MPWB1K/6-31+G(d,p) <sup>c</sup>	0.951	0.28
MPWB1K/MG3S <sup>c</sup>	0.954	0.28
PBE1KCIS/MG3S <sup>c</sup>	0.981	0.23
PBE1KCIS/MG3S <sup>c</sup>	0.981	0.22
PM3 <sup>b</sup>	0.940	3.71 <sup>f</sup>
PM6 <sup>b,d</sup>	1.078	9.35 <sup>f</sup>
PW6B95/6-31+G(d,p) <sup>c</sup>	0.970	0.21
QCISD(FC)/6-31G(d) <sup>b</sup>	0.973	0.47
X1B95/6-31+G(d,p) <sup>c</sup>	0.968	0.30
X1B95/MG3S <sup>c</sup>	0.971	0.24
XB1K/6-31+G(d,p) <sup>c</sup>	0.952	0.30
XB1K/MG3S <sup>c</sup>	0.955	0.30

<sup>a</sup> Values for  $\lambda^{\text{H}}$  and  $\lambda^{\text{F}}$  can be obtained by multiplying  $\lambda^{\text{ZPE}}$  by 1.014 and 0.974, respectively, and rounding to the nearest thousandth. <sup>b</sup> Obtained using the reduced scale factor optimization model. <sup>c</sup> Obtained by decreasing the value in Table S1 (Supporting Information) by 0.0025 (see text). <sup>d</sup> Computed using Gaussian 09.<sup>122</sup> <sup>e</sup> Absolute percent deviations between  $\lambda^{\text{ZPE}}$  values in Table 7 and Table S1 (Supporting Information). <sup>f</sup> Absolute percent deviations between  $\lambda^{\text{F}}$  values in Table 7 (0.974  $\times$   $\lambda^{\text{ZPE}}$ ) and Table S1 (Supporting Information).

we compute  $\lambda^{\text{ZPE}}$  by steps (i) and (ii) in Section 3.2. The resulting  $\lambda^{\text{ZPE}}$  values are given in Table 7.

We also used the ZPE6 database to find  $\lambda^{\text{ZPE}}$  for electronic model chemistries not in either Tables 3 or 7. These  $\lambda^{\text{ZPE}}$  values are given in Table 8. Note that  $\lambda^{\text{H}}$  and  $\lambda^{\text{F}}$  for any electronic model chemistry in Tables 7 or 8 can be obtained by multiplying  $\lambda^{\text{ZPE}}$  by 1.014 or 0.974, respectively, and then rounding to the nearest thousandth. For example,  $\lambda^{\text{H}}$  and  $\lambda^{\text{F}}$  for MPW3LYP/6-31G(d) are 0.990 and 0.951.

Most of the scale factors in Table 7 have changed from the original scale factors in Table S1 (Supporting Information) by less than 0.6%, with the exception of PM3 and PM6,

**Table 8.** Additional  $\lambda^{\text{ZPE}}$  Values Obtained with the Reduced Scale Factor Optimization Model<sup>a</sup>

model chemistry	$\lambda^{\text{ZPE}}$
B3LYP/ma-TZVP	0.986
B97-3/ma-TZVP <sup>b</sup>	0.975
B98/def2-TZVP	0.984
B98/ma-TZVP	0.985
BMK/ma-TZVP	0.972
BP86/ma-TZVP	1.014
CAM-B3LYP/ma-TZVP <sup>c</sup>	0.976
CCSD(T)/jul-cc-pVTZ	0.984
CCSD(T)-F12/jul-cc-pVTZ <sup>d</sup>	0.981
CCSD/jul-cc-pVTZ	0.973
CCSD-F12/jul-cc-pVTZ <sup>d</sup>	0.971
HSEh1PBE/ma-TZVP	0.979
M05/aug-cc-pVTZ	0.978
M05/ma-TZVP	0.979
M05/maug-cc-pVTZ	0.978
M05-2X/aug-cc-pVTZ	0.964
M05-2X/ma-TZVP	0.965
M05-2X/maug-cc-pVTZ	0.964
M06/aug-cc-pVTZ	0.984
M06/ma-TZVP	0.982
M06/maug-cc-pVTZ	0.982
M06-2X/ma-TZVP	0.972
M06-HF/aug-cc-pVTZ	0.961
M06-HF/ma-TZVP	0.957
M06-HF/maug-cc-pVTZ	0.959
M06-L/aug-cc-pVTZ	0.980
M06-L/ma-TZVP	0.977
M06-L/maug-cc-pVTZ	0.977
M08-HX/aug-cc-pVTZ	0.975
M08-HX/ma-TZVP	0.976
M08-HX/maug-cc-pVTZ	0.976
M08-SO/aug-cc-pVTZ	0.985
M08-SO/ma-TZVP	0.984
M08-SO/maug-cc-pVTZ	0.983
MOHLYP/ma-TZVP	1.027
MOHLYP/MG3S	1.022
MP4(SDQ)/jul-cc-pVTZ	0.973
MPW1K/ma-TZVP	0.956
MPW1K/MIDI	0.953
MPW1K/MIDIY	0.947
MPW3LYP/6-311+G(2d,p)	0.986
MPW3LYP/6-31G(d)	0.976
MPW3LYP/ma-TZVP	0.986
MPWLYP1M/ma-TZVP	1.009
SOGGA/ma-TZVP	1.017
$\tau$ -HCTHhyb/ma-TZVP	0.989
TPSS1KCIS/def2-TZVP	0.982
TPSS1KCIS/ma-TZVP	0.983
$\omega$ B97/def2-TZVP <sup>c</sup>	0.969
$\omega$ B97/ma-TZVP <sup>c</sup>	0.970
$\omega$ B97X/def2-TZVP <sup>c</sup>	0.970
$\omega$ B97X/ma-TZVP <sup>c</sup>	0.971
$\omega$ B97X-D/def2-TZVP <sup>c</sup>	0.975
$\omega$ B97X-D/ma-TZVP <sup>c</sup>	0.975
$\omega$ B97X-D/maug-cc-pVTZ <sup>c</sup>	0.974

<sup>a</sup> Values for  $\lambda^{\text{H}}$  and  $\lambda^{\text{F}}$  can be obtained by multiplying  $\lambda^{\text{ZPE}}$  by 1.014 and 0.974, respectively, and rounding to the nearest thousandth. <sup>b</sup> Computed using locally modified version of Gaussian 03.<sup>106,123</sup> <sup>c</sup> Computed using Gaussian 09.<sup>122</sup> <sup>d</sup> Computed using MOLPRO 2009.1.<sup>124</sup>

where the percentage changes are 4 and 9%, respectively. For methods based on the neglect-of-diatomic differential overlap, the percentage changes we report in Table 7 are actually for  $\lambda^{\text{F}}$  (obtained by multiplying  $\lambda^{\text{ZPE}}$  by 0.974), since this is the quantity that is reported for these methods in Table S1 (Supporting Information). The  $\lambda^{\text{F}}$  values in Table S1 (Supporting Information) come from the work of Scott and Radom<sup>11</sup> for AM1 and PM3 and from the work of Fekete et al.<sup>120</sup> for PM6 and were directly obtained from rms deviation minimization procedures, rather than the indirect way in which we obtain them here via the reduced scale factor optimization model (steps i–iii of Section 3.2). Although the difference between the  $\lambda^{\text{F}}$  values in Tables 7 and S1 (Supporting Information) for AM1 is reasonable, 0.6%, the



**Table 9.** Comparison between Experimental and Calculated ZPEs Used in Deriving Scale Factors and Universal Scale Factor Ratios in the Present Study

species	ZPE <sub>(exp)</sub> <sup>b</sup> (cm <sup>-1</sup> )	SD (1σ) (cm <sup>-1</sup> )	ZPE <sub>(calc)</sub> (cm <sup>-1</sup> )	absolute deviation <sup>a</sup>		
				cm <sup>-1</sup>	kcal mol <sup>-1</sup>	%
CO <sub>2</sub>	2554	80	2575	21	0.06	0.81
H <sub>2</sub> O	4636	10	4624	12	0.03	0.25
N <sub>2</sub> O	2368	N/A	2406	38	0.11	1.62
HCN	3508	111	3504	4	0.01	0.13
C <sub>2</sub> H <sub>2</sub>	5768	2	5812	43	0.12	0.75
NH <sub>3</sub>	7415	N/A	7407	8	0.02	0.10
CH <sub>4</sub>	9692	N/A	9733	41	0.12	0.43
average				24	0.07	0.58

<sup>a</sup> These values represent the absolute deviations from the central value from the range of the experimental ZPE ± 1σ. <sup>b</sup> See text for references.

large discrepancies between the  $\lambda^F$  values obtained for PM3 and PM6 from the reduced scale factor optimization model and the original direct rms deviation minimization procedures suggest that errors in the PM3 and PM6 methods are less systematic than those in the other methods studied here. In addition, we note that even upon scaling, neglect-of-diatomic differential-overlap methods give very unreliable vibrational frequencies, with rms deviations of 126, 159, and 96 cm<sup>-1</sup> for AM1, PM3, and PM6, respectively,<sup>11,120</sup> and such methods should be used for computational thermochemistry with extreme caution or even avoided.

#### 4. Applications of Universal Scale Factor Ratios

The universal scale factor ratios can have a wide range of applications. In addition to providing a much more convenient and inexpensive method for obtaining all three scale factors discussed in this paper for any given electronic model chemistry without appreciably compromising the accuracy, the universal scale factor ratios can also be used to estimate the ZPE of any molecule directly from its observed fundamental and/or true harmonic vibrational frequencies:

$$\varepsilon_{\text{vib}}^G \cong \frac{\hbar c}{2\alpha^{F/ZPE}} \sum_m v_m \quad (15)$$

$$\varepsilon_{\text{vib}}^G \cong \frac{\hbar c}{2\alpha^{H/ZPE}} \sum_m \omega_m \quad (16)$$

The above equations can be useful for a wide range of scenarios, but eq 15 is especially valuable for approximating the ZPE of polyatomic species whose fundamental frequencies are known, but the ZPEs of which may not be available due to insufficient spectroscopic data. In turn, knowledge of the ZPE can be useful for a number of applications. For instance, to more accurately gauge the performance of a given electronic model chemistry with regards to heats of reactions, subtracting the experimental ZPEs from the  $\theta$  K heats of reaction of the products and reactants will allow for the direct comparison of the resulting electronic energies.

As a practical example, we now aim to quantify the degree of accuracy that can be achieved for predicting the ZPEs of polyatomic molecules through the use of  $\alpha^{F/ZPE}$  (i.e., via eq 15). We do this through two separate analyses. In the first analysis, we directly compare the ZPEs calculated via eq 15

**Table 10.** Comparison between Experimental and Calculated ZPEs Not Used in Deriving Scale Factors and Universal Scale Factor Ratios in the Present Study

species	ZPE <sub>(exp)</sub> <sup>b</sup> (cm <sup>-1</sup> )	SD (1σ) (cm <sup>-1</sup> )	ZPE <sub>(calc)</sub> (cm <sup>-1</sup> )	absolute deviation <sup>a</sup>		
				cm <sup>-1</sup>	kcal mol <sup>-1</sup>	%
OCS	2016	63	2033	17	0.05	0.86
SO <sub>2</sub>	1542	48	1556	14	0.04	0.88
H <sub>2</sub> S	3316	107	3298	18	0.05	0.54
CS <sub>2</sub>	1520	48	1533	14	0.04	0.91
NO <sub>2</sub>	1889	62	1892	3	0.01	0.15
CICN	1888	59	1908	20	0.06	1.06
HOCl	2863	9	2860	3	0.01	0.10
HOF	3026	96	2986	40	0.11	1.32
average				16	0.05	0.73

<sup>a</sup> These values represent the absolute deviations from the central value of the range from the experimental ZPE ± 1σ. <sup>b</sup> See text for references.

with their experimental counterparts for the polyatomic species in the ZPVE15/10 database, with the exception of H<sub>2</sub>CO, the experimental ZPE of which has an uncertainty that is too large for a meaningful comparison. In the second analysis of this process, we compare the calculated and experimental ZPEs of eight polyatomic species that were not used in the scale factor optimization or universal scale factor ratio analyses in this work, namely OCS, SO<sub>2</sub>, H<sub>2</sub>S, CS<sub>2</sub>, NO<sub>2</sub>, CICN, HOCl, and HOF. The experimental ZPEs of these species constitute the only remaining available new estimates from Irkura et al.,<sup>21</sup> with the exception of C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>Cl, whose experimental ZPEs we omit because they have very large error bars. The accuracy with which the ZPEs of these eight species can be predicted, via eq 15, should be a reasonable indicator of the general reliability and transferability of  $\alpha^{F/ZPE}$ . All experimentally observed fundamental frequencies needed for these two analyses were taken from the Computational Chemistry Comparison and Benchmark Database,<sup>15</sup> and the ensuing results are given in Tables 9 and 10. The excellent agreement between the calculated and experimental ZPEs, in both cases of ZPEs, which were used to establish scale factors and universal scale factor ratios, mean absolute deviation of 0.07 kcal mol<sup>-1</sup> (0.58%), and of the ZPEs that were not used to establish these quantities, mean absolute deviation of 0.05 kcal mol<sup>-1</sup> (0.73%), indicates that  $\alpha^{F/ZPE}$  is reasonably transferable and reliable for predicting accurate ZPEs for stable covalently bound polyatomic species from their observed fundamental frequen-



cies, provided that these frequencies are also reliable. Averaging over the results in both tables (i.e., all 15 polyatomic ZPEs) leads to the value of 0.06 kcal mol<sup>-1</sup> (0.66%) for the mean absolute deviation and 0.07 kcal mol<sup>-1</sup> (0.80%) for the rms deviation. We suggest taking twice the rms deviation as the 95% confidence limits ( $2\sigma = 1.6\%$ ) when using eq 15 to approximate experimental ZPEs.

## 5. Concluding Remarks

Although we encourage the use of these newly optimized scale factors and their ratios, we point out that while these can usually lead to accurate predictions of the quantities of interest, for some specific problems, the use of a general scale factor can result in large discrepancies between the computed and experimental properties of interest. For example, some of the electronic model chemistries tested in this work overestimated the harmonic and/or fundamental stretching frequency in F<sub>2</sub> by more than 20% and its ZPE by more than 0.3 kcal mol<sup>-1</sup> (23%). An error of this magnitude can propagate and lead to a significant contribution to the overall error of a thermochemical quantity of interest. It is important to keep in mind that throughout this study, the minimizations of the rms deviations are done with respect to absolute errors, which are generally the greatest for the largest members in the set. Therefore, because the values of the vibrational frequency and ZPE in F<sub>2</sub> are quite small, even a 20% error in either of these quantities does not amount to as much as just a 5% error in the frequency of H<sub>2</sub> or a 1% error in the ZPE of CH<sub>4</sub>. An alternative would be to minimize the rms deviations of a set of relative errors, in which case the large fractional deviations in F<sub>2</sub> discussed above would receive more weight than the smaller percentage errors in the equivalent properties of other molecules.

It should also be emphasized that because vibrational frequencies and ZPEs of weakly bound and/or noncovalent species are generally not available, these types of species have been excluded from the present study. Due to the loose vibrations possessed by these species, the scale factors and scale factor ratios established in this work based on species predominantly characterized by strong covalent interactions are probably inapplicable to thermochemical calculations dominated by the low frequencies of noncovalently bonded species.

Finally, it is well recognized that for severely anharmonic frequencies, simply scaling frequencies computed within the harmonic approximation can often be inadequate. These types of frequencies include many torsions and most inversions, such as the umbrella modes of halomethyl radicals.<sup>121</sup> More sophisticated scaling methods which treat these kinds of modes separately in the scaling procedure or, indeed, which treat several different classes of internal coordinates separately can improve upon the accuracy that can be achieved with just one general scale factor, though this improvement is often just marginal in the case of fundamental frequencies, and as has been noted, “for the calculation of zero-point energies and thermodynamic parameters, single scale factors are adequate.”<sup>110</sup> However, in principle, precautionary diagnostic analyses should always be conducted beforehand, when feasible, to determine the degree of applicability of these scale factors and universal ratios to the systems of interest.

## 6. Summary

The optimal scale factors for reproducing vibrational harmonic frequencies, fundamental frequencies, and zero-point energies (ZPEs) from computed harmonic frequencies have been obtained for 145 electronic model chemistries, where an electronic model chemistry is a combination of an electronic structure level or density functional approximation with a one-electron basis or is a multicoefficient correlation method, a doubly hybrid density functional, or a neglect-of-diatomic differential-overlap model. Extensive statistics for large databases were used for 40 of these electronic model chemistries. In these cases, the experimental values for true harmonic frequencies can be reproduced to typically within 2.9%, fundamental frequencies can be predicted typically to within 2.4%, and the ZPE can be estimated to typically within 0.14 kcal mol<sup>-1</sup> from the appropriately scaled computed harmonic frequencies. The frequencies computed with the balanced multicoefficient correlation method based on coupled cluster theory with single and double excitations (BMC-CCSD) multilevel method, scaled accordingly, were found to give the most reliable results overall. The M06-L and VSXC functionals also consistently yielded high-quality results.

The scale factor ratios  $\lambda^H/\lambda^{ZPE}$  and  $\lambda^F/\lambda^{ZPE}$  were found to be invariant to a good approximation with respect to the electronic model chemistry used to compute the scale factors. In light of this, we denote these universal quantities as  $\alpha^{H/ZPE}$  and  $\alpha^{F/ZPE}$ , and we recommend using their respective average values of 1.014 and 0.974. These values can be used to interconvert between scale factors optimized for various properties, thereby allowing the extraction of all three scale factors for the cost of just one. Additional computational cost can be saved when the  $\lambda^{ZPE}$  used to obtain the other scale factors is obtained from the small representative database (called ZPE6) presented here.

**Acknowledgment.** This material is based on work supported as part of the Combustion Energy Frontier Research Center, funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC 0001198.

**Supporting Information Available:** Previous scale factors and absolute ZPE deviations for new scale factors. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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CT100326H