



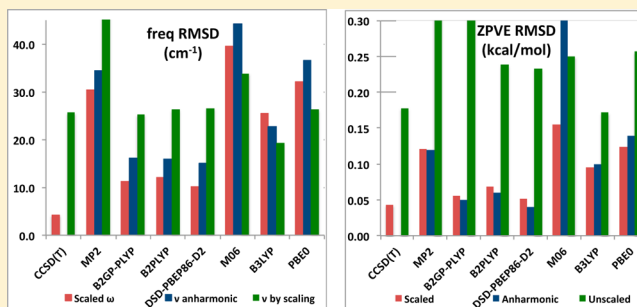
# Frequency and Zero-Point Vibrational Energy Scale Factors for Double-Hybrid Density Functionals (and Other Selected Methods): Can Anharmonic Force Fields Be Avoided?

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## S Supporting Information

**ABSTRACT:** We have obtained uniform frequency scaling factors  $\lambda_{\text{harm}}$  (for harmonic frequencies),  $\lambda_{\text{fund}}$  (for fundamentals), and  $\lambda_{\text{ZPVE}}$  (for zero-point vibrational energies (ZPVEs)) for the Weigend–Ahlrichs and other selected basis sets for MP2, SCS-MP2, and a variety of DFT functionals including double hybrids. For selected levels of theory, we have also obtained scaling factors for true anharmonic fundamentals and ZPVEs obtained from quartic force fields. For harmonic frequencies, the double hybrids B2PLYP, B2GP-PLYP, and DSD-PBEP86 clearly yield the best performance at  $\text{RMSD} = 10\text{--}12\text{ cm}^{-1}$  for def2-TZVP and larger basis sets, compared to  $5\text{ cm}^{-1}$  at the CCSD(T) basis set limit. For ZPVEs, again, the double hybrids are the best performers, reaching root-mean-square deviations (RMSDs) as low as 0.05 kcal/mol, but even mainstream functionals like B3LYP can get down to 0.10 kcal/mol. Explicitly anharmonic ZPVEs only are marginally more accurate. For fundamentals, however, simple uniform scaling is clearly inadequate.



## INTRODUCTION AND THEORETICAL BACKGROUND

Recently, remarkable progress has been made in the area of high-accuracy computational thermochemistry on small molecules, as witnessed by W4 theory,<sup>1–3</sup> the HEAT approach,<sup>4,5</sup> the focal point approximation,<sup>6</sup> and the Feller–Peterson–Dixon (FPD) approach.<sup>7–11</sup> Likewise, a number of options now exist for chemical accuracy (generally defined as  $\pm 1$  kcal/mol) on medium-sized molecules, such as Gn theory (reviewed in ref 12), CBS-QB3,<sup>13,14</sup> and the ccCA approach,<sup>15–17</sup> as well as W1-F12 and W2-F12 theory.<sup>18</sup> As such, approaches are extended to larger organic and biomolecules, such as benzene<sup>5</sup> and the amino acids;<sup>19</sup> it is becoming increasingly clear<sup>20</sup> that the limiting factor for thermochemical accuracy in such systems may well be the nuclear motion rather than the electronic structure. By far, the largest nuclear motion term is the zero-point vibrational energy (ZPVE); for instance, it reaches 62.14 kcal/mol for benzene<sup>5</sup> and goes up to about 138.2 kcal/mol for arginine.<sup>19</sup> This situation will only get worse as applications move to larger systems.

For small molecules, the calculation of accurate anharmonic force fields is a practical option (see, e.g., refs 1 and 21–23). For systems the size of arginine, however, other options clearly need to be sought.

Traditionally, one approximation has been to multiply one-half of the sum of harmonic frequencies by a scaling factor appropriate for the level of theory and basis set.<sup>24–28</sup> Some theoretical background may be appropriate here.

Limiting ourselves for the moment to asymmetric tops and neglecting higher-order anharmonicity and vibrational resonances,

the vibrational energy levels of a polyatomic molecule are given by the expression

$$E(\mathbf{n}) = G_0 + \sum_i \omega_i \left( n_i + \frac{1}{2} \right) + \sum_{i \geq j} X_{ij} \left( n_i + \frac{1}{2} \right) \left( n_j + \frac{1}{2} \right) + O(\mathbf{n}^3) \quad (1)$$

where  $G_0$  is the polyatomic equivalent of the Dunham  $Y_{00}$  constant,<sup>30</sup> while the  $n_i$ ,  $\omega_i$ , and  $X_{ij}$  have their usual meanings (e.g., ref 31) of vibrational quantum numbers, harmonic frequencies, and first-order anharmonicity constants, respectively. For simplicity, we will henceforth drop the remainder term cubic in the vibrational quantum numbers,  $O(\mathbf{n}^3)$ .

Eliminating the cumbersome restricted summation from eq 1, we obtain

$$E(\mathbf{n}) = G_0 + \sum_i \left( n_i + \frac{1}{2} \right) \left( \omega_i + X_{ii} \left( n_i + \frac{1}{2} \right) + \frac{1}{2} \sum_{j \neq i} X_{ij} \left( n_j + \frac{1}{2} \right) \right) \quad (2)$$

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The anharmonic ZPVE trivially becomes

$$\begin{aligned} \text{ZPVE}_{\text{anhar}} &\equiv E(\mathbf{0}) = G_0 + \frac{1}{2} \sum_i \omega_i + \frac{1}{4} \sum_{i \geq j} X_{ij} \\ &= G_0 + \sum_i \left( \frac{\omega_i}{2} + \frac{X_{ii}}{4} \right) + \frac{1}{8} \sum_{j \neq i} X_{ij} \end{aligned} \quad (3)$$

In experimental vibrational spectroscopy of polyatomics, vibrational energy levels are often fitted to Dunham-style power series in the vibrational quantum numbers

$$\begin{aligned} E(\mathbf{n}) - \text{ZPVE}_{\text{anhar}} &= \sum_i \left( \omega_i^0 n_i + X_{ii} n_i^2 + \frac{1}{2} \sum_{j \neq i} X_{ij} n_i n_j \right) \\ &= \sum_i (\omega_i^0 n_i + X_{ii} n_i^2) + \sum_{i > j} X_{ij} n_i n_j \end{aligned} \quad (4)$$

where the linear polyatomic Dunham coefficients are given by

$$\omega_i^0 = \omega_i + X_{ii} + \frac{1}{2} \sum_{j \neq i} X_{ij} + O(\mathbf{n}^3) \quad (5)$$

and obviously the vibrational fundamentals  $\nu_i$  (in the absence of resonances) are  $\nu_i = \omega_i^0 + X_{ii}$ . If we now define

$$\begin{aligned} \text{ZPVE}_{\text{harm}} &= \frac{1}{2} \sum_i \omega_i & \text{ZPVE}_{\text{fund}} &= \frac{1}{2} \sum_i \nu_i \\ \text{ZPVE}_{\text{linear}} &= \frac{1}{2} \sum_i \omega_i^0 \end{aligned} \quad (6)$$

Then it is easily shown that<sup>27</sup>

$$\begin{aligned} \frac{\text{ZPVE}_{\text{harm}} + \text{ZPVE}_{\text{linear}}}{2} &= \frac{1}{4} \sum_i \left( \omega_i + X_{ii} + \frac{1}{2} \sum_{j \neq i} X_{ij} \right) \\ &+ \frac{1}{4} \sum_i \omega_i = \frac{1}{2} \sum_i \omega_i + \frac{1}{4} \sum_i X_{ii} + \frac{1}{8} \sum_{i,j \neq i} X_{ij} \\ &= \frac{1}{2} \sum_i \omega_i + \frac{1}{4} \sum_i X_{ii} + \frac{1}{4} \sum_{i > j} X_{ij} = \text{ZPVE}_{\text{anhar}} - G_0 \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{\text{ZPVE}_{\text{harm}} + \text{ZPVE}_{\text{fund}}}{2} &= \frac{\text{ZPVE}_{\text{harm}} + \text{ZPVE}_{\text{linear}}}{2} + \frac{1}{4} \sum_i X_{ii} \\ &= \text{ZPVE}_{\text{anhar}} + \frac{1}{4} \sum_i X_{ii} - G_0 \end{aligned} \quad (8)$$

The anharmonicity constants can be compactly expressed in terms of the quartic force field in reduced normal coordinates ( $\text{cm}^{-1}$  units) as

$$\begin{aligned} X_{ij} &= \frac{\phi_{ijj}}{4} - \sum_k \frac{\phi_{ik} \phi_{ijk}}{4\omega_k} - \sum_k \frac{\phi_{ijk}^2}{8} [D(k, i, j) \\ &+ D(k, -i, -j) + D(k, i, -j) + D(k, -i, j)] \\ &+ \sum_\alpha B_\alpha (\zeta_{ij}^{(\alpha)}) \left( \frac{\omega_i}{\omega_j} + \frac{\omega_j}{\omega_i} \right) \end{aligned} \quad (9)$$

where the  $\omega_i$ ,  $\phi_{ijk}$  and  $\phi_{ijkb}$  have their customary meanings (e.g., ref 31) of harmonic frequencies, cubic, and quartic force constants, respectively, the  $B_\alpha$  are the rotational constants about the three principal axes of inertia, and the  $\zeta_{ij}^{(\alpha)}$  are the Coriolis coupling constants. The inverse denominators  $D$  are defined by<sup>32,33</sup>

$$D(\pm i, \pm j, \pm k) = \frac{1}{\pm \omega_i \pm \omega_j \pm \omega_k} \quad (10)$$

The  $D$  array can be precomputed; Fermi resonances will correspond to very large  $D$  elements [e.g.,  $2\omega_i \approx \omega_k$  corresponds to a very large  $D(k, -i, -i)$ ], and the anharmonicity constants can be easily deperturbed by simply zeroing the affected  $D$  element.<sup>32,33</sup>

Note that typically, the negative cubic terms outweigh the positive quartic term, making the  $X_{ij}$  negative overall. If we take this into account, then the following inequality will generally be obeyed

$$\begin{aligned} \text{ZPVE}_{\text{harm}} &> \text{ZPVE}_{\text{anhar}} \approx \frac{\text{ZPVE}_{\text{harm}} + \text{ZPVE}_{\text{linear}}}{2} \\ &> \text{ZPVE}_{\text{linear}} > \text{ZPVE}_{\text{fund}} \end{aligned} \quad (11)$$

While the  $X_{ij}$  are not invariant under deperturbation for Fermi interactions (and neither is  $G_0$ ), it can be shown<sup>22</sup> that the invariances cancel each other in eq 3, and thus,  $\text{ZPVE}_{\text{anhar}}$  is invariant. Allen and co-workers derived the following expression<sup>22</sup>

$$\begin{aligned} \text{ZPVE}_{\text{anhar}} &= \frac{1}{2} \sum_i \omega_i - \sum_{ijk} \frac{\phi_{ik} \phi_{ijk}}{32\omega_k} \\ &- \frac{1}{48} \sum_{ijk} \frac{\phi_{ijk}^2}{\omega_i + \omega_j + \omega_k} + \sum_{ij} \frac{\phi_{ijj}}{32} + Z_{\text{kinetic}} \end{aligned} \quad (12)$$

where the typically small kinetic energy term is

$$\begin{aligned} Z_{\text{kinetic}} &= -\frac{1}{4} \sum_\alpha B_\alpha^{(\alpha)} \\ &\times \left\{ 1 + \sum_{i > j} (\zeta_{ij}^{(\alpha)})^2 \frac{[B_\alpha^{(\alpha)}(\omega_i + \omega_j) - (\omega_i - \omega_j)^2]}{\omega_i \omega_j} \right\} \end{aligned} \quad (13)$$

Equivalent expressions were derived by Vázquez and Stanton (cf. ref 30 in ref 34) as well as by Barone,<sup>35</sup> the latter of which is implemented<sup>36</sup> in Gaussian 09, revision D.

(Explicit evaluation of eq 12 requires the full cubic force field and a semidiagonal quartic force field. For methods where analytical second derivatives are available, numerical central differences of the Hessian in normal coordinates permit evaluation of all required force constants in at most  $2N + 1$  Hessian evaluations.<sup>37</sup>)

The relatively high computational cost of determining harmonic force fields early on led to approximations in which force constants determined at a low level of theory were rescaled. While the SQM (scaled quantum mechanical) approach of Pulay and co-workers<sup>38,39</sup> employs different scaling factors for different types of force constants and different functional groups, by far, the most popular approach has been the use of a single global scaling factor  $\lambda$ .<sup>25,29,40,41</sup>

When using a simple scaling factor to fit harmonic frequencies  $\omega_{\text{true}} \approx \omega_{\text{calc}}(\text{level}) \lambda_{\text{harm}}(\text{level})$ , one seeks to compensate for the

intrinsic biases of the theoretical level. For instance, it has been well-known since the 1970s (see, for example, ref 41) that at the HF level with small basis sets, bonds are too short and stretching frequencies thus (as a special case of Badger's rule<sup>42,43</sup>) intrinsically too high. (In fact, it was found empirically that such low-level harmonic frequencies could be brought much closer to experiment by evaluating them at the [nonstationary] experimental geometry.<sup>44–46</sup>)

The common use of scaled harmonic frequencies to predict approximate fundamental frequencies  $\nu_{\text{true}} \approx \omega_{\text{calc}}(\text{level}) \cdot \lambda_{\text{fund}}(\text{level})$  goes a step further in that it also attempts to subsume the generally negative anharmonicity into the scaling factor. In practice, it is indeed seen in the near-IR range that vibrational anharmonicities are roughly proportional to harmonic frequencies, which is why such a crude correction as a scaling factor “has any prayer of working at all”.

Grev et al.<sup>27</sup> first showed that  $\text{ZPVE}_{\text{harm}} > \text{ZPVE}_{\text{anhar}} > \text{ZPVE}_{\text{fund}}$  as well as deriving an expression equivalent to eq 8, and it has been argued<sup>27</sup> on that basis that the average of  $\lambda_{\text{harm}}(\text{level})$  and  $\lambda_{\text{fund}}(\text{level})$  would be a good approximation to  $\lambda_{\text{ZPVE}}(\text{level})$ .

Large compendia of scale factors were published by Radom and co-workers<sup>25,40</sup> as well as by Truhlar and co-workers;<sup>28</sup> additional sets of scale factors have been published for the correlation-consistent basis sets,<sup>47</sup> the polarization-consistent basis sets,<sup>48</sup> and the Sadlej<sup>49–52</sup> electrical properties basis set;<sup>53</sup> the rationale behind this latter study was the performance of these basis sets for Raman activities.

No discussion would be complete without mentioning the more elaborate SQM or SQMFF (scaled quantum mechanical force field) approach<sup>38</sup> pioneered by Boggs, Pulay, and co-workers.

To the best of our knowledge, no consistent set of scale factors for harmonics, fundamentals, or ZPVEs has ever been proposed for the Weigend–Ahlrichs<sup>54</sup> def2 basis sets. The def2 family of basis sets not only covers most of the periodic table (presently H–Rn) but holds a middle ground between ab initio optimized basis sets like the correlation-consistent family<sup>55–58</sup> and DFT-specific basis sets like Jensen's polarization-consistent<sup>59–63</sup> family. (For two recent reviews on Gaussian basis sets, see Hill<sup>64</sup> and Jensen.<sup>65</sup>) As such, they are especially well-suited for application in conjunction with double-hybrid functionals,<sup>66,67</sup> where the correlation energy is a hybrid of DFT correlation and MP2 correlation in the basis of Kohn–Sham orbitals.<sup>68</sup> One purpose of the present paper is to report appropriate frequency ( $\lambda_{\text{harm}}$ ,  $\lambda_{\text{fund}}$ ) and ZPVE ( $\lambda_{\text{ZPVE}}$ ) scaling factors for the def2 family and a variety of ab initio and DFT methods.

Second, while it has been reported<sup>38,39</sup> that double-hybrid<sup>66,67,69,70</sup> and particularly DSD<sup>71–73</sup> density functionals perform quite well (between CCSD and CCSD(T) in quality) for calculated vibrational frequencies, no systematic set of scale factors has been proposed (aside from some ad hoc values<sup>71,73</sup> for  $\lambda_{\text{harm}}$  with polarization-consistent basis sets). A consistent set of  $\lambda_{\text{harm}}$ ,  $\lambda_{\text{fund}}$ ,  $\lambda_{\text{ZPVE}}$  for a variety of basis sets will be derived and reported in the present paper.

Third, we will address the question as to whether quartic force fields (perhaps enhanced by appropriate scaling factors) offer an actual advantage over scaled harmonic frequencies. We will show that the answer is generally affirmative for fundamentals, especially if the quartic force field is augmented with higher-level harmonic frequencies, but that for ZPVEs of at least semirigid molecules,  $\text{ZPVE}_{\text{harm}} \lambda_{\text{ZPVE}}$  works almost as well. The reason for the different behaviors is obvious from comparing the coefficients of the anharmonicities in eqs 3 and 4.

A number of basis set correlation methods or basis set–DFT functional combinations overlap with previous studies in the literature; our values for those are not intended to supersede the earlier work but to serve as a “sanity check” on the values obtained for the previously uncovered combinations. The principal resources for comparison are the large compilations of Radom and co-workers<sup>25</sup> and of Alecu et al.;<sup>28</sup> additionally, scale factors obtained using a different fitting procedure are available for HF, B3LYP, and MP2 with the correlation-consistent basis sets<sup>47</sup> and for various DFT functionals (including the B2GP-PLYP double hybrid<sup>69</sup>) with Jensen's polarization-consistent basis sets.<sup>48</sup>

## ■ COMPUTATIONAL DETAILS

Most calculations were performed using the Gaussian 09, revision D01 program system<sup>36</sup> running on the Faculty of Chemistry computing cluster at the Weizmann Institute of Science. Some CCSD(T) frequency calculations were carried out using MOLPRO 2012.1<sup>74</sup> running on the same hardware platform.

Aside from conventional CCSD(T),<sup>75</sup> we considered the following levels of theory:

- regular MP2 and spin-component-scaled SCS-MP2<sup>76,77</sup>
- on rung two of the “Jacob's Ladder of DFT”,<sup>78</sup> the GGA functionals BP86<sup>79</sup> and PBE<sup>80</sup>
- on rung three, the meta-GGA functionals TPSS<sup>81</sup> and M06L<sup>82</sup>
- on rung four, the hybrid GGAs B3LYP,<sup>83,84</sup> PBE0,<sup>85</sup> and B97-1<sup>86,87</sup> and hybrid meta-GGAs TPSS0,<sup>88,89</sup> M06,<sup>82</sup> and M06-2X<sup>82</sup>
- on rung five, the double hybrids (see Grimme<sup>67</sup> for a very recent review) B2PLYP,<sup>66</sup> B2GP-PLYP,<sup>69</sup> and the spin-component-scaled double-hybrid DSD-PBEP86-D2<sup>90</sup>
- the range-separated hybrid  $\omega$ B97X-D<sup>91</sup>

As the “training set”, we considered a slight modification of the HFREQ2014 data set,<sup>92</sup> which was compiled by two of us in a paper on explicitly correlated harmonic frequencies; for details of the experimental and “semi-experimental” reference data, the reader is referred to p 2086 of that paper. The modifications consist of deleting F<sub>2</sub> (which is a statistical outlier for all DFT and lower-level ab initio methods owing to severe static correlation), HNO (which has an anomalously high anharmonicity in the H–N stretch), and CF<sub>2</sub> and compensating by adding the open-shell diatomics S<sub>2</sub> and SO (reference data taken from Huber and Herzberg<sup>93</sup>).

In ref 92, we found that the valence CCSD(T) limit still has a root-mean-square deviation (RMSD) of 4.7 cm<sup>−1</sup> from the reference data, which actually increases to 7.0 cm<sup>−1</sup> if inner-shell correlation is accounted for; the remaining error is primarily due to neglect of higher-order correlation effects (particularly connected quadruples). This means in practice that a RMSD of 7 cm<sup>−1</sup> represents the lower limit of what we can reasonably expect.

The following basis sets have been considered:

(a) From the correlation-consistent family,<sup>55–58</sup> cc-pVDZ, cc-pV(T+d)Z, cc-pV(Q+d)Z, and the latter two's augmented counterparts aug'-cc-pV(T+d)Z and aug'-cc-pV(Q+d)Z, where the “+d” refers to the addition of a high-exponent d function on second-row elements; this has repeatedly been found<sup>58,94,95</sup> to be essential for the description of the 3d orbital, which in high oxidation states lies low enough to become a back-donation acceptor from oxygen and fluorine.

(b) From the Weigend–Ahlrichs family, the def2-SVP, def2-TZVP, def2-TZVPP, and def2-QZVP basis sets,<sup>54</sup> as well as their diffuse-augmented variants<sup>96</sup> def2-SVPD, def2-TZVPD,

Table 1. Optimal Scale Factors for Harmonic Frequencies

|                 | aug-cc-pV(Q+d)Z | aug-cc-pV(T+d)Z | cc-pV(Q+d)Z | cc-pV(T+d)Z | aug'-pc3+d | aug'-pc2 + 2d | CBSB7     | 6-31G(2df,p) | cc-pVDZ  | cc-pVQZ-F12 |
|-----------------|-----------------|-----------------|-------------|-------------|------------|---------------|-----------|--------------|----------|-------------|
| CCSD(T)-F12c    |                 |                 |             |             |            |               |           |              |          | 0.9999      |
| CCSD(T)         | 1.0012          |                 | 1.0002      | 1.0007      |            |               |           |              |          |             |
| SCS-MP2         | 0.9933          | 0.9957          | 0.9920      | 0.9926      | 0.9915     | 0.9894        | 0.9915    | 0.9843       | 0.9955   |             |
| MP2             | 0.9930          | 0.9952          | 0.9916      | 0.9919      | 0.9913     | 0.9891        | 0.9896    | 0.9831       | 0.9934   |             |
| B2GP-PLYP       | 0.9906          | 0.9916          | 0.9899      | 0.9897      | 0.9898     | 0.9885        | 0.9887    | 0.9835       | 0.9924   |             |
| B2PLYP          | 0.9991          | 0.9999          | 0.9985      | 0.9983      | 0.9985     | 0.9973        | 0.9976    | 0.9925       | 1.0018   |             |
| DSD-PBEP86-D2   | 0.9982          | 0.9993          | 0.9973      | 0.9973      | 0.9972     | 0.9957        | 0.9959    | 0.9904       | 0.9992   |             |
| M06-2X          | 0.9874          | 0.9877          | 0.9873      | 0.9870      | 0.9873     | 0.9871        | 0.9863    | 0.9837       | 0.9911   |             |
| M06             | 0.9957          | 0.9990          | 0.9959      | 0.9979      | 0.9951     | 0.9962        | 0.9985    | 0.9938       | 1.0027   |             |
| TPSS0           | 0.9875          | 0.9875          | 0.9874      | 0.9871      | 0.9870     | 0.9864        | 0.9863    | 0.9871       | 0.9894   |             |
| B3LYP           | 1.0041          | 1.0043          | 1.0040      | 1.0038      | 1.0039     | 1.0034        | 1.0042    | 1.0004       | 1.0096   |             |
| PBE0            | 0.9947          | 0.9948          | 0.9945      | 0.9942      | 0.9944     | 0.9938        | 0.9931    | 0.9895       | 0.9962   |             |
| B97-1           | 1.0033          | 1.0039          | 1.0032      | 1.0033      | 1.0031     | 1.0026        | 1.0027    | 0.9992       | 1.0075   |             |
| TPSS            | 1.0198          | 1.0198          | 1.0197      | 1.0194      | 1.0192     | 1.0188        | 1.0193    | 1.0158       | 1.0248   |             |
| M06L            | 0.9944          | 0.9981          | 0.9947      | 0.9971      | 0.9934     | 0.9951        | 0.9980    | 0.9925       | 1.0002   |             |
| BP86            | 1.0339          | 1.0340          | 1.0338      | 1.0334      | 1.0337     | 1.0332        | 1.0338    | 1.0299       | 1.0393   |             |
| PBE             | 1.0309          | 1.0310          | 1.0308      | 1.0305      | 1.0308     | 1.0302        | 1.0300    | 1.0260       | 1.0353   |             |
| $\omega$ B97X-D | 0.9913          | 0.9917          | 0.9912      | 0.9909      | 0.9910     | 0.9900        | 0.9912    | 0.9874       | 0.9942   |             |
|                 | def2-SVP        | def2-SVPD       | def2-TZVP   | def2-TZVPD  | def2-TZVPP | def2-TZVPPD   | def2-QZVP | def2-QZVPD   | 6-31G(d) | N07D        |
| SCS-MP2         | 0.9854          | 0.9938          | 0.9960      | 0.9987      | 0.9920     | 0.9936        | 0.9919    | 0.9923       | 0.9896   | 0.9864      |
| MP2             | 0.9835          | 0.9928          | 0.9946      | 0.9976      | 0.9913     | 0.9931        | 0.9915    | 0.9920       | 0.9869   | 0.9856      |
| B2GP-PLYP       | 0.9854          | 0.9901          | 0.9911      | 0.9926      | 0.9892     | 0.9900        | 0.9897    | 0.9900       | 0.9841   | 0.9865      |
| B2PLYP          | 0.9952          | 0.9989          | 0.9995      | 1.0008      | 0.9977     | 0.9985        | 0.9983    | 0.9987       | 0.9932   | 0.9957      |
| DSD-PBEP86-D2   | 0.9917          | 0.9972          | 0.9989      | 1.0007      | 0.9967     | 0.9977        | 0.9971    | 0.9975       | 0.9918   | 0.9931      |
| M06-2X          | 0.9855          | 0.9873          | 0.9871      | 0.9876      | 0.9865     | 0.9867        | 0.9869    | 0.9870       | 0.9827   | 0.9862      |
| M06             | 0.9992          | 1.0007          | 0.9980      | 0.9985      | 0.9959     | 0.9961        | 0.9959    | 0.9960       | 0.9955   | 0.9978      |
| TPSS0           | 0.9842          | 0.9860          | 0.9871      | 0.9876      | 0.9865     | 0.9867        | 0.9869    | 0.9871       | 0.9810   | 0.9855      |
| B3LYP           | 1.0044          | 1.0045          | 1.0044      | 1.0047      | 1.0029     | 1.0030        | 1.0037    | 1.0039       | 1.0008   | 1.0032      |
| PBE0            | 0.9915          | 0.9930          | 0.9944      | 0.9949      | 0.9935     | 0.9937        | 0.9942    | 0.9944       | 0.9885   | 0.9919      |
| B97-1           | 1.0023          | 1.0031          | 1.0034      | 1.0038      | 1.0023     | 1.0025        | 1.0029    | 1.0031       | 0.9993   | 1.0021      |
| TPSS            | 1.0190          | 1.0193          | 1.0194      | 1.0198      | 1.0188     | 1.0190        | 1.0192    | 1.0194       | 1.0153   | 1.0188      |
| M06L            | 0.9958          | 0.9978          | 0.9965      | 0.9970      | 0.9949     | 0.9954        | 0.9945    | 0.9946       | 0.9959   | 0.9967      |
| BP86            | 1.0340          | 1.0341          | 1.0337      | 1.0342      | 1.0325     | 1.0327        | 1.0336    | 1.0338       | 1.0316   | 1.0329      |
| PBE             | 1.0303          | 1.0302          | 1.0306      | 1.0311      | 1.0295     | 1.0297        | 1.0306    | 1.0308       | 1.0273   | 1.0288      |
| $\omega$ B97X-D | 0.9891          | 0.9910          | 0.9914      | 0.9920      | 0.9901     | 0.9903        | 0.9910    | 0.9911       | 0.9867   | 0.9903      |

def2-TZVPPD, and def2-QZVPD, respectively. (We note that def2-QZVPP is equivalent to def2-QZVP for the elements presently under consideration.)

(c) From the Jensen polarization-consistent family, the aug'-pc2+2d and aug'-pc3+d basis sets, which consist of pc-2 and pc-3, respectively, on hydrogen combined with aug-pc2 and aug-pc3, respectively, on nonhydrogen atoms and where second-row basis sets have been augmented with two and one set of high-exponent d functions, respectively, the exponent being obtained by successively multiplying the highest *d* exponent already present by a factor of 2.5. These basis set combinations should be close to the basis set limit for DFT calculations and were employed in previous DFT benchmarking papers by our group (see, for example, refs 69, 71, 73, 90, 97, and 98).

(d) Several Pople-family basis sets that are routinely used for zero-point and thermal corrections in various composite ab initio thermochemistry schemes, such as 6-31G(d) in G2 and G3 theory, GTBas3 (effectively 6-31G(2df,p)) in G4 and G4MP2 theory, and CBSB7 (effectively 6-311G(d) on first row and 6-311G(2d) on second row) in CBS-QB3. In addition, we also considered the N07D basis set, which has been advocated by Barone and co-workers<sup>99</sup> as a good compromise between

accuracy and computational cost for DFT anharmonic force fields.

Finally, the scaling factors were obtained by regression through the origin according to eqs (6.1.5) through (6.1.8) in ref 100, as implemented in the LINEST function of Microsoft Excel.

## RESULTS AND DISCUSSION

**Approximate Harmonic Frequencies to Exact Harmonic Frequencies.** RMSDs from the HFREQ2014 reference values<sup>92</sup> for unscaled harmonic frequencies can be found in the Supporting Information; optimal scaling factors  $\lambda_{\text{harm}}(\text{level})$  for  $\omega_{\text{true}} \approx \omega_{\text{calc}}(\text{level})\lambda_{\text{harm}}(\text{level})$  are given in Table 1, while the corresponding RMSD values are given in Table 2.

First of all, the largest basis sets of each of the three families, that is, aug-cc-pV(Q+d)Z, aug'-pc3+d, and def2-QZVPD, all yield similar error statistics for both raw and scaled harmonic frequencies. As a probe for performance near the basis set limit of a given method, we shall single out def2-QZVPD on the grounds of not being specifically biased toward either ab initio or DFT methods.

Of the DFT functionals considered, M06, M06-2X, and (barely)  $\omega$ B97X-D have RMSDs larger than the 30 cm<sup>-1</sup> of MP2;



Table 2. RMSD ( $\text{cm}^{-1}$ ) for Harmonic Frequencies after Scaling

|                 | aug-cc-pV(Q<br>+d)Z | aug-cc-pV(T<br>+d)Z | cc-pV(Q<br>+d)Z | cc-pV(T<br>+d)Z | aug'-pc3+d | aug'-pc2 +<br>2d | CBSB7     | 6-31G<br>(2df,p) | cc-<br>pVDZ | cc-pVQZ-<br>F12 |
|-----------------|---------------------|---------------------|-----------------|-----------------|------------|------------------|-----------|------------------|-------------|-----------------|
| CCSD(T)-F12c    |                     |                     |                 |                 |            |                  |           |                  |             | 4.63            |
| CCSD(T)         | 4.22                |                     | 7.13            | 11.51           |            |                  |           |                  |             |                 |
| SCS-MP2         | 21.97               | 24.35               | 21.24           | 22.81           | 21.45      | 26.04            | 30.29     | 31.37            | 34.96       |                 |
| MP2             | 30.48               | 32.44               | 29.40           | 30.22           | 30.13      | 34.50            | 37.47     | 38.41            | 42.57       |                 |
| B2GP-PLYP       | 11.20               | 11.26               | 9.88            | 10.06           | 10.93      | 12.70            | 18.19     | 19.59            | 25.13       |                 |
| B2PLYP          | 12.10               | 12.78               | 10.89           | 11.51           | 11.87      | 14.07            | 20.26     | 22.50            | 28.82       |                 |
| DSD-PBEP86-D2   | 10.25               | 10.50               | 9.66            | 10.54           | 9.95       | 12.04            | 18.89     | 20.65            | 26.52       |                 |
| M06-2X          | 37.09               | 36.25               | 37.12           | 36.98           | 36.82      | 36.55            | 36.39     | 39.10            | 41.88       |                 |
| M06             | 39.47               | 41.97               | 39.56           | 43.47           | 38.55      | 40.72            | 44.84     | 43.88            | 44.31       |                 |
| TPSS0           | 27.76               | 27.41               | 28.15           | 28.97           | 27.86      | 27.18            | 29.43     | 28.08            | 34.51       |                 |
| B3LYP           | 25.43               | 25.10               | 25.62           | 26.63           | 25.44      | 25.55            | 29.70     | 31.92            | 37.03       |                 |
| PBE0            | 32.03               | 31.57               | 32.22           | 32.90           | 32.21      | 31.67            | 33.42     | 33.94            | 38.35       |                 |
| B97-1           | 23.48               | 23.26               | 24.06           | 25.45           | 23.76      | 23.15            | 27.81     | 28.71            | 32.23       |                 |
| TPSS            | 24.25               | 24.30               | 25.31           | 26.49           | 24.12      | 24.58            | 30.91     | 36.34            | 44.02       |                 |
| M06L            | 28.88               | 31.23               | 28.92           | 32.88           | 27.99      | 30.51            | 34.65     | 36.58            | 38.91       |                 |
| BP86            | 22.60               | 22.87               | 23.30           | 24.67           | 22.65      | 23.66            | 29.57     | 34.91            | 41.29       |                 |
| PBE             | 23.33               | 23.51               | 24.17           | 25.46           | 23.45      | 24.28            | 30.27     | 35.45            | 42.80       |                 |
| $\omega$ B97X-D | 33.52               | 32.40               | 33.73           | 33.63           | 33.63      | 32.65            | 34.74     | 34.17            | 35.15       |                 |
|                 | def2-SVP            | def2-SVPD           | def2-TZVP       | def2-TZVPD      | def2-TZVPP | def2-TZVPPD      | def2-QZVP | def2-QZVPD       | 6-31G(d)    | N07D            |
| SCS-MP2         | 28.58               | 30.91               | 24.64           | 23.61           | 22.84      | 23.89            | 21.13     | 21.37            | 53.72       | 48.34           |
| MP2             | 35.87               | 39.28               | 31.78           | 31.02           | 30.78      | 32.05            | 29.73     | 30.03            | 60.08       | 55.70           |
| B2GP-PLYP       | 21.70               | 23.83               | 12.29           | 12.57           | 10.45      | 11.17            | 10.46     | 10.71            | 37.54       | 29.41           |
| B2PLYP          | 23.07               | 25.52               | 14.04           | 14.03           | 11.71      | 12.53            | 11.30     | 11.58            | 40.78       | 31.99           |
| DSD-PBEP86-D2   | 22.53               | 23.81               | 12.24           | 11.57           | 10.20      | 10.56            | 9.78      | 9.93             | 38.33       | 31.02           |
| M06-2X          | 49.57               | 47.76               | 37.26           | 37.59           | 37.46      | 37.17            | 36.84     | 36.85            | 40.34       | 35.75           |
| M06             | 51.30               | 51.25               | 41.71           | 41.52           | 42.32      | 41.85            | 39.71     | 39.28            | 36.34       | 40.33           |
| TPSS0           | 37.02               | 33.64               | 28.08           | 28.12           | 28.27      | 27.90            | 27.65     | 27.62            | 38.75       | 28.47           |
| B3LYP           | 38.89               | 36.10               | 26.76           | 26.66           | 25.96      | 25.58            | 25.34     | 25.37            | 41.58       | 30.31           |
| PBE0            | 43.87               | 42.28               | 32.22           | 32.29           | 32.53      | 32.30            | 32.05     | 32.08            | 36.25       | 32.54           |
| B97-1           | 35.75               | 34.25               | 23.96           | 23.33           | 24.10      | 23.57            | 23.75     | 23.65            | 35.22       | 27.25           |
| TPSS            | 37.54               | 31.64               | 26.33           | 25.13           | 24.76      | 24.10            | 24.19     | 24.07            | 52.92       | 33.74           |
| M06L            | 42.58               | 41.21               | 32.38           | 32.77           | 31.50      | 31.00            | 28.76     | 27.98            | 39.86       | 33.38           |
| BP86            | 38.38               | 36.03               | 25.64           | 24.63           | 23.74      | 23.31            | 22.69     | 22.69            | 46.92       | 32.63           |
| PBE             | 40.70               | 38.49               | 26.68           | 25.14           | 24.64      | 24.14            | 23.44     | 23.48            | 46.75       | 33.03           |
| $\omega$ B97X-D | 43.10               | 41.64               | 33.33           | 33.21           | 33.91      | 33.49            | 33.59     | 33.52            | 33.61       | 32.50           |

SCS-MP2 outperforms not just MP2 itself but all non-double-hybrid DFT functionals. Somewhat surprising, perhaps, are the low RMSDs for the simple GGAs BP86 and PBE. DSD-PBEP86, at  $9.9 \text{ cm}^{-1}$ , is the best performer in the table short of CCSD(T) itself.

Not surprisingly, RMSDs for (meta)GGA and hybrid DFT functionals display much less basis set sensitivity than the correlated ab initio methods. The double hybrids take an intermediate position but are apparently closer to the ab initio than to the DFT end of the spectrum.

Among the small basis set DFT results, N07D appears to be clearly superior to def2-SVP, 6-31G(d), and even CBSB7.

With the double hybrids, on the other hand, 6-31G(d) and N07D are clearly inferior to def2-SVP and CBSB7. Here, however, the extra computational effort for a larger basis set clearly pays off; for instance, for B2PLYP, replacing def2-SVP by def2-TZVP nearly cuts RMSD in half, and def2-TZVPP actually does better still. Still larger basis sets appear to be past the point of diminishing returns. Comparing def2-TZVPP to similar-sized basis sets from the other families, it would seem that the pc-*n* family is less suited to double-hybrid frequency calculations than the other options.

After scaling, B2PLYP, B2GP-PLYP, and DSD-PBEP86 deliver similar performances, with a slight edge for DSD-PBEP86. For unscaled harmonic frequencies, B2GP-PLYP is clearly inferior to the two other double hybrids.

What about the scaling factors themselves? Unsurprisingly, those for CCSD(T) are effectively within statistical uncertainty from unity; near the basis set limit, the pure (meta)GGAs BP86, PBE, and TPSS all have scaling factors significantly greater than unity, while B3LYP, B97-1, B2PLYP, DSD-PBEP86-D2, and M06 have scale factors close to unity, and a number of other functionals (such as TPSS0) appear to overestimate frequencies on average.

Optimal scaling factors for the DFT methods are rather weakly dependent on the basis set, to the point that scaling factors can be considered transferable to similar-sized basis sets not listed in the table. Obviously, there is more variation for MP2, with smaller basis sets corresponding to smaller optimum scaling factors (i.e., blue-shifted frequencies on average), while again the double hybrids take a middle position in terms of basis set sensitivity.

By way of a “sanity check” for our procedure, for the M06 family and the def2-TZVPP basis sets, the Truhlar group,<sup>28</sup> fitting against the F38/06 database,<sup>82</sup> found scaling factors of 0.992 for M06, 0.983 for M06-2X, and 0.995 for M06L. These

Table 3. Optimal Scale Factors for Fundamentals

|                 | aug-cc-pV(Q<br>+d)/Z | aug-cc-pV(T<br>+d)/Z | cc-pV(Q<br>+d)/Z | cc-pV(T<br>+d)/Z | aug'-pc3+d | aug'-pc2 +<br>2d | CBSB7     | 6-31G<br>(2dfp) | cc-<br>pVDZ | cc-pVQZ-<br>F12 |
|-----------------|----------------------|----------------------|------------------|------------------|------------|------------------|-----------|-----------------|-------------|-----------------|
| CCSD(T)-F12c    |                      |                      |                  |                  |            |                  |           |                 |             | 0.9627          |
| CCSD(T)         | 0.9639               |                      | 0.9629           | 0.9635           |            |                  |           |                 |             |                 |
| SCS-MP2         | 0.9563               | 0.9586               | 0.9550           | 0.9556           | 0.9545     | 0.9525           | 0.9545    | 0.9476          | 0.9584      |                 |
| MP2             | 0.9559               | 0.9581               | 0.9546           | 0.9548           | 0.9543     | 0.9521           | 0.9527    | 0.9464          | 0.9563      |                 |
| B2GP-PLYP       | 0.9537               | 0.9547               | 0.9530           | 0.9529           | 0.9529     | 0.9517           | 0.9518    | 0.9469          | 0.9554      |                 |
| B2PLYP          | 0.9619               | 0.9627               | 0.9613           | 0.9611           | 0.9613     | 0.9602           | 0.9604    | 0.9555          | 0.9645      |                 |
| DSD-PBEP86-D2   | 0.9610               | 0.9621               | 0.9602           | 0.9602           | 0.9600     | 0.9586           | 0.9588    | 0.9535          | 0.9620      |                 |
| M06-2X          | 0.9508               | 0.9510               | 0.9507           | 0.9503           | 0.9506     | 0.9505           | 0.9497    | 0.9472          | 0.9543      |                 |
| M06             | 0.9588               | 0.9619               | 0.9589           | 0.9609           | 0.9581     | 0.9592           | 0.9615    | 0.9569          | 0.9655      |                 |
| TPSS0           | 0.9508               | 0.9509               | 0.9507           | 0.9504           | 0.9504     | 0.9498           | 0.9497    | 0.9505          | 0.9527      |                 |
| B3LYP           | 0.9668               | 0.9670               | 0.9667           | 0.9665           | 0.9666     | 0.9661           | 0.9669    | 0.9633          | 0.9721      |                 |
| PBE0            | 0.9577               | 0.9579               | 0.9576           | 0.9573           | 0.9575     | 0.9569           | 0.9562    | 0.9528          | 0.9592      |                 |
| B97-1           | 0.9661               | 0.9666               | 0.9659           | 0.9661           | 0.9658     | 0.9654           | 0.9654    | 0.9621          | 0.9700      |                 |
| TPSS            | 0.9819               | 0.9819               | 0.9818           | 0.9816           | 0.9813     | 0.9809           | 0.9814    | 0.9780          | 0.9867      |                 |
| M06L            | 0.9574               | 0.9611               | 0.9577           | 0.9601           | 0.9565     | 0.9582           | 0.9609    | 0.9556          | 0.9630      |                 |
| BP86            | 0.9954               | 0.9955               | 0.9954           | 0.9950           | 0.9953     | 0.9948           | 0.9954    | 0.9916          | 1.0006      |                 |
| PBE             | 0.9926               | 0.9927               | 0.9925           | 0.9922           | 0.9925     | 0.9919           | 0.9917    | 0.9879          | 0.9968      |                 |
| $\omega$ B97X-D | 0.9545               | 0.9549               | 0.9544           | 0.9542           | 0.9542     | 0.9533           | 0.9544    | 0.9508          | 0.9573      |                 |
|                 | def2-SVP             | def2-SVPD            | def2-TZVP        | def2-TZVPD       | def2-TZVPP | def2-TZVPPD      | def2-QZVP | def2-QZVPPD     | 6-31G(d)    | N07D            |
| SCS-MP2         | 0.9487               | 0.9567               | 0.9589           | 0.9615           | 0.9550     | 0.9565           | 0.9549    | 0.9553          | 0.9527      | 0.9495          |
| MP2             | 0.9468               | 0.9557               | 0.9575           | 0.9604           | 0.9543     | 0.9560           | 0.9545    | 0.9550          | 0.9501      | 0.9488          |
| B2GP-PLYP       | 0.9487               | 0.9532               | 0.9542           | 0.9557           | 0.9523     | 0.9532           | 0.9529    | 0.9532          | 0.9474      | 0.9497          |
| B2PLYP          | 0.9581               | 0.9617               | 0.9623           | 0.9636           | 0.9605     | 0.9613           | 0.9612    | 0.9615          | 0.9563      | 0.9586          |
| DSD-PBEP86-D2   | 0.9548               | 0.9601               | 0.9617           | 0.9634           | 0.9596     | 0.9606           | 0.9600    | 0.9604          | 0.9549      | 0.9561          |
| M06-2X          | 0.9490               | 0.9507               | 0.9505           | 0.9510           | 0.9499     | 0.9501           | 0.9503    | 0.9504          | 0.9463      | 0.9496          |
| M06             | 0.9621               | 0.9636               | 0.9610           | 0.9614           | 0.9589     | 0.9591           | 0.9589    | 0.9590          | 0.9585      | 0.9607          |
| TPSS0           | 0.9477               | 0.9494               | 0.9505           | 0.9509           | 0.9499     | 0.9501           | 0.9503    | 0.9504          | 0.9446      | 0.9489          |
| B3LYP           | 0.9671               | 0.9671               | 0.9671           | 0.9674           | 0.9657     | 0.9658           | 0.9665    | 0.9666          | 0.9636      | 0.9659          |
| PBE0            | 0.9547               | 0.9561               | 0.9575           | 0.9580           | 0.9566     | 0.9568           | 0.9573    | 0.9575          | 0.9518      | 0.9550          |
| B97-1           | 0.9651               | 0.9658               | 0.9661           | 0.9665           | 0.9651     | 0.9652           | 0.9657    | 0.9658          | 0.9622      | 0.9648          |
| TPSS            | 0.9811               | 0.9814               | 0.9815           | 0.9819           | 0.9810     | 0.9811           | 0.9814    | 0.9815          | 0.9776      | 0.9809          |
| M06L            | 0.9588               | 0.9607               | 0.9595           | 0.9599           | 0.9580     | 0.9584           | 0.9575    | 0.9576          | 0.9589      | 0.9596          |
| BP86            | 0.9956               | 0.9956               | 0.9953           | 0.9958           | 0.9941     | 0.9943           | 0.9951    | 0.9953          | 0.9932      | 0.9945          |
| PBE             | 0.9920               | 0.9919               | 0.9923           | 0.9928           | 0.9912     | 0.9914           | 0.9922    | 0.9925          | 0.9891      | 0.9905          |
| $\omega$ B97X-D | 0.9524               | 0.9542               | 0.9546           | 0.9552           | 0.9533     | 0.9536           | 0.9542    | 0.9543          | 0.9501      | 0.9535          |

agree to within overlapping uncertainties with the values obtained presently of 0.9959, 0.9865, and 0.9949, respectively.

**Approximate Harmonic Frequencies to Exact Fundamental Frequencies.** The compiled experimental fundamentals can be found in the Supporting Information. For the diatomics  $\text{Cl}_2$ ,  $\text{ClF}$ ,  $\text{CO}$ ,  $\text{CS}$ ,  $\text{S}_2$ ,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{N}_2$ ,  $\text{SiO}$ , and  $\text{SO}$ , the data were taken from Huber and Herzberg,<sup>93</sup> while detailed source references are as follows:  $\text{C}_2\text{H}_2$ ,<sup>101,102</sup>  $\text{C}_2\text{H}_4$ ,<sup>103–107</sup>  $\text{CH}_3\text{OH}$ ,<sup>108</sup>  $\text{H}_2\text{CS}$ ,<sup>109,110</sup>  $\text{CH}_4$ ,<sup>111</sup>  $\text{ClCN}$ ,<sup>112,113</sup>  $\text{CO}_2$ ,<sup>114</sup>  $\text{H}_2\text{CO}$ ,<sup>115–117</sup>  $\text{H}_2\text{O}$ ,<sup>118</sup>  $\text{H}_2\text{S}$ ,<sup>119,120</sup>  $\text{HCN}$ ,<sup>121</sup>  $\text{HOCl}$ ,<sup>122</sup>  $\text{N}_2\text{O}$ ,<sup>123</sup>  $\text{NH}_3$ ,<sup>124–127</sup>  $\text{OCS}$ ,<sup>128</sup>  $\text{PH}_3$ ,<sup>129,130</sup>  $\text{SO}_2$ ,<sup>131</sup>  $\text{CS}_2$ ,<sup>132</sup>  $\text{BH}_3$ ,<sup>22</sup> and  $\text{CCl}_4$ .<sup>133</sup>

Scaling factors are given in Table 3, while RMSDs are given in Table 4. As a sanity check, we may attempt to fit experimental (ly extracted) harmonics to experimentally observed fundamentals. For the data set<sup>71</sup> considered in the present paper, we find  $\lambda_{\text{fund}}(\text{expt.}) = 0.9627(11)$ , where the number in parentheses refers to the standard deviation in the fit parameter. The RMSD in the scaled frequencies is  $24.9 \text{ cm}^{-1}$  (compared to  $79.8 \text{ cm}^{-1}$  unscaled, i.e., “RMS anharmonicity” in this special case), the max + D and max – D (maximum positive and negative errors) being  $56.9$  and  $-59.2 \text{ cm}^{-1}$ , respectively.

A very similar RMSD is obtained if the experimental harmonics are replaced by CCSD(T)-F12c harmonic frequencies

taken from ref 92. For CCSD(T) with smaller basis sets, RMSD slightly rises to reach  $28.8 \text{ cm}^{-1}$  for cc-pV(T+d)/Z.

Interestingly, a number of functional/basis set combinations have RMSDs considerably lower than  $24.9 \text{ cm}^{-1}$ , for example, B3LYP, TPSS0, and B97-1 with def2-TZVP or larger basis sets. Clearly a “better answer for the wrong reasons” is obtained here. SCS-MP2 is now clearly inferior to most DFT functionals, unlike the case for harmonic frequencies.

For the double hybrids, error statistics with sufficiently large basis sets are comparable to those of CCSD(T) and about 2.5 times worse than can be achieved for harmonic frequencies. Clearly, uniformly scaling harmonics to reproduce fundamentals erases any advantage that such functionals have for harmonic frequencies.

Interestingly, the scaling factors for the simple BP86 and PBE functionals are close to unity, and again, RMSDs in the  $25 \text{ cm}^{-1}$  range can be obtained with def2-TZVP or better basis sets. (We note that the corresponding scaling factors for harmonic frequencies are in the 1.03–1.04 range.) The low cost of these methods (if density fitting<sup>134–138</sup> is employed) obviously makes them a viable option for large systems.

The scale factors for the PBE, PBE0, B97-1, BP86, TPSS, B3LYP, and MP2 methods with the 6-31G(2dfp) basis set

Table 4. RMSD (cm<sup>-1</sup>) for Fundamentals after Scaling

|               | aug-cc-pV(Q<br>+d)Z | aug-cc-pV(T<br>+d)Z | cc-pV(Q<br>+d)Z | cc-pV(T<br>+d)Z | aug'-pc3+d | aug'-pc2 +<br>2d | CBSB7     | 6-31G<br>(2df,p) | cc-<br>pVDZ | cc-pVQZ-<br>F12 |
|---------------|---------------------|---------------------|-----------------|-----------------|------------|------------------|-----------|------------------|-------------|-----------------|
| CCSD(T)-F12c  |                     |                     |                 |                 |            |                  |           |                  |             | 24.14           |
| CCSD(T)       | 25.67               |                     | 26.55           | 28.79           |            |                  |           |                  |             |                 |
| SCS-MP2       | 37.12               | 39.27               | 36.77           | 37.86           | 37.07      | 41.30            | 45.31     | 44.31            | 49.40       |                 |
| MP2           | 45.94               | 47.88               | 45.32           | 46.05           | 45.86      | 49.95            | 53.48     | 52.36            | 57.89       |                 |
| B2GP-PLYP     | 25.32               | 26.31               | 24.72           | 24.67           | 25.32      | 27.74            | 32.11     | 30.88            | 37.99       |                 |
| B2PLYP        | 26.30               | 27.52               | 25.66           | 25.70           | 26.32      | 28.77            | 33.44     | 32.94            | 40.35       |                 |
| DSD-PBEP86-D2 | 26.57               | 27.59               | 26.32           | 26.59           | 26.63      | 29.02            | 33.88     | 33.10            | 40.07       |                 |
| M06-2X        | 27.81               | 27.67               | 27.73           | 27.60           | 27.87      | 28.21            | 28.26     | 29.61            | 35.42       |                 |
| M06           | 33.88               | 35.10               | 33.86           | 36.02           | 32.87      | 35.68            | 40.02     | 40.09            | 42.04       |                 |
| TPSS0         | 18.45               | 18.91               | 18.60           | 19.29           | 18.67      | 19.14            | 22.50     | 18.39            | 30.21       |                 |
| B3LYP         | 19.34               | 19.95               | 19.13           | 19.61           | 19.51      | 20.99            | 25.72     | 26.63            | 34.54       |                 |
| PBE0          | 26.30               | 26.42               | 26.29           | 26.56           | 26.59      | 26.93            | 29.25     | 29.10            | 36.04       |                 |
| B97-1         | 20.63               | 20.93               | 20.87           | 21.40           | 20.91      | 21.70            | 26.56     | 26.52            | 32.32       |                 |
| TPSS          | 23.32               | 24.21               | 23.86           | 24.50           | 23.38      | 24.76            | 30.73     | 34.78            | 43.17       |                 |
| M06L          | 25.74               | 26.13               | 25.49           | 27.15           | 24.77      | 26.80            | 32.60     | 35.95            | 40.34       |                 |
| BP86          | 24.50               | 25.49               | 24.75           | 25.40           | 24.70      | 26.41            | 31.68     | 35.37            | 42.74       |                 |
| PBE           | 25.85               | 26.69               | 26.17           | 26.50           | 26.12      | 27.67            | 32.66     | 36.37            | 44.13       |                 |
| ωB97X-D       | 26.51               | 25.52               | 26.54           | 25.71           | 26.63      | 26.85            | 28.89     | 27.64            | 31.32       |                 |
|               | def2-SVP            | def2-SVPD           | def2-TZVP       | def2-TZVPD      | def2-TZVPP | def2-TZVPPD      | def2-QZVP | def2-QZVPD       | 6-31G(d)    | N07D            |
| SCS-MP2       | 41.77               | 45.91               | 36.61           | 35.98           | 38.04      | 39.18            | 37.03     | 37.08            | 59.88       | 61.61           |
| MP2           | 50.17               | 54.51               | 45.35           | 44.79           | 46.46      | 47.68            | 45.77     | 45.88            | 67.61       | 69.24           |
| B2GP-PLYP     | 31.27               | 36.50               | 24.35           | 24.52           | 25.46      | 26.36            | 25.43     | 25.43            | 42.95       | 42.82           |
| B2PLYP        | 32.21               | 37.99               | 25.98           | 26.07           | 26.51      | 27.49            | 26.35     | 26.37            | 45.87       | 44.74           |
| DSD-PBEP86-D2 | 33.48               | 37.63               | 25.79           | 25.52           | 26.96      | 27.69            | 26.79     | 26.74            | 44.37       | 45.08           |
| M06-2X        | 40.63               | 42.07               | 27.72           | 28.37           | 28.22      | 28.37            | 27.99     | 28.01            | 30.24       | 30.29           |
| M06           | 46.39               | 49.16               | 34.42           | 34.41           | 36.56      | 36.43            | 34.10     | 33.76            | 30.62       | 40.25           |
| TPSS0         | 29.11               | 29.61               | 18.39           | 18.79           | 19.22      | 19.52            | 18.67     | 18.65            | 31.61       | 25.87           |
| B3LYP         | 32.39               | 35.13               | 19.65           | 20.11           | 20.11      | 20.69            | 19.63     | 19.64            | 36.18       | 31.74           |
| PBE0          | 38.49               | 40.42               | 25.84           | 26.24           | 26.91      | 27.29            | 26.61     | 26.62            | 29.86       | 32.21           |
| B97-1         | 32.00               | 35.38               | 20.30           | 20.10           | 21.46      | 21.79            | 21.21     | 21.07            | 31.52       | 30.84           |
| TPSS          | 33.85               | 33.31               | 25.07           | 24.26           | 23.72      | 23.98            | 23.57     | 23.51            | 50.23       | 37.02           |
| M06L          | 40.85               | 41.99               | 26.65           | 26.95           | 27.69      | 27.05            | 25.49     | 25.03            | 37.13       | 36.52           |
| BP86          | 37.02               | 39.72               | 26.44           | 25.87           | 25.55      | 26.01            | 24.87     | 24.84            | 45.20       | 38.51           |
| PBE           | 39.33               | 42.13               | 28.00           | 27.07           | 26.82      | 27.32            | 26.27     | 26.28            | 45.18       | 39.14           |
| ωB97X-D       | 36.32               | 38.35               | 25.38           | 25.50           | 27.20      | 27.31            | 26.64     | 26.60            | 25.26       | 30.75           |

suggested early on by Radom and co-workers<sup>25</sup> are close enough to our fitted values, the greatest difference being 0.003. However, with the 6-31G(d) basis set, the differences are 0.004 and 0.006 for the TPSS and MP2 methods, respectively.

The wave number linear scaling fit proposed in ref 139 was found not to yield better results.

**Approximate Harmonic Frequencies to Exact Anharmonic ZPVEs.** Detailed values are again given in the Supporting Information. The values for the diatomics are simply obtained as  $(\omega_e/2) - (\omega_e x_e/4) + (\omega_e y_e/8) + Y_{00}$  from the Huber and Herzberg<sup>93</sup> spectroscopic constants; the small  $Y_{00}$  can be obtained as (see Herzberg<sup>140</sup> or eq 5 in ref 141)

$$Y_{00} \cong \frac{B_e}{4} - \frac{\omega_e x_e}{4} + \frac{\alpha_e \omega_e}{12 B_e} + \frac{\alpha_e^2 \omega_e^2}{144 B_e^3} \quad (14)$$

Anharmonic ZPVEs for the polyatomic molecules were compiled from a variety of experimental and “semi-experimental” source, the latter referring to fitting of an adjustable anharmonic force field for best reproduction of experimental vibrational levels using either a variational or high-order perturbative vibrational Hamiltonian. The specific literature references are C<sub>2</sub>H<sub>2</sub>,<sup>142</sup> C<sub>2</sub>H<sub>4</sub>,<sup>143</sup> CH<sub>3</sub>OH,<sup>108</sup> CH<sub>4</sub>,<sup>144,145</sup> ClCN,<sup>146</sup> CO<sub>2</sub>,<sup>147</sup> H<sub>2</sub>CO,<sup>148</sup> H<sub>2</sub>O,<sup>149</sup> H<sub>2</sub>S,<sup>150</sup> HCN,<sup>151</sup> HOCl,<sup>152</sup> N<sub>2</sub>O,<sup>153</sup> NH<sub>3</sub>,<sup>154</sup> OCS,<sup>146</sup>

PH<sub>3</sub>,<sup>155,156</sup> SO<sub>2</sub>,<sup>149</sup> CS<sub>2</sub> (from spectroscopic constants in ref 157), H<sub>2</sub>CS (ref 158 adjusted for the difference between calculated and more recent fundamentals<sup>110</sup>), BH<sub>3</sub>,<sup>22</sup> and CCl<sub>2</sub>.<sup>133</sup> Some additional details are given as footnotes to the Supporting Information.

Scaling factors are given in Table 5, while RMSDs are given in Table 6. In light of the greatly reduced dependence (compared to the fundamentals) of the ZPVE<sub>anhar</sub> on the  $X_{ij}$ , it is presumably not surprising that not only are scaling factors  $\lambda_{ZPVE}(\text{expt.})$  closer to unity, but the uncertainty on them is much smaller. For instance, fitting ZPVE<sub>anhar</sub>  $\approx \omega_{\text{expt}} \lambda_{ZPVE}(\text{expt.})$  over our training set, we found  $\lambda_{ZPVE}(\text{expt.}) = 0.9856(5)$ , with a RMSD of just 0.04 kcal/mol (compared to 0.20 kcal/mol unscaled), a max + D of 0.08 kcal/mol, and a max − D of −0.07 kcal/mol. Considering eq 12, we can expect for the scaling factors that

$$\lambda_{\text{harm}} > \lambda_{ZPVE} \approx \frac{\lambda_{\text{harm}} + \lambda_{\text{linear}}}{2} > \frac{\lambda_{\text{harm}} + \lambda_{\text{fund}}}{2} > \lambda_{\text{linear}} > \lambda_{\text{fund}} \quad (15)$$

Obviously, for the experimental frequencies  $\lambda_{\text{harm}}(\text{expt.}) = 1$  by definition, and we found  $\lambda_{\text{fund}}(\text{expt.}) = 0.9627$  earlier; therefore,  $\lambda_{ZPVE}(\text{expt.}) = 0.9856$  is, as we may expect, somewhat larger than  $(\lambda_{\text{harm}} + \lambda_{\text{fund}})/2 = 0.9814$ . Our  $\lambda_{ZPVE}(\text{expt.})$  is very close to the value of 0.9863 found by Perdew and co-workers<sup>159</sup> for a

Table 5. Optimal Scale Factors for ZPVEs

|                 | aug-cc-pV(Q+d)Z | aug-cc-pV(T+d)Z | cc-pV(Q+d)Z | cc-pV(T+d)Z | aug'-pc3+d | aug'-pc2 + 2d | CBSB7     | 6-31G (2dfp) | cc-pVDZ  | cc-pVQZ-F12 |
|-----------------|-----------------|-----------------|-------------|-------------|------------|---------------|-----------|--------------|----------|-------------|
| CCSD(T)-F12c    |                 |                 |             |             |            |               |           |              |          | 0.9859      |
| CCSD(T)         | 0.9871          |                 | 0.9862      | 0.9868      |            |               |           |              |          |             |
| SCS-MP2         | 0.9772          | 0.9792          | 0.9763      | 0.9767      | 0.9756     | 0.9727        | 0.9759    | 0.9684       | 0.9794   |             |
| MP2             | 0.9774          | 0.9792          | 0.9764      | 0.9765      | 0.9760     | 0.9730        | 0.9746    | 0.9676       | 0.9778   |             |
| B2GP-PLYP       | 0.9750          | 0.9758          | 0.9744      | 0.9742      | 0.9743     | 0.9727        | 0.9733    | 0.9683       | 0.9768   |             |
| B2PLYP          | 0.9830          | 0.9837          | 0.9825      | 0.9822      | 0.9824     | 0.9811        | 0.9817    | 0.9769       | 0.9856   |             |
| DSD-PBEP86-D2   | 0.9831          | 0.9840          | 0.9824      | 0.9823      | 0.9822     | 0.9803        | 0.9811    | 0.9756       | 0.9841   |             |
| M06-2X          | 0.9756          | 0.9760          | 0.9756      | 0.9752      | 0.9756     | 0.9754        | 0.9744    | 0.9724       | 0.9797   |             |
| M06             | 0.9853          | 0.9891          | 0.9856      | 0.9879      | 0.9844     | 0.9865        | 0.9891    | 0.9850       | 0.9932   |             |
| TPSS0           | 0.9730          | 0.9732          | 0.9729      | 0.9726      | 0.9725     | 0.9719        | 0.9715    | 0.9729       | 0.9745   |             |
| B3LYP           | 0.9893          | 0.9896          | 0.9892      | 0.9889      | 0.9891     | 0.9887        | 0.9894    | 0.9862       | 0.9945   |             |
| PBE0            | 0.9832          | 0.9834          | 0.9830      | 0.9827      | 0.9830     | 0.9823        | 0.9814    | 0.9783       | 0.9845   |             |
| B97-1           | 0.9899          | 0.9905          | 0.9897      | 0.9898      | 0.9897     | 0.9892        | 0.9891    | 0.9861       | 0.9938   |             |
| TPSS            | 1.0021          | 1.0022          | 1.0019      | 1.0016      | 1.0015     | 1.0012        | 1.0011    | 0.9984       | 1.0059   |             |
| M06L            | 0.9812          | 0.9849          | 0.9815      | 0.9837      | 0.9797     | 0.9818        | 0.9853    | 0.9812       | 0.9876   |             |
| BP86            | 1.0192          | 1.0195          | 1.0191      | 1.0187      | 1.0192     | 1.0188        | 1.0190    | 1.0159       | 1.0240   |             |
| PBE             | 1.0172          | 1.0175          | 1.0172      | 1.0167      | 1.0172     | 1.0167        | 1.0160    | 1.0128       | 1.0210   |             |
| $\omega$ B97X-D | 0.9791          | 0.9793          | 0.9790      | 0.9784      | 0.9787     | 0.9778        | 0.9789    | 0.9756       | 0.9819   |             |
|                 | def2-SVP        | def2-SVPD       | def2-TZVP   | def2-TZVPD  | def2-TZVPP | def2-TZVPPD   | def2-QZVP | def2-QZVPD   | 6-31G(d) | N07D        |
| SCS-MP2         | 0.9710          | 0.9798          | 0.9791      | 0.9818      | 0.9760     | 0.9775        | 0.9762    | 0.9766       | 0.9700   | 0.9705      |
| MP2             | 0.9697          | 0.9791          | 0.9784      | 0.9812      | 0.9760     | 0.9775        | 0.9764    | 0.9769       | 0.9672   | 0.9701      |
| B2GP-PLYP       | 0.9716          | 0.9773          | 0.9752      | 0.9766      | 0.9737     | 0.9746        | 0.9743    | 0.9746       | 0.9649   | 0.9707      |
| B2PLYP          | 0.9808          | 0.9859          | 0.9832      | 0.9844      | 0.9818     | 0.9825        | 0.9824    | 0.9827       | 0.9735   | 0.9794      |
| DSD-PBEP86-D2   | 0.9784          | 0.9848          | 0.9834      | 0.9852      | 0.9818     | 0.9827        | 0.9823    | 0.9827       | 0.9731   | 0.9779      |
| M06-2X          | 0.9762          | 0.9795          | 0.9754      | 0.9760      | 0.9748     | 0.9751        | 0.9753    | 0.9754       | 0.9678   | 0.9745      |
| M06             | 0.9916          | 0.9951          | 0.9876      | 0.9881      | 0.9860     | 0.9863        | 0.9856    | 0.9858       | 0.9829   | 0.9886      |
| TPSS0           | 0.9710          | 0.9741          | 0.9729      | 0.9733      | 0.9723     | 0.9725        | 0.9725    | 0.9727       | 0.9632   | 0.9706      |
| B3LYP           | 0.9912          | 0.9935          | 0.9896      | 0.9898      | 0.9883     | 0.9885        | 0.9891    | 0.9892       | 0.9825   | 0.9883      |
| PBE0            | 0.9817          | 0.9848          | 0.9830      | 0.9834      | 0.9821     | 0.9824        | 0.9828    | 0.9830       | 0.9733   | 0.9802      |
| B97-1           | 0.9903          | 0.9929          | 0.9900      | 0.9903      | 0.9890     | 0.9892        | 0.9896    | 0.9897       | 0.9822   | 0.9884      |
| TPSS            | 1.0019          | 1.0041          | 1.0020      | 1.0023      | 1.0013     | 1.0016        | 1.0015    | 1.0017       | 0.9941   | 1.0005      |
| M06L            | 0.9858          | 0.9893          | 0.9824      | 0.9829      | 0.9817     | 0.9823        | 0.9813    | 0.9814       | 0.9812   | 0.9850      |
| BP86            | 1.0207          | 1.0232          | 1.0192      | 1.0196      | 1.0181     | 1.0193        | 1.0191    | 1.0193       | 1.0131   | 1.0181      |
| PBE             | 1.0179          | 1.0203          | 1.0171      | 1.0175      | 1.0160     | 1.0163        | 1.0171    | 1.0173       | 1.0095   | 1.0149      |
| $\omega$ B97X-D | 0.9788          | 0.9821          | 0.9791      | 0.9796      | 0.9779     | 0.9782        | 0.9788    | 0.9789       | 0.9709   | 0.9777      |

different set of mostly diatomic molecules; those authors proposed determining  $\text{ZPVE}_{\text{anhar}} \approx (5/8)\text{ZPVE}_{\text{harm,calc}} + (3/8)\text{ZPVE}_{\text{fund,expt}}$  which works out to be 0.9861 in this case.

Using yet another set of small molecules, Alecu et al.<sup>28</sup> surveyed scaling factors for harmonic frequencies and ZPVEs for a very large number of levels of theory and proposed a “universal scaling factor ratio” of  $\lambda_{\text{harm}}/\lambda_{\text{ZPVE}} = 1.014 \pm 0.002$ , which would lead to  $0.9862 \pm 0.0019$  for  $\text{ZPVE}_{\text{true}}(\text{expt.})/\text{ZPVE}_{\text{harm}}(\text{expt.})$ , essentially the same as Perdew et al.<sup>159</sup> and the present authors. (As an aside, Irikura et al.<sup>160</sup> found  $0.9949 \pm 0.0124$  for the same ratio, using a very different reference set that contains many second and third row diatomics, and pessimistic error bars on the reference data.)

If we were to use CCSD(T)-F12c/cc-pVQZ-F12 harmonic frequencies, which effectively represent the valence CCSD(T) basis set limit, we would have a fitted scale factor of 0.9859 (essentially the same as that for experimental frequencies) and an associated  $\text{RMSD} = 0.037$  kcal/mol. Using conventional CCSD(T), we reach  $\text{RMSD} = 0.043$  kcal/mol with the aug'-cc-pV(Q+d)Z basis set, which increases to 0.059 kcal/mol with the cc-pV(T+d)Z basis set.

For the lower-level methods, let us turn again to the def2-QZVPD basis set for performance near the basis set limit. Two of

the double hybrids reach RMSDs as low as 0.049 (DSD-PBEP86-D2) and 0.052 (B2GP-PLYP) kcal/mol, followed by 0.065 kcal/mol for B2PLYP. Especially the former two numbers are gratifyingly close to the much more expensive values for CCSD(T); we note that B2GP-PLYP has a noticeably smaller scaling factor than the two other double hybrids, that is, there is more overestimation in the harmonic frequencies that needs to be compensated for by scaling down.

SCS-MP2 performs somewhat better than straight MP2, but both have twice the RMSD of the double hybrids. Still, with the def2-QZVPD basis set, many conventional DFT functionals outperform MP2 and yield performances similar to SCS-MP2; the exceptions are M06, M06-2X, PBE0, and  $\omega$ B97X-D.

Unsurprisingly perhaps, many of the smaller basis sets are wholly inadequate for MP2 and SCS-MP2; for the double hybrids, def2-TZVP appears to be a good compromise between RMSD and computational cost. Basis set sensitivity is weaker for the conventional DFT functionals, but still, one would like something better than 6-31G(d) or even N07D; again, def2-TZVP appears to be an attractive choice.

The CBS-QB3 thermochemistry protocol<sup>13</sup> specifies a B3LYP/CBSB7 ZPVE scaled by 0.9900, which is basically identical to the 0.9894 obtained in the present work. Likewise, the



Table 6. RMSD (kcal/mol) for ZPVEs after Scaling

|                 | aug-cc-pV(Q<br>+d)Z | aug-cc-pV(T<br>+d)Z | cc-pV(Q<br>+d)Z | cc-pV(T<br>+d)Z | aug'-pc3+d | aug'-pc2 +<br>2d | CBSB7     | 6-31G<br>(2df,p) | cc-<br>pVDZ | cc-pVQZ-<br>F12 |
|-----------------|---------------------|---------------------|-----------------|-----------------|------------|------------------|-----------|------------------|-------------|-----------------|
| CCSD(T)-F12c    |                     |                     |                 |                 |            |                  |           |                  |             | 0.0374          |
| CCSD(T)         | 0.043               |                     | 0.051           | 0.059           |            |                  |           |                  |             |                 |
| SCS-MP2         | 0.100               | 0.114               | 0.099           | 0.102           | 0.098      | 0.114            | 0.137     | 0.118            | 0.144       |                 |
| MP2             | 0.121               | 0.134               | 0.119           | 0.122           | 0.119      | 0.134            | 0.158     | 0.141            | 0.168       |                 |
| B2GP-PLYP       | 0.056               | 0.060               | 0.048           | 0.048           | 0.054      | 0.062            | 0.082     | 0.056            | 0.101       |                 |
| B2PLYP          | 0.068               | 0.072               | 0.060           | 0.060           | 0.066      | 0.075            | 0.091     | 0.068            | 0.116       |                 |
| DSD-PBEP86-D2   | 0.051               | 0.056               | 0.047           | 0.047           | 0.049      | 0.058            | 0.085     | 0.061            | 0.101       |                 |
| M06-2X          | 0.133               | 0.130               | 0.132           | 0.134           | 0.132      | 0.134            | 0.130     | 0.153            | 0.154       |                 |
| M06             | 0.155               | 0.163               | 0.152           | 0.170           | 0.147      | 0.156            | 0.168     | 0.176            | 0.175       |                 |
| TPSS0           | 0.097               | 0.099               | 0.095           | 0.100           | 0.098      | 0.100            | 0.107     | 0.094            | 0.125       |                 |
| B3LYP           | 0.095               | 0.096               | 0.091           | 0.096           | 0.094      | 0.099            | 0.109     | 0.099            | 0.140       |                 |
| PBE0            | 0.123               | 0.123               | 0.123           | 0.127           | 0.123      | 0.124            | 0.131     | 0.127            | 0.145       |                 |
| B97-1           | 0.079               | 0.078               | 0.078           | 0.082           | 0.079      | 0.080            | 0.096     | 0.084            | 0.112       |                 |
| TPSS            | 0.100               | 0.101               | 0.095           | 0.099           | 0.100      | 0.107            | 0.119     | 0.103            | 0.160       |                 |
| M06L            | 0.109               | 0.113               | 0.100           | 0.116           | 0.096      | 0.112            | 0.115     | 0.133            | 0.125       |                 |
| BP86            | 0.090               | 0.091               | 0.087           | 0.091           | 0.088      | 0.095            | 0.108     | 0.097            | 0.142       |                 |
| PBE             | 0.091               | 0.092               | 0.086           | 0.091           | 0.090      | 0.096            | 0.111     | 0.099            | 0.146       |                 |
| $\omega$ B97X-D | 0.122               | 0.120               | 0.122           | 0.125           | 0.123      | 0.120            | 0.129     | 0.129            | 0.133       |                 |
|                 | def2-SVP            | def2-SVPD           | def2-TZVP       | def2-TZVPD      | def2-TZVPP | def2-TZVPPD      | def2-QZVP | def2-QZVPD       | 6-31G(d)    | N07D            |
| SCS-MP2         | 0.119               | 0.138               | 0.110           | 0.104           | 0.103      | 0.108            | 0.097     | 0.097            | 0.223       | 0.222           |
| MP2             | 0.140               | 0.159               | 0.132           | 0.125           | 0.123      | 0.128            | 0.117     | 0.118            | 0.256       | 0.245           |
| B2GP-PLYP       | 0.079               | 0.089               | 0.053           | 0.061           | 0.052      | 0.057            | 0.052     | 0.053            | 0.144       | 0.133           |
| B2PLYP          | 0.087               | 0.098               | 0.065           | 0.073           | 0.063      | 0.069            | 0.064     | 0.065            | 0.155       | 0.144           |
| DSD-PBEP86-D2   | 0.079               | 0.088               | 0.051           | 0.053           | 0.050      | 0.053            | 0.049     | 0.049            | 0.147       | 0.142           |
| M06-2X          | 0.179               | 0.162               | 0.134           | 0.139           | 0.139      | 0.137            | 0.132     | 0.132            | 0.116       | 0.130           |
| M06             | 0.193               | 0.178               | 0.155           | 0.159           | 0.165      | 0.163            | 0.152     | 0.148            | 0.112       | 0.147           |
| TPSS0           | 0.127               | 0.112               | 0.094           | 0.100           | 0.101      | 0.101            | 0.097     | 0.097            | 0.108       | 0.110           |
| B3LYP           | 0.143               | 0.123               | 0.092           | 0.102           | 0.099      | 0.099            | 0.094     | 0.094            | 0.113       | 0.122           |
| PBE0            | 0.161               | 0.142               | 0.119           | 0.124           | 0.127      | 0.127            | 0.123     | 0.123            | 0.102       | 0.129           |
| B97-1           | 0.119               | 0.105               | 0.070           | 0.078           | 0.082      | 0.083            | 0.080     | 0.079            | 0.085       | 0.101           |
| TPSS            | 0.131               | 0.121               | 0.096           | 0.101           | 0.098      | 0.100            | 0.098     | 0.099            | 0.170       | 0.142           |
| M06L            | 0.142               | 0.137               | 0.110           | 0.117           | 0.116      | 0.113            | 0.102     | 0.095            | 0.116       | 0.118           |
| BP86            | 0.128               | 0.112               | 0.087           | 0.094           | 0.094      | 0.092            | 0.088     | 0.088            | 0.134       | 0.131           |
| PBE             | 0.137               | 0.115               | 0.086           | 0.094           | 0.094      | 0.096            | 0.090     | 0.090            | 0.132       | 0.131           |
| $\omega$ B97X-D | 0.154               | 0.138               | 0.120           | 0.122           | 0.127      | 0.125            | 0.122     | 0.122            | 0.092       | 0.123           |

0.9854 scale factor for B3LYP/6-31G(2df,p) specified in G4 and G4MP2 theory agrees almost perfectly with 0.9862. The 0.985 scaling factor for B3LYP/cc-pV(T+d)Z in W1 theory, however, should be increased to about 0.989, as previously concluded<sup>19</sup> in our study on the amino acids. The scale factor for MP2/6-31G(d) advocated early on by Pople et al.<sup>29</sup> (0.9646) is also close to our fitted value (0.9672). As an additional sanity check, we can compare with the Radom database<sup>25</sup> for the PBE, PBE0, B97-1, BP86, TPSS, B3LYP, and MP2 methods with the 6-31G(2df,p) basis set; our scaling factors agree to one unit on the third decimal place, several of them to 1–2 units in the fourth decimal place.

**Approximate Anharmonic ZPVE to Exact Anharmonic ZPVE.** Would calculating actual anharmonic force fields yield materially better ZPVEs than simply scaling  $\text{ZPVE}_{\text{harm}}$  by an appropriate factor? We decided to investigate this for the def2-TZVP basis set and various methods (Table 7). The acetylene molecule had to be removed from the sample on account of its well-known pathological basis set dependence for the bending anharmonic corrections.<sup>161</sup> The Allen  $\text{ZPVE}_{\text{anharm}}$  expression,<sup>22</sup> being free of resonance denominators, is independent of any operator decisions concerning which anharmonic resonances to include or exclude.

Particularly for the meta-GGA functionals, the results display a surprising degree of grid sensitivity, as was found previously<sup>162</sup> for vibrational anharmonicities. Consequently, we used the “superfine” pruned (150,974) grid combination throughout.

Somewhat expectedly, the scaling factors  $\lambda_{\text{ZPVE,anharm}}$  are generally found to be quite close to  $\lambda_{\text{harm}}$ , typically slightly smaller.

For semirigid molecules like (aside from internal rotations and the  $\text{NH}_3$  inversion) the molecules in the present set, the performance benefit of anharmonic over scaled harmonic ZPVEs appears to be quite small. We may, however, expect the situation to be different for less rigid molecules, where the quartic force field calculation may be preferable.

**Approximate Fundamentals to Observed Fundamentals.** Finally, we consider, for just the def2-TZVP basis set (see however below), the case of fundamental frequencies calculated using second-order rotation–vibration perturbation theory (Table 8).

In the fundamentals, the anharmonic contribution is of course much larger than that in the ZPVE, and here, at least for some levels of theory, we do see a significant improvement over harmonic frequencies uniformly scaled by  $\lambda_{\text{fund}}$ . For instance, for B2PLYP, RMSD goes down from  $26 \text{ cm}^{-1}$  for uniformly scaled harmonics to  $16 \text{ cm}^{-1}$  for an anharmonic force field, and for

Table 7. Scale Factors<sup>a</sup>, Standard Deviations, RMSDs, and Sum of Maximum Positive and Negative Errors for ZPVE<sub>anharmonic</sub>

|                     | SCS-MP2 | MP2    | B2GP-PLYP | B2PLYP | DSD-PBEP86-D2     | M06-2X <sup>b</sup> | M06 <sup>b</sup> | TPSS0           |
|---------------------|---------|--------|-----------|--------|-------------------|---------------------|------------------|-----------------|
| scale factor        | 0.9917  | 0.9907 | 0.9886    | 0.9968 | 0.9968            | 0.9753              | 1.0059           | 0.9875          |
| standard deviation  | 0.0014  | 0.0017 | 0.0007    | 0.0008 | 0.0006            | 0.0097              | 0.0061           | 0.0018          |
| RMSD(unscaled)      | 0.15    | 0.17   | 0.16      | 0.07   | 0.06              | 0.76                | 0.43             | 0.21            |
| RMSD(scaled)        | 0.10    | 0.12   | 0.05      | 0.06   | 0.04              | 0.69                | 0.42             | 0.12            |
| (max +D) + (max -D) | 0.46    | 0.54   | 0.25      | 0.27   | 0.20              | 4.06                | 2.59             | 0.64            |
|                     | B3LYP   | PBE0   | B97-1     | TPSS   | M06L <sup>b</sup> | BP86                | PBE              | $\omega$ B97X-D |
| scale factor        | 1.0040  | 0.9974 | 1.0048    | 1.0177 | 0.9864            | 1.0346              | 1.0328           | 0.9921          |
| standard deviation  | 0.0015  | 0.0021 | 0.0017    | 0.0018 | 0.0073            | 0.0014              | 0.0018           | 0.0017          |
| RMSD(unscaled)      | 0.11    | 0.15   | 0.13      | 0.26   | 0.54              | 0.45                | 0.43             | 0.16            |
| RMSD(scaled)        | 0.10    | 0.14   | 0.11      | 0.12   | 0.51              | 0.09                | 0.12             | 0.12            |
| (max +D) + (max -D) | 0.40    | 0.72   | 0.66      | 0.58   | 3.11              | 0.38                | 0.62             | 0.51            |

<sup>a</sup>Calculations were performed using def2-TZVP basis sets. <sup>b</sup>The PH<sub>3</sub> molecule was omitted owing to insurmountable integration grid convergence issues with this functional.

Table 8. Scale Factors<sup>a</sup>, Standard Deviations, RMSDs, and Sum of Maximum Positive and Negative Errors for Anharmonic Frequencies

|                     | SCS-MP2 | MP2    | B2GP-PLYP | B2PLYP | DSD-PBEP86-D2     | M06-2X <sup>b</sup> | M06 <sup>b</sup> | TPSS0           |
|---------------------|---------|--------|-----------|--------|-------------------|---------------------|------------------|-----------------|
| scale factor        | 0.9945  | 0.9930 | 0.9903    | 0.9992 | 0.9981            | 0.9840              | 0.9946           | 0.9870          |
| standard deviation  | 0.0012  | 0.0017 | 0.0008    | 0.0008 | 0.0007            | 0.0021              | 0.0022           | 0.0019          |
| RMSD(unscaled)      | 28.05   | 37.18  | 25.02     | 16.01  | 15.48             | 54.24               | 45.54            | 46.67           |
| RMSD(scaled)        | 25.90   | 34.53  | 16.18     | 15.94  | 15.00             | 43.88               | 44.27            | 38.88           |
| (max +D) + (max -D) | 180.18  | 246.17 | 88.74     | 83.70  | 101.39            | 294.28              | 244.31           | 343.61          |
|                     | B3LYP   | PBE0   | B97-1     | TPSS   | M06L <sup>b</sup> | BP86                | PBE              | $\omega$ B97X-D |
| scale factor        | 1.0050  | 0.9937 | 1.0040    | 1.0240 | 0.9992            | 1.0370              | 1.0343           | 0.9881          |
| standard deviation  | 0.0014  | 0.0018 | 0.0017    | 0.0021 | 0.0037            | 0.0014              | 0.0018           | 0.0018          |
| RMSD(unscaled)      | 29.38   | 38.60  | 35.71     | 62.60  | 74.82             | 75.11               | 73.71            | 44.10           |
| RMSD(scaled)        | 27.70   | 36.52  | 34.83     | 42.55  | 74.80             | 27.63               | 34.92            | 37.25           |
| (max +D) + (max -D) | 200.87  | 251.11 | 263.72    | 336.03 | 866.83            | 197.07              | 230.88           | 230.21          |

<sup>a</sup>Calculations were performed using def2-TZVP basis sets. <sup>b</sup>The PH<sub>3</sub> molecule was omitted owing to insurmountable integration grid convergence issues with this functional.

DSD-PBEP86, it goes from 26 to 15 cm<sup>-1</sup>. For functionals like B3LYP and PBE0, no great improvement is seen, but that can be attributed to deficiencies in the harmonic frequencies. If CCSD(T)-F12c/cc-pVQZ-F12 harmonic frequencies are combined with the B3LYP anharmonicities, RMSD drops to just 12.5 cm<sup>-1</sup>; if DSD-PBEP86 anharmonicities are used instead, RMSD drops to 9 cm<sup>-1</sup>.

Most of the meta-GGAs turn out to be quite problematic for anharmonicities owing to excessive grid sensitivity. Fitted scaling factors, once again, are quite close to the “harmonic-to-harmonic” ones.

## CONCLUSIONS

We have obtained a collection of uniform frequency scaling factors  $\lambda_{\text{harm}}$  (approximate to true harmonic frequencies),  $\lambda_{\text{ZPVE}}$  (ZPVE<sub>harm</sub> to ZPVE<sub>true</sub>), and  $\lambda_{\text{fund}}$  (calculated harmonics to true fundamentals) for the Weigend–Ahlich and other selected basis sets for MP2, SCS-MP2, and a variety of DFT functionals including double hybrids. In addition, we have obtained, for selected levels of theory, scaling factors for true anharmonic ZPVEs and fundamental frequencies obtained from quartic force fields.

Where comparison is possible, our scaling factors generally agree well with those previously obtained by the Radom and Truhlar groups.

For “harmonic to harmonic” scaling, the double hybrids B2PLYP, B2GP-PLYP, and DSD-PBEP86 clearly yield the best performance at RMSDs of around 10–12 cm<sup>-1</sup> for sufficiently

large basis sets. For comparison, the valence CCSD(T) basis set limit represents a RMSD of 4.6 cm<sup>-1</sup>.

For “harmonic to ZPVE<sub>anharmonic</sub>” scaling, again the double hybrids are the best performers (reaching a RMSD of 0.05 kcal/mol with large basis sets, compared to 0.04 kcal/mol for valence CCSD(T) at the basis set limit), but functionals like B3LYP and B97-1 can still reach RMSDs in the 0.10 and 0.08 kcal/mol range, respectively. The use of explicit anharmonic ZPVEs from quartic force fields yields only a fairly marginal further improvement.

For “harmonic to fundamental” scaling, simple uniform scaling factors leave something to be desired in terms of performance; here, explicit calculation of anharmonicities does offer considerably better RMSDs. This becomes especially true if, in addition, the harmonic frequencies are replaced by basis set limit CCSD(T) values.

Among the various basis sets considered, def2-TZVP appears to offer the best compromise between quality and computational cost.

## ASSOCIATED CONTENT

### Supporting Information

Unabridged refs 36, 74, and 107; (quasi-)experimental harmonic frequencies, fundamentals, and ZPVEs for the test molecules, and computed harmonic frequencies, ZPVE<sub>harm</sub>, anharmonic frequencies, and ZPVE<sub>anharmonic</sub> for the studied molecules at the levels of theory considered in this article. Tables containing unscaled RMSDs, standard deviations, and sum of the max+ and

max– deviations are also given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The article was written through contributions of all authors. All authors have given approval to the final version of the article.

### Notes

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## REFERENCES

- (1) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. W4 Theory for Computational Thermochemistry: In Pursuit of Confident Sub-kJ/mol Predictions. *J. Chem. Phys.* **2006**, *125*, 144108.
- (2) Karton, A.; Taylor, P. R.; Martin, J. M. L. Basis Set Convergence of Post-CCSD Contributions to Molecular Atomization Energies. *J. Chem. Phys.* **2007**, *127*, 064104.
- (3) Karton, A.; Daon, S.; Martin, J. M. L. W4-11: A High-Confidence Benchmark Dataset for Computational Thermochemistry Derived from First-Principles W4 Data. *Chem. Phys. Lett.* **2011**, *510*, 165–178.
- (4) Harding, M. E.; Vázquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F. High-Accuracy Extrapolated Ab Initio Thermochemistry. III. Additional Improvements and Overview. *J. Chem. Phys.* **2008**, *128*, 114111.
- (5) Harding, M. E.; Vázquez, J.; Gauss, J.; Stanton, J. F.; Kállay, M. Towards Highly Accurate Ab Initio Thermochemistry of Larger Systems: Benzene. *J. Chem. Phys.* **2011**, *135*, 044513.
- (6) Allen, W. D.; East, A. L. L.; Császár, A. G. Ab Initio Anharmonic Vibrational Analyses of Non-Rigid Molecules. In *Structures and Conformations of Non-Rigid Molecules (NATO ASI Series 410)*; Laane, J., Dakkouri, M., Veken, B., Oberhammer, H., Eds.; Springer: Dordrecht, The Netherlands, 1993; pp 343–373.
- (7) Feller, D.; Peterson, K. A.; Dixon, D. A. A Survey of Factors Contributing to Accurate Theoretical Predictions of Atomization Energies and Molecular Structures. *J. Chem. Phys.* **2008**, *129*, 204105.
- (8) Li, S.; Hennigan, J. M.; Dixon, D. A.; Peterson, K. A. Accurate Thermochemistry for Transition Metal Oxide Clusters. *J. Phys. Chem. A* **2009**, *113*, 7861–7877.
- (9) Bross, D. H.; Hill, J. G.; Werner, H.-J.; Peterson, K. A. Explicitly Correlated Composite Thermochemistry of Transition Metal Species. *J. Chem. Phys.* **2013**, *139*, 094302.
- (10) Dixon, D.; Feller, D.; Peterson, K. A Practical Guide to Reliable First Principles Computational Thermochemistry Predictions Across the Periodic Table. *Annu. Rev. Comput. Chem.* **2012**, *8*, 1–28.
- (11) Feller, D.; Peterson, K. A.; Ruscic, B. Improved Accuracy Benchmarks of Small Molecules Using Correlation Consistent Basis Sets. *Theor. Chem. Acc.* **2013**, *133*, 1407.
- (12) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. Gn Theory. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1*, 810–825.
- (13) Wood, G. P. F.; Radom, L.; Petersson, G. A.; Barnes, E. C.; Frisch, M. J.; Montgomery, J. A. A Restricted-Open-Shell Complete-Basis-Set Model Chemistry. *J. Chem. Phys.* **2006**, *125*, 094106.
- (14) Barnes, E. C.; Petersson, G. A.; Montgomery, J. A.; Frisch, M. J.; Martin, J. M. L. Unrestricted Coupled Cluster and Brueckner Doubles Variations of W1 Theory. *J. Chem. Theory Comput.* **2009**, *5*, 2687–2693.
- (15) DeYonker, N. J.; Cundari, T. R.; Wilson, A. K. The Correlation Consistent Composite Approach (ccCA): An Alternative to the Gaussian-N Methods. *J. Chem. Phys.* **2006**, *124*, 114104.
- (16) DeYonker, N. J.; Wilson, B. R.; Pierpont, A. W.; Cundari, T. R.; Wilson, A. K. Towards the Intrinsic Error of the Correlation Consistent Composite Approach (ccCA). *Mol. Phys.* **2009**, *107*, 1107–1121.
- (17) Prascher, B. P.; Lai, J. D.; Wilson, A. K. The Resolution of the Identity Approximation Applied to the Correlation Consistent Composite Approach. *J. Chem. Phys.* **2009**, *131*, 044130.
- (18) Karton, A.; Martin, J. M. L. Explicitly Correlated Wn Theory: W1-F12 and W2-F12. *J. Chem. Phys.* **2012**, *136*, 124114.
- (19) Karton, A.; Yu, L.-J.; Kesharwani, M. K.; Martin, J. M. L. Heats of Formation of the Amino Acids Re-Examined by Means of W1-F12 and W2-F12 Theories. *Theor. Chem. Acc.* **2014**, *133*, 1483.
- (20) Pfeiffer, F.; Rauhut, G.; Feller, D.; Peterson, K. A. Anharmonic Zero Point Vibrational Energies: Tipping the Scales in Accurate Thermochemistry Calculations? *J. Chem. Phys.* **2013**, *138*, 044311.
- (21) Karton, A.; Ruscic, B.; Martin, J. M. L. Benchmark Atomization Energy of Ethane: Importance of Accurate Zero-Point Vibrational Energies and Diagonal Born–Oppenheimer Corrections for a “Simple” Organic Molecule. *J. Mol. Struct.: THEOCHEM* **2007**, *811*, 345–353.
- (22) Schuurman, M. S.; Allen, W. D.; Schaefer, H. F. The Ab Initio Limit Quartic Force Field of BH<sub>3</sub>. *J. Comput. Chem.* **2005**, *26*, 1106–1112.
- (23) Császár, A. G. Anharmonic Molecular Force Fields. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 273–289.
- (24) Del Bene, J. E.; Aue, D. H.; Shavitt, I. Stabilities of Hydrocarbons and Carbocations. 1. A Comparison of Augmented 6-31G, 6-311G, and Correlation Consistent Basis Sets. *J. Am. Chem. Soc.* **1992**, *114*, 1631–1640.
- (25) Merrick, J. P.; Moran, D.; Radom, L. An Evaluation of Harmonic Vibrational Frequency Scale Factors. *J. Phys. Chem. A* **2007**, *111*, 11683–11700.
- (26) Martin, J. M. L.; de Oliveira, G. Towards Standard Methods for Benchmark Quality Ab Initio Thermochemistry—W1 and W2 Theory. *J. Chem. Phys.* **1999**, *111*, 1843–1856.
- (27) Grev, R. S.; Janssen, C. L.; Schaefer, H. F. Concerning Zero-Point Vibrational Energy Corrections to Electronic Energies. *J. Chem. Phys.* **1991**, *95*, 5128–5132.
- (28) Alecu, I.; Zheng, J.; Zhao, Y.; Truhlar, D. G. Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries. *J. Chem. Theory Comput.* **2010**, *6*, 2872–2887.
- (29) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. Scaling Factors for Obtaining Fundamental Vibrational Frequencies and Zero-Point Energies from HF/6-31G\* and MP2/6-31G\* Harmonic Frequencies. *Isr. J. Chem.* **1993**, *33*, 345–350.
- (30) Dunham, J. The Energy Levels of a Rotating Vibrator. *Phys. Rev.* **1932**, *41*, 721–731.
- (31) Papoušek, D.; Aliev, M. R. *Molecular Vibrational–Rotational Spectra: Theory and Applications of High Resolution Infrared, Microwave and Raman Spectroscopy of Polyatomic Molecules (Studies in Physical and Theoretical Chemistry 17)*; Elsevier: New York, 1982; pp 1–324.
- (32) Davisson, J. L.; Brinkmann, N. R.; Polik, W. F. Accurate and Efficient Calculation of Excited Vibrational States from Quartic Potential Energy Surfaces. *Mol. Phys.* **2012**, *110*, 2587–2598.
- (33) Martin, J. M. L.; Taylor, P. R. Accurate Ab Initio Quartic Force Field for trans-HNNH and Treatment of Resonance Polyads. *Spectrochim. Acta, Part A* **1997**, *53*, 1039–1050.
- (34) Bomble, Y. J.; Vázquez, J.; Kállay, M.; Michauk, C.; Szalay, P. G.; Császár, A. G.; Gauss, J.; Stanton, J. F. High-Accuracy Extrapolated Ab Initio Thermochemistry. II. Minor Improvements to the Protocol and a Vital Simplification. *J. Chem. Phys.* **2006**, *125*, 64108.
- (35) Barone, V. Vibrational Zero-Point Energies and Thermodynamic Functions beyond the Harmonic Approximation. *J. Chem. Phys.* **2004**, *120*, 3059–3065.
- (36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.;



Petersson, G. A.; et al. *Gaussian 09*, revision D01, 2012; Gaussian, Inc.: Wallingford, CT, 2009. See also <http://www.gaussian.com>.

(37) Schneider, W.; Thiel, W. Anharmonic Force Fields from Analytic Second Derivatives: Method and Application to Methyl Bromide. *Chem. Phys. Lett.* **1989**, *157*, 367–373.

(38) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. Combination of Theoretical Ab Initio and Experimental Information to Obtain Reliable Harmonic Force Constants. Scaled Quantum Mechanical (QM) Force Fields for Glyoxal, Acrolein, Butadiene, Formaldehyde, and Ethylene. *J. Am. Chem. Soc.* **1983**, *105*, 7037–7047.

(39) Rauhut, G.; Pulay, P. Transferable Scaling Factors for Density Functional Derived Vibrational Force Fields. *J. Phys. Chem.* **1995**, *99*, 3093–3100.

(40) Scott, A. P.; Radom, L. Harmonic Vibrational Frequencies: An Evaluation of Hartree–Fock, Møller–Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors. *J. Phys. Chem.* **1996**, *100*, 16502–16513.

(41) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; Defrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. Molecular Orbital Studies of Vibrational Frequencies. *Int. J. Quantum Chem.* **1981**, *S20*, 269–278.

(42) Badger, R. M. A Relation Between Internuclear Distances and Bond Force Constants. *J. Chem. Phys.* **1934**, *2*, 128–131.

(43) Cioslowski, J.; Liu, G.; Mosquera Castro, R. A. Badger's Rule Revisited. *Chem. Phys. Lett.* **2000**, *331*, 497–501.

(44) Schwendeman, R. H. Comparison of Experimentally Derived and Theoretically Calculated Derivatives of the Energy, Kinetic Energy, and Potential Energy for CO. *J. Chem. Phys.* **1966**, *44*, 2115–2119.

(45) Schwendeman, R. H. Application of the Hellmann–Feynman and Virial Theorems to the Theoretical Calculation of Molecular Potential Constants. *J. Chem. Phys.* **1966**, *44*, 556–561.

(46) Allen, W. D.; Császár, A. G. On the Ab Initio Determination of Higher-Order Force Constants at Nonstationary Reference Geometries. *J. Chem. Phys.* **1993**, *98*, 2983–3015.

(47) Sinha, P.; Boesch, S. E.; Gu, C.; Wheeler, R. A.; Wilson, A. K. Harmonic Vibrational Frequencies: Scaling Factors for HF, B3LYP, and MP2 Methods in Combination with Correlation Consistent Basis Sets. *J. Phys. Chem. A* **2004**, *108*, 9213–9217.

(48) Laury, M. L.; Carlson, M. J.; Wilson, A. K. Vibrational Frequency Scale Factors for Density Functional Theory and the Polarization Consistent Basis Sets. *J. Comput. Chem.* **2012**, *33*, 2380–2387.

(49) Sadlej, A. J. Medium-Size Polarized Basis Sets for High-Level Correlated Calculations of Molecular Electric Properties. *Collect. Czech. Chem. Commun.* **1988**, *53*, 1995–2016.

(50) Sadlej, A. J. Medium-Size Polarized Basis Sets for High-Level-Correlated Calculations of Molecular Electric Properties. *Theor. Chim. Acta* **1991**, *81*, 45–63.

(51) Sadlej, A. J. Medium-Size Polarized Basis Sets for High-Level-Correlated Calculations of Molecular Electric Properties. *Theor. Chim. Acta* **1991**, *79*, 123–140.

(52) Sadlej, A. J. Medium-Size Polarized Basis Sets for High-Level-Correlated Calculations of Molecular Electric Properties. *Theor. Chim. Acta* **1992**, *81*, 339–354.

(53) Halls, M. D.; Velkovski, J.; Schlegel, H. B. Harmonic Frequency Scaling Factors for Hartree–Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2 with the Sadlej pVTZ Electric Property Basis Set. *Theor. Chem. Acc.* **2001**, *105*, 413–421.

(54) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(55) Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(56) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron Affinities of the First-Row Atoms Revisited. Systematic Basis Sets and Wave Functions. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(57) Woon, D. E.; Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. III. The Atoms Aluminum through Argon. *J. Chem. Phys.* **1993**, *98*, 1358–1371.

(58) Dunning, T. H.; Peterson, K. A.; Wilson, A. K. Gaussian Basis Sets for Use in Correlated Molecular Calculations. X. The Atoms Aluminum through Argon Revisited. *J. Chem. Phys.* **2001**, *114*, 9244–9253.

(59) Jensen, F. Polarization Consistent Basis Sets. VIII. The Transition Metals Sc–Zn. *J. Chem. Phys.* **2013**, *138*, 014107.

(60) Jensen, F. Polarization Consistent Basis Sets. 4: The Elements He, Li, Be, B, Ne, Na, Mg, Al, and Ar. *J. Phys. Chem. A* **2007**, *111*, 11198–11204.

(61) Jensen, F. Polarization Consistent Basis Sets. VII. The Elements K, Ca, Ga, Ge, As, Se, Br, and Kr. *J. Chem. Phys.* **2012**, *136*, 094110.

(62) Jensen, F.; Helgaker, T. Polarization Consistent Basis Sets. V. The Elements Si–Cl. *J. Chem. Phys.* **2004**, *121*, 3463–3470.

(63) Jensen, F. Polarization Consistent Basis Sets: Principles. *J. Chem. Phys.* **2001**, *115*, 9113–9125.

(64) Hill, J. G. Gaussian Basis Sets for Molecular Applications. *Int. J. Quantum Chem.* **2013**, *113*, 21–34.

(65) Jensen, F. Atomic Orbital Basis Sets. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2013**, *3*, 273–295.

(66) Grimme, S. Semiempirical Hybrid Density Functional with Perturbative Second-Order Correlation. *J. Chem. Phys.* **2006**, *124*, 034108.

(67) Goerigk, L.; Grimme, S. Double-Hybrid Density Functionals. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014**, DOI: 10.1002/wcms.1193.

(68) Görling, A.; Levy, M. Exact Kohn–Sham Scheme Based on Perturbation Theory. *Phys. Rev. A* **1994**, *50*, 196–204.

(69) Karton, A.; Tarnopolsky, A.; Lamère, J.-F.; Schatz, G. C.; Martin, J. M. L. Highly Accurate First-Principles Benchmark Data Sets for the Parametrization and Validation of Density Functional and Other Approximate Methods. Derivation of a Robust, Generally Applicable, Double-Hybrid Functional for Thermochemistry and Thermochemical. *J. Phys. Chem. A* **2008**, *112*, 12868–12886.

(70) Zhang, I. Y.; Xu, X. Doubly Hybrid Density Functional for Accurate Description of Thermochemistry, Thermochemical Kinetics and Nonbonded Interactions. *Int. Rev. Phys. Chem.* **2011**, *30*, 115–160.

(71) Kozuch, S.; Gruzman, D.; Martin, J. M. L. DSD-BLYP: A General Purpose Double Hybrid Density Functional Including Spin Component Scaling and Dispersion Correction. *J. Phys. Chem. C* **2010**, *114*, 20801–20808.

(72) Kozuch, S.; Martin, J. M. L. What Makes for a Bad Catalytic Cycle? A Theoretical Study on the Suzuki–Miyaura Reaction within the Energetic Span Model. *ACS Catal.* **2011**, *1*, 246–253.

(73) Kozuch, S.; Martin, J. M. L. Spin-Component-Scaled Double Hybrids: An Extensive Search for the Best Fifth-Rung Functionals Blending DFT and Perturbation Theory. *J. Comput. Chem.* **2013**, *34*, 2327–2344.

(74) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. et al. *MOLPRO*, version 2012.1, a Package of Ab Initio Programs; University of Cardiff Chemical Consultants (UC3), Cardiff, U.K., 2012. See also <http://www.molpro.net>.

(75) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A Fifth-Order Perturbation Comparison of Electron Correlation Theories. *Chem. Phys. Lett.* **1989**, *157*, 479–483.

(76) Grimme, S.; Goerigk, L.; Fink, R. F. Spin-Component-Scaled Electron Correlation Methods. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 886–906.

(77) Grimme, S. Improved Second-Order Møller–Plesset Perturbation Theory by Separate Scaling of Parallel- and Antiparallel-Spin Pair Correlation Energies. *J. Chem. Phys.* **2003**, *118*, 9095–9102.

(78) Perdew, J. P. Jacob's Ladder of Density Functional Approximations for the Exchange–Correlation Energy. In *AIP Conference Proceedings*, Antwerp, Belgium, 2001; Van Doren, V., Van Alsenoy, C., Geerlings, P., Eds.; 2001; Vol. 577, pp 1–20.

(79) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.



- (80) Perdew, J.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (81) Tao, J.; Perdew, J.; Staroverov, V.; Scuseria, G. Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- (82) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Non-covalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Function. *Theor. Chem. Acc.* **2007**, *120*, 215–241.
- (83) Becke, A. D. A New Mixing of Hartree–Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- (84) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
- (85) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- (86) Becke, A. D. Density-Functional Thermochemistry. V. Systematic Optimization of Exchange–Correlation Functionals. *J. Chem. Phys.* **1997**, *107*, 8554–8560.
- (87) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. Development and Assessment of New Exchange–Correlation Functionals. *J. Chem. Phys.* **1998**, *109*, 6264–6271.
- (88) Grimme, S. Accurate Calculation of the Heats of Formation for Large Main Group Compounds with Spin-Component Scaled MP2 Methods. *J. Phys. Chem. A* **2005**, *109*, 3067–3077.
- (89) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. Benchmark Study of DFT Functionals for Late-Transition-Metal Reactions. *J. Phys. Chem. A* **2006**, *110*, 709–716.
- (90) Kozuch, S.; Martin, J. M. L. DSD-PBEP86: In Search of the Best Double-Hybrid DFT with Spin-Component Scaled MP2 and Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20104–20107.
- (91) Chai, J.-D.; Head-Gordon, M. Systematic Optimization of Long-Range Corrected Hybrid Density Functionals. *J. Chem. Phys.* **2008**, *128*, 84106.
- (92) Martin, J. M. L.; Kesharwani, M. K. Assessment of CCSD(T)-F12 Approximations and Basis Sets for Harmonic Vibrational Frequencies. *J. Chem. Theory Comput.* **2014**, *10*, 2085–2090.
- (93) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
- (94) Bauschlicher, C. W.; Partridge, H. The Sensitivity of B3LYP Atomization Energies to the Basis Set and a Comparison of Basis Set Requirements for CCSD(T) and B3LYP. *Chem. Phys. Lett.* **1995**, *240*, 533–540.
- (95) Martin, J. M. L. Basis Set Convergence Study of the Atomization Energy, Geometry, and Anharmonic Force Field of SO<sub>2</sub>: The Importance of Inner Polarization Functions. *J. Chem. Phys.* **1998**, *108*, 2791–2800.
- (96) Rappoport, D.; Furche, F. Property-Optimized Gaussian Basis Sets for Molecular Response Calculations. *J. Chem. Phys.* **2010**, *133*, 134105.
- (97) Boese, A. D.; Martin, J. M. L. Development of Density Functionals for Thermochemical Kinetics. *J. Chem. Phys.* **2004**, *121*, 3405–3416.
- (98) Karton, A.; Gruzman, D.; Martin, J. M. L. Benchmark Thermochemistry of the C<sub>n</sub>H<sub>2n+2</sub> Alkane Isomers (*n* = 2–8) and Performance of DFT and Composite Ab Initio Methods for Dispersion-Driven Isomeric Equilibria. *J. Phys. Chem. A* **2009**, *113*, 8434–8447.
- (99) Barone, V.; Cimino, P. Accurate and Feasible Computations of Structural and Magnetic Properties of Large Free Radicals: The PBE0/N07D Model. *Chem. Phys. Lett.* **2008**, *454*, 139–143.
- (100) Gujarati, D. *Basic Econometrics*, 4th ed.; Tata McGraw Hill: Noida, India, 2004; Chapter 6.
- (101) Bramley, M. J.; Carter, S.; Handy, N. C.; Mills, I. M. A Refined Quartic Forcefield for Acetylene: Accurate Calculation of the Vibrational Spectrum. *J. Mol. Spectrosc.* **1993**, *157*, 301–336.
- (102) Vanderauwera, J.; Hurtmans, D.; Carleer, M.; Herman, M. The  $\nu_3$  Fundamental in C<sub>2</sub>H<sub>2</sub>. *J. Mol. Spectrosc.* **1993**, *157*, 337–357.
- (103) Willaert, F.; Demaison, J.; Margules, L.; Mäder, H.; Spahn, H.; Giesen, T.; Fayt, A. The Spectrum of Ethylene from Microwave to Submillimetre-Wave. *Mol. Phys.* **2006**, *104*, 273–292.
- (104) Bermejo, D.; Cané, E.; Di Lonardo, G.; Luis Domenech, J.; Escribano, R.; Martínez, R. Z.; Fusina, L. The  $\nu_2$ ,  $\nu_3$  and  $2\nu_{10}$  Raman Bands of Ethylene (<sup>12</sup>C<sub>2</sub>H<sub>4</sub>). *Mol. Phys.* **2004**, *102*, 1659–1669.
- (105) Lebron, G. B.; Tan, T. L. High-Resolution Fourier Transform Infrared Spectrum of the  $\nu_{11}$  Band of Ethylene (<sup>12</sup>C<sub>2</sub>H<sub>4</sub>). *J. Mol. Spectrosc.* **2013**, *288*, 11–13.
- (106) Aouididi, H.; Rotger, M.; Bermejo, D.; Martínez, R. Z.; Boudon, V. High-Resolution Stimulated Raman Spectroscopy and Analysis of the  $\nu_1/\nu_5$  (C–H) Stretching Dyad of C<sub>2</sub>H<sub>4</sub>. *J. Raman Spectrosc.* **2013**, *44*, 590–596.
- (107) Loroño Gonzalez, M. A.; Boudon, V.; Loëte, M.; Rotger, M.; Bourgeois, M.-T.; Didriche, K.; Herman, M.; Kapitanov, V. A.; Ponomarev, Y. N.; Solodov, A. A.; et al. High-Resolution Spectroscopy and Preliminary Global Analysis of C–H Stretching Vibrations of C<sub>2</sub>H<sub>4</sub> in the 3000 and 6000 cm<sup>−1</sup> Regions. *J. Quant. Spectrosc. Radiat. Transfer* **2010**, *111*, 2265–2278.
- (108) Hänninen, V.; Halonen, L. Calculation of Spectroscopic Parameters and Vibrational Overtones of Methanol. *Mol. Phys.* **2003**, *101*, 2907–2916.
- (109) Clouthier, D. J.; Ramsay, D. A. The Spectroscopy of Formaldehyde and Thioformaldehyde. *Annu. Rev. Phys. Chem.* **1983**, *34*, 31–58.
- (110) Yachmenev, A.; Yurchenko, S. N.; Ribeyre, T.; Thiel, W. High-Level Ab Initio Potential Energy Surfaces and Vibrational Energies of H<sub>2</sub>CS. *J. Chem. Phys.* **2011**, *135*, 074302.
- (111) Gray, D. L.; Robiette, A. G. The Anharmonic Force Field and Equilibrium Structure of Methane. *Mol. Phys.* **1979**, *37*, 1901–1920.
- (112) Meyer, F.; Dupre, J.; Meyer, C.; Koivusaari, M.; Blanquet, G. A Complete Study of the  $\nu_1$ ,  $\nu_2$ ,  $2\nu_2$  Bands of ClCN with Their Associated Hot Bands. *Mol. Phys.* **1994**, *83*, 741–756.
- (113) Lafferty, W. J.; Lide, D. R.; Toth, R. A. Infrared and Microwave Spectra of ClCN. *J. Chem. Phys.* **1965**, *43*, 2063–2070.
- (114) Teffo, J.-L.; Sulakshina, O. N.; Perevalov, V. I. Effective Hamiltonian for Rovibrational Energies and Line Intensities of Carbon Dioxide. *J. Mol. Spectrosc.* **1992**, *156*, 48–64.
- (115) Brown, L. R.; Hunt, R. H.; Pine, A. S. Wavenumbers, Line Strengths, and Assignments in the Doppler-Limited Spectrum of Formaldehyde from 2700 to 3000 cm<sup>−1</sup>. *J. Mol. Spectrosc.* **1979**, *75*, 406–428.
- (116) Bréchignac, C.; Johns, J. W. C.; McKellar, A. R. W.; Wong, M. The  $\nu_2$  Fundamental Band of H<sub>2</sub>CO. *J. Mol. Spectrosc.* **1982**, *96*, 353–361.
- (117) Allegrini, M.; Johns, J. W. C.; McKellar, A. R. W. A Study of the Coriolis-Coupled  $\nu_4$ ,  $\nu_6$ , and  $\nu_3$  Fundamental Bands and the  $\nu_5 \leftarrow \nu_6$  Difference Band of H<sub>2</sub>CO; Measurement of the Dipole Moment for  $\nu_5 = 1$ . *J. Mol. Spectrosc.* **1977**, *67*, 476–495.
- (118) Shirin, S. V.; Zobov, N. F.; Ovsyannikov, R. I.; Polyansky, O. L.; Tennyson, J. Water Line Lists Close to Experimental Accuracy Using a Spectroscopically Determined Potential Energy Surface for H<sub>2</sub><sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, and H<sub>2</sub><sup>18</sup>O. *J. Chem. Phys.* **2008**, *128*, 224306.
- (119) Gillis, J. R.; Edwards, T. H. Analysis of  $2\nu_2$ ,  $\nu_1$ , and  $\nu_3$  of H<sub>2</sub>S. *J. Mol. Spectrosc.* **1981**, *85*, 55–73.
- (120) Lane, W. C.; Edwards, T. H.; Gillis, J. R.; Bonomo, F. S.; Murcray, F. J. Analysis of  $\nu_2$  of H<sub>2</sub>S. *J. Mol. Spectrosc.* **1982**, *95*, 365–380.
- (121) Smith, A. M.; Coy, S. L.; Klemperer, W.; Lehmann, K. K. Fourier Transform Spectra of Overtone Bands of HCN from 5400 to 15100 cm<sup>−1</sup>. *J. Mol. Spectrosc.* **1989**, *134*, 134–153.
- (122) Skokov, S.; Peterson, K. A.; Bowman, J. M. An Accurate Ab Initio HOCl Potential Energy Surface, Vibrational and Rotational Calculations, and Comparison with Experiment. *J. Chem. Phys.* **1998**, *109*, 2662–2671.
- (123) Teffo, J.-L.; Chédin, A. Internuclear Potential and Equilibrium Structure of the Nitrous Oxide Molecule from Rovibrational Data. *J. Mol. Spectrosc.* **1989**, *135*, 389–409.

- (124) Hoy, A. R.; Mills, I. M.; Strey, G. Anharmonic Force Constant Calculations. *Mol. Phys.* **1972**, *24*, 1265–1290.
- (125) Morino, Y.; Kuchitsu, K.; Yamamoto, S. The Anharmonic Constants and Average Structure of Ammonia. *Spectrochim. Acta, Part A* **1968**, *24*, 335–352.
- (126) Guelachvili, G.; Abdullah, A. H.; Tu, N.; Narahari Rao, K.; Urban, Š.; Papoušek, D. Analysis of High-Resolution Fourier Transform Spectra of  $^{14}\text{NH}_3$  at  $3.0\ \mu\text{m}$ . *J. Mol. Spectrosc.* **1989**, *133*, 345–364.
- (127) Job, V. A.; Patel, N. D.; D'Cunha, R.; Kartha, V. B. High Resolution Diode Laser Measurements on the  $\nu_2$  Bands of  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$ . *J. Mol. Spectrosc.* **1983**, *101*, 48–60.
- (128) Martin, J. M. L.; François, J.-P.; Gijbels, R. Accurate Ab-Initio Quartic Force Fields for the Sulfur Compounds  $\text{H}_2\text{S}$ ,  $\text{CS}_2$ ,  $\text{OCS}$ , and  $\text{CS}$ . *J. Mol. Spectrosc.* **1995**, *169*, 445–457.
- (129) Ainetschian, A.; Häring, U.; Spiegel, G.; Kreiner, W. A. The  $\nu_2/\nu_4$  Diad of  $\text{PH}_3$ . *J. Mol. Spectrosc.* **1997**, *181*, 99–107.
- (130) Tarrago, G.; Lacombe, N.; Lévy, A.; Guelachvili, G.; Bézard, B.; Drossart, P. Phosphine Spectrum at  $4\text{--}5\ \mu\text{m}$ : Analysis and Line-by-Line Simulation of  $2\nu_2$ ,  $\nu_2 + \nu_4$ ,  $2\nu_4$ ,  $\nu_1$ , and  $\nu_3$  Bands. *J. Mol. Spectrosc.* **1992**, *154*, 30–42.
- (131) Lafferty, W. J.; Pine, A. S.; Flaud, J. M.; Camy-Peyret, C. The  $2\nu_3$  Band of  $^{32}\text{S}^{16}\text{O}_2$ : Line Positions and Intensities. *J. Mol. Spectrosc.* **1993**, *157*, 499–511.
- (132) Liou, H. T.; Huang, K. L. Fermi-Resonances, Potential Energy Function, and Cluster-Like Spectra of the Ground Electronic State of  $\text{CS}_2$ . *Chem. Phys.* **1999**, *246*, 391–431.
- (133) Tarczay, G.; Miller, T. A.; Czako, G.; Császár, A. G. Accurate Ab Initio Determination of Spectroscopic and Thermochemical Properties of Mono- and Dichlorocarbenes. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2881–2893.
- (134) Vahtras, O.; Almlöf, J.; Feyereisen, M. W. Integral Approximations for LCAO-SCF Calculations. *Chem. Phys. Lett.* **1993**, *213*, 514–518.
- (135) Weigend, F.; Häser, M. RI-MP2: First Derivatives and Global Consistency. *Theor. Chem. Acc.* **1997**, *97*, 331–340.
- (136) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. RI-MP2: Optimized Auxiliary Basis Sets and Demonstration of Efficiency. *Chem. Phys. Lett.* **1998**, *294*, 143–152.
- (137) Kendall, R. A.; Früchtl, H. A. The Impact of the Resolution of the Identity Approximate Integral Method on Modern Ab Initio Algorithm Development. *Theor. Chem. Acc.* **1997**, *97*, 158–163.
- (138) Bernholdt, D. E. Scalability of Correlated Electronic Structure Calculations on Parallel Computers: A Case Study of the RI-MP2 Method. *Parallel Comput.* **2000**, *26*, 945–963.
- (139) Yoshida, H.; Takeda, K.; Okamura, J.; Ehara, A.; Matsuur, H. A New Approach to Vibrational Analysis of Large Molecules by Density Functional Theory: Wavenumber-Linear Scaling Method. *J. Phys. Chem. A* **2002**, *106*, 3580–3586.
- (140) Herzberg, G. *Molecular Spectra and Molecular Structure. Vol. 1: Spectra of Diatomic Molecules*, 2nd ed.; Krieger: Malabar, FL, 1989.
- (141) Irikura, K. K. Experimental Vibrational Zero-Point Energies: Diatomic Molecules. *J. Phys. Chem. Ref. Data* **2007**, *36*, 389–397.
- (142) Xu, D.; Guo, H.; Zou, S.; Bowman, J. M. A Scaled Ab Initio Potential Energy Surface for Acetylene and Vinylidene. *Chem. Phys. Lett.* **2003**, *377*, 582–588.
- (143) Avila, G.; Carrington, T. Using a Pruned Basis, a Non-Product Quadrature Grid, and the Exact Watson Normal-Coordinate Kinetic Energy Operator to Solve the Vibrational Schrödinger Equation for  $\text{C}_2\text{H}_4$ . *J. Chem. Phys.* **2011**, *135*, 064101.
- (144) Wang, X.-G.; Carrington, T. A Contracted Basis-Lanczos Calculation of Vibrational Levels of Methane: Solving the Schrödinger Equation in Nine Dimensions. *J. Chem. Phys.* **2003**, *119*, 101–117.
- (145) Schwenke, D. W.; Partridge, H. Vibrational Energy Levels for  $\text{CH}_4$  from an Ab Initio Potential. *Spectrochim. Acta, Part A* **2001**, *57*, 887–895.
- (146) Pak, Y.; Woods, R. C. Spectroscopic Constants and Potential Energy Functions of  $\text{OCCl}^+$ ,  $\text{ONP}$ ,  $\text{ONS}^+$ ,  $\text{ArCN}^+$ ,  $\text{OCS}$ , and  $\text{NCCl}$  Using the Coupled Cluster Method. *J. Chem. Phys.* **1997**, *107*, 5094–5102.
- (147) Huang, X.; Schwenke, D. W.; Tashkun, S. A.; Lee, T. J. An Isotopic-Independent Highly Accurate Potential Energy Surface for  $\text{CO}_2$  Isotopologues and an Initial  $^{12}\text{C}^{16}\text{O}_2$  Infrared Line List. *J. Chem. Phys.* **2012**, *136*, 124311.
- (148) Avila, G.; Carrington, T. Solving the Schrödinger Equation Using Smolyak Interpolants. *J. Chem. Phys.* **2013**, *139*, 134114.
- (149) Fortenberry, R. C.; Huang, X.; Schwenke, D. W.; Lee, T. J. Limited Rotational and Rovibrational Line Lists Computed with Highly Accurate Quartic Force Fields and Ab Initio Dipole Surfaces. *Spectrochim. Acta, Part A* **2014**, *119*, 76–83.
- (150) Kozin, I. N.; Jensen, P. Fourfold Clusters of Rovibrational Energy Levels for  $\text{H}_2\text{S}$  Studied with a Potential Energy Surface Derived from Experiment. *J. Mol. Spectrosc.* **1994**, *163*, 483–509.
- (151) Wu, Q.; Zhang, J. Z. H.; Bowman, J. M. Inverse Perturbation via Singular Value Decomposition: Application to Correction of Potential Surface for  $\text{HCN}$ . *J. Chem. Phys.* **1997**, *107*, 3602–3610.
- (152) Peterson, K. A.; Skokov, S.; Bowman, J. M. A Theoretical Study of the Vibrational Energy Spectrum of the  $\text{HOCl}/\text{HClO}$  System on an Accurate Ab Initio Potential Energy Surface. *J. Chem. Phys.* **1999**, *111*, 7446–7456.
- (153) Czako, G.; Furtenbacher, T.; Császár, A. G.; Szalay, V. Variational Vibrational Calculations Using High-Order Anharmonic Force Fields. *Mol. Phys.* **2004**, *102*, 2411–2423.
- (154) Huang, X.; Schwenke, D. W.; Lee, T. J. An Accurate Global Potential Energy Surface, Dipole Moment Surface, and Rovibrational Frequencies for  $\text{NH}_3$ . *J. Chem. Phys.* **2008**, *129*, 214304.
- (155) Nikitin, A. V.; Holka, F.; Tyuterev, V. G.; Fremont, J. Vibration Energy Levels of the  $\text{PH}_3$ ,  $\text{PH}_2\text{D}$ , and  $\text{PHD}_2$  Molecules Calculated from High Order Potential Energy Surface. *J. Chem. Phys.* **2009**, *130*, 244312.
- (156) Wang, D.; Shi, Q.; Zhu, Q.-S. An Ab Initio Quartic Force Field of  $\text{PH}_3$ . *J. Chem. Phys.* **2000**, *112*, 9624–9631.
- (157) Zúñiga, J.; Bastida, A.; Requena, A.; Sibert, E. L. A Theoretical Study of the Vibrational Spectrum of the  $\text{CS}_2$  Molecule. *J. Chem. Phys.* **2002**, *116*, 7495–7508.
- (158) Martin, J. M. L.; François, J.-P.; Gijbels, R. The Anharmonic Force Field of Thioformaldehyde,  $\text{H}_2\text{CS}$ , by Ab Initio Methods. *J. Mol. Spectrosc.* **1994**, *168*, 363–373.
- (159) Csonka, G. I.; Ruzsinszky, A.; Perdew, J. P. Estimation, Computation, and Experimental Correction of Molecular Zero-Point Vibrational Energies. *J. Phys. Chem. A* **2005**, *109*, 6779–6789.
- (160) Irikura, K. K.; Johnson, R. D.; Kacker, R. N.; Kessel, R. Uncertainties in Scaling Factors for Ab Initio Vibrational Zero-Point Energies. *J. Chem. Phys.* **2009**, *130*, 114102.
- (161) Martin, J. M. L.; Lee, T. J.; Taylor, P. R. A Purely Ab Initio Spectroscopic Quality Quartic Force Field for Acetylene. *J. Chem. Phys.* **1998**, *108*, 676–691.
- (162) Boese, A. D.; Klopper, W.; Martin, J. M. L. Anharmonic Force Fields and Thermodynamic Functions Using Density Functional Theory. *Mol. Phys.* **2005**, *103*, 863–876.