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An Evaluation of Harmonic Vibrational Frequency Scale Factors

Jeffrey P. Merrick, Damian Moran,*,† and Leo Radom*

School of Chemistry and Centre of Excellence in Free Radical Chemistry and Biotechnology, University of Sydney, Sydney, New South Wales 2006, Australia

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Scale factors for obtaining fundamental vibrational frequencies, low-frequency vibrational frequencies, zero-point vibrational energies (ZPVEs), and thermal contributions to enthalpy and entropy have been derived through a least-squares approach from harmonic frequencies determined at more than 100 levels of theory. Wave function procedures (HF, MP2, QCISD, QCISD(T), CCSD, and CCSD(T)) and a large and representative range of density functional theory (DFT) approaches (B3-LYP, BMK, EDF2, M05-2X, MPWB1K, O3-LYP, PBE, TPSS, etc.) have been examined in conjunction with basis sets such as 6-31G(d), 6-31+G(d,p), 6-31G(2df,p), 6-311+G(d,p), and 6-311+G(2df,p). The vibrational frequency scale factors were determined by a comparison of theoretical harmonic frequencies with the corresponding experimental fundamentals utilizing a standard set of 1066 individual vibrations. ZPVE scale factors were generally obtained from a comparison of the computed ZPVEs with experimental ZPVEs for a smaller standard set of 39 molecules, though the effect of expansion to a 48 molecule data set was also examined. In addition to evaluating the scale factors for a wide range of levels of theory, we have also probed the effect on scale factors of varying the percentage of incorporated exact exchange in hybrid DFT calculations using a modified B3-LYP functional. This has revealed a near-linear relationship between the magnitude of the scale factor and the proportion of exact exchange. Finally, we have investigated the effect of basis set size on HF, MP2, B3-LYP, and BMK scale factors by deriving values with basis sets ranging from 6-31G(d) up to 6-311++G(3df,3pd) as well as with basis sets in the cc-pVnZ and aug-cc-pVnZ series and with the TZV2P basis.

1. Introduction

Computed quantum chemical harmonic vibrational frequencies (ω) are typically larger than the fundamentals ($\tilde{\nu}$) observed experimentally.[1] A major source of this disagreement is the neglect of anharmonicity effects in the theoretical treatment. Errors also arise because of incomplete incorporation of electron correlation and the use of finite basis sets. The relatively uniform nature of the overestimation of quantum chemical harmonic vibrational frequencies for a particular theoretical procedure allows the application of generic frequency scale factors (λ). For instance, in previous work[2,3] we developed λ values suitable for obtaining fundamentals, low-frequency vibrational frequencies, zero-point vibrational energies (ZPVEs), and thermal contributions to enthalpy ($\Delta H_{\mathrm{vib}}(T)$) and entropy ($S_{\mathrm{vib}}(T)$) with HF, MP2, QCISD, and density functional theory (DFT) procedures (Table 1).

TABLE 1: Summary of Recommended Frequency Scale Factors from Our Previous Work[a]

level of theory	$\omega^{b,c}$	$1/\omega^{d,e}$	ZPVE^{f,g}	$\Delta H_{\mathrm{vib}}(T)^{d,h}$	$S_{\mathrm{vib}}(T)^{d,i}$
AM1	0.9532				
PM3	0.9761				
HF/3-21G	0.9085	1.0075	0.9207	0.9444	0.9666
HF/6-31G(d)	0.8953[j]	0.9061	0.9135	0.8905	0.8978
HF/6-31+G(d)	0.8970	0.9131	0.9153	0.8945	0.9027
HF/6-31G(d,p)	0.8992	0.9089	0.9181	0.8912	0.8990
HF/6-311G(d,p)	0.9051	0.9110	0.9248	0.8951	0.9021
HF/6-311G(df,p)	0.9054	0.9085	0.9247	0.8908	0.8981
MP2-fu/6-31G(d)	0.9427	1.0214	0.9661[k]	1.0084	1.0228
MP2-fc/6-31G(d)	0.9434	1.0485	0.9670[k]	1.0211	1.0444
MP2/6-31G(d,p)	0.9370	1.0229	0.9608[k]	1.0084	1.0232
MP2/6-311G(d,p)	0.9496	1.0127	0.9748[k]	1.0061	1.0175
QCISD-fc/6-31G(d)	0.9538	1.0147	0.9776	1.0080	1.0187
B-LYP/6-31G(d)	0.9945	1.0620	1.0126	1.0633	1.0670
B-LYP/6-311G(df,p)	0.9986	1.0667	1.0167	1.0593	1.0641
B-P86/6-31G(d)	0.9914	1.0512	1.0108	1.0478	1.0527
B3-LYP/6-31G(d)	0.9614	1.0013	0.9806	0.9989	1.0015
B3-P86/6-31G(d)	0.9558	0.9923	0.9759	0.9864	0.9902
B3-PW91/6-31G(d)	0.9573	0.9930	0.9774	0.9885	0.9920

[a] From ref 2. [b] From the F1 set, 122 molecules and 1066 frequencies. [c] Suitable for relating theoretical harmonic frequencies to observed fundamentals. [d] From the F1′ set, 122 molecules and 1062 frequencies. [e] Suitable for the prediction of low-frequency vibrations. [f] From the Z1 set. [g] Suitable for the prediction of zero-point vibrational energies (ZPVEs). [h] Suitable for the prediction of the thermal contributions to enthalpy, $\Delta H_{\mathrm{vib}}(T)$. [i] Suitable for the prediction of the thermal contributions to entropy, $S_{\mathrm{vib}}(T)$. [j] The previous “standard” value of 0.8929 should continue to be used, as employed, for example, in G3 theory. [k] Values obtained with NO and CN removed from the analysis; see text.

Since our previous paper,[2] a number of other reports have appeared in the literature on the development of harmonic vibrational frequency scale factors. For example, Wong[4] used the molecular test set from our 1993 paper[3] to develop scale factors for fundamental frequencies and ZPVEs for a range of methods (MP2-fu, S-VWN, B-LYP, B-VWN, B3-LYP, and B3-P86) in conjunction with the 6-31G(d) basis set. Truhlar and co-workers[5−10] used a metal-free set of 49 molecules based on the G2 set to develop a number of ZPVE scale factors for use with contemporary DFT methods developed in his research group (e.g., MPW1K, MPWB1K, and BB1K). Curtiss et al.[11] produced a single ZPVE scale factor for B3-LYP/6-31G(2df,p)

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* Authors to whom correspondence should be addressed. E-mail: dmoran@chem.mq.edu.au; radom@chem.usyd.edu.au.

† Current address: Department of Chemistry and Biomolecular Sciences, Macquarie University, NSW 2109, Australia.

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TABLE 2: Frequency Scale Factors Suitable for Fundamental Vibrations and Corresponding rms_{ov} Values Derived from a Least-Squares Fit[a]

	6-31G(d)		6-31+G(d,p)		6-31G(2df,p)		6-311+G(d,p)		6-311+G(2df,p)	
method	scale factor[b]	rms_{ov}[c]	scale factor[b]	rms_{ov}[c]	scale factor[b]	rms_{ov}[c]	scale factor[b]	rms_{ov}[c]	scale factor[b]	rms_{ov}[c]
HF	0.8953	50	0.9007	51	0.9035	55	0.9059	53	0.9073	54
MP2	0.9441[d]	47[d]	0.9418[d]	52[d]	0.9462[d]	41[d]	0.9523[d]	46[d]	0.9569[d]	40[d]
QCISD	0.9536[d]	35[d]	0.9454[d]	39[d]	*e*	*e*	0.9560[d]	33[d]	*e*	*e*
QCISD(T)	0.9611[d]	41[d]	0.9529[d]	47[d]	*e*	*e*	0.9647[d]	40[d]	*e*	*e*
CCSD	0.9516[d]	34[d]	0.9436[d]	37[d]	*e*	*e*	0.9542[d]	32[d]	*e*	*e*
CCSD(T)	0.9603[d]	40[d]	0.9522[d]	46[d]	*e*	*e*	0.9639[d]	38[d]	*e*	*e*
B-B95	0.9919	43	0.9944	46	0.9943	41	*e*	*e*	*e*	*e*
B-LYP	0.9940	45	0.9969	47	0.9964	40	1.0001	47	0.9994	41
B-P86	0.9914	40	0.9939	43	0.9943	39	0.9978	43	0.9976	37
G96-LYP	0.9923	43	0.9944	45	0.9948	39	0.9977	45	0.9970	39
HCTH147	0.9748	39	0.9771	43	0.9781	39	0.9812	43	0.9820	38
HCTH407	0.9698	41	0.9728	45	0.9735	41	0.9765	45	0.9778	40
HCTH93	0.9734	40	0.9760	44	0.9768	40	0.9799	44	0.9810	39
O-LYP	0.9775	41	0.9802	44	0.9811	40	0.9842	44	0.9854	39
PBE	0.9875	40	0.9904	44	0.9907	40	0.9944	43	0.9948	38
TPSS	0.9741	42	0.9767	42	0.9787	36	0.9818	41	0.9821	36
VSXC	0.9681	42	0.9700	47	0.9700	42	0.9738	48	0.9746	42
B1-B95	0.9501	35	0.9535	37	0.9544	37	*e*	*e*	*e*	*e*
B1-LYP	0.9561	33	0.9599	34	0.9603	32	0.9640	34	0.9639	30
B3-LYP	0.9613	34	0.9648	35	0.9652	32	0.9688	35	0.9686	31
B3-P86	0.9557	34	0.9588	36	0.9600	35	0.9632	35	0.9635	33
B3-PW91	0.9571	33	0.9602	36	0.9615	35	0.9648	35	0.9652	33
B971	0.9609	33	0.9644	35	0.9651	34	0.9684	35	0.9685	32
B972	0.9512	33	0.9543	36	0.9558	35	0.9587	36	0.9596	34
B98	0.9602	33	0.9635	35	0.9642	33	0.9676	34	0.9675	31
BB1K	0.9322	36	0.9359	39	*e*	*e*	*e*	*e*	*e*	*e*
BHandH	0.9270	45	0.9320	46	0.9330	51	0.9368	46	0.9376	47
BHandH-LYP	0.9244	34	0.9288	36	0.9301	37	0.9335	35	0.9339	35
BMK	0.9475	39	0.9533	41	0.9520	41	0.9566	38	0.9551	36
EDF1	0.9798	40	0.9820	43	*e*	*e*	0.9858[f]	43[f]	*e*	*e*
EDF2	0.9595	34	0.9627	37	*e*	*e*	0.9668	36	*e*	*e*
M05	0.9492	39	0.9542	42	0.9582	40	0.9601	41	0.9614	39
M05-2X	0.9373	39	0.9419	40	0.9450	38	0.9446	38	0.9444	37
MPW1K	0.9278	36	0.9315	39	0.9336	40	0.9365	38	0.9375	38
mPW1PW91	0.9499	34	0.9532	36	0.9546	36	0.9580	36	0.9587	34
MPWB1K	0.9295	37	0.9335	39	0.9348	41	*e*	*e*	*e*	*e*
O3-LYP	0.9617	35	0.9648	39	0.9658	36	0.9690	38	0.9701	35
PBE0	0.9512	34	0.9547	37	0.9561	38	0.9594	36	0.9602	35

[a] Using the F1 set of 1066 frequencies unless otherwise noted. [b] As defined by eq 2. [c] Overall root-mean-square error, as defined by eq 5, in units of cm^{-1}. [d] Values obtained with the F″ set; see text. [e] Scale factors and rms_{ov} values not determined at these levels of theory. [f] Values obtained with Cl_2CS removed from the analysis due to SCF convergence problems.

to use in conjunction with the G3X procedure. Schlegel and co-workers[12] developed high- (>1800 cm^{-1}) and low-frequency (<1800 cm^{-1}) scale factors for use with the Sadlej pVTZ basis set in conjunction with the HF, S-VWN, B-LYP, B3-LYP, B3-PW91, and MP2 methods. Their scale factor test set involved 111 molecules (900 vibrations) that contained only elements from the first and second row.

More recently, Wilson and co-workers[13] derived frequency scale factors for the correlation-consistent basis sets cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ in combination with the HF, B3-LYP, and MP2 methods. For the development of scale factors for low- (<1000 cm^{-1}) and high-frequency (>1000 cm^{-1}) vibrations and thermal contributions to enthalpy and entropy, they employed a molecular test set of 41 common organic molecules that was based on earlier work by Healy and Holder.[14] They determined their ZPVE scale factors with the set of 24 molecules from Schaefer and co-workers.[15] Andersson and Uvdal[16] have recently reported three scale factors suitable for scaling fundamentals, low-frequency vibrational modes, and ZPVEs for B3-LYP/6-311+G-(d,p). Interestingly, they noted that the B3-LYP scale factor did not change significantly when evaluated for basis sets larger than 6-311+G(d,p) (i.e., the scale factor "converges" with respect to increasing basis set size). As a consequence, Andersson and Uvdal[16] recommended the B3-LYP/6-311+G(d,p) scale factor for use with B3-LYP computations employing larger basis sets. Csonka, Ruzsinsky, and Perdew[17] carried out a detailed study on the determination of ZPVEs using the B3-LYP, B3-PW91, PBE, PBE0, TPSS, and TPSSh methods, combined with the 6-31G(d), 6-31+G(d), 6-31+G-(d,p), and 6-31G(2df,p) basis sets. One interesting result noted in their study is the different relationships between the true ZPVE and anharmonic/harmonic ZPVEs for diatomic and polyatomic molecules. Another interesting result that they report is that experimental harmonic ZPVEs are related to true experimental ZPVEs by a scale factor of 0.9859 with a mean absolute deviation (MAD) of just 0.2 kJ mol^{-1}. Finally, scale factors suitable for scaling fundamentals and ZPVEs have most recently been reported by Tantirungrotechai et al.[18] They employed a number of different density functionals (B972, B98, G96-LYP, HCTH, O-LYP, O3-LYP, VSXC, and PBE0) and basis sets (3-21G, 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-311G-(d,p), 6-311G(df,p), 6-311+G(df,p), cc-pVDZ, and aug-cc-pVDZ) in combination with the test sets from our previous work.[2]

In the present article, we report the results of our most recent scale factor development efforts. We have extended our previous extensive study[2] by examining (a) a variety of more recently formulated DFT procedures, (b) a wider range of basis sets, and (c) the effect of varying the amount of exact exchange in hybrid DFT calculations.

2. Theoretical Procedures

The calculations performed in the present study were carried out with either the Gaussian 03,[19] Q-Chem 3.0,[20] ACES II,[21] or NWChem[22] program packages. Harmonic vibrational frequencies were determined by the analytical evaluation of second derivatives of the energy with respect to nuclear displacement, except for the coupled cluster and quadratic configuration interaction methods where finite central differences of the analytical gradients were employed.

The effect of integration grid density on the computed DFT frequencies was examined with additional Gaussian 03 computations performed for a variety of grids at the B3-LYP/6-31G(d), BMK/6-31G(d), MPWB1K/6-31G(d), B3-LYP/6-311+G(d,p), BMK/6-311+G(d,p), PBE/6-31G(d), B972/6-31G(d), BHandH/6-31G(d), BLYP/6-31G(d), and HCTH407/6-31G(d) levels of theory in conjunction with the F1 molecule set (described below). In addition to the default pruned (75,302)p grid, two further grids were considered, (a) a pruned (99,590)p grid and (b) a spherical product grid (96,32,64), defined as having 96 radial shells per atom and 32 θ points and 2×32 φ points in each shell. As a result of this preliminary investigation (details of which are reported below), all BMK results in the main body of the paper are reported using the (ultrafine) pruned (99,590)p grid, while the pruned (75,302)p grid is employed with all other functionals.

An extensive range of methods has been considered in this study, which we can categorize in broad terms as follows. The first group is comprised of the wave function methods. We have built on our previous study[2] by examining the archetypal HF, MP2, and QCISD methods with a wider range of basis sets. In addition, we have extended the previous study by including the higher-level methods, CCSD, CCSD(T), and QCSID(T).

The second category that we have considered consists of the pure DFT procedures (containing no HF exact exchange). As in our previous study, we have examined both B-LYP[23−25] and B-P86.[23,26] In addition, we have considered G96-LYP,[24,25,27,28] O-LYP,[24,25,29] PBE,[30,31] EDF1,[32] the Handy functional family of HCTH93, HCTH147, and HCTH407,[33−35] the τ-dependent TPSS,[36] B-B95[23,37] and VSXC[38] functionals, and finally the stand-alone exchange functionals HFB[23] and HFS.[39−41]

The third and final category that we have considered is comprised of hybrid DFT procedures (including HF exact exchange). We have extended our previous examination of the well-known B3-LYP,[23,24,25,42] B3-P86,[23,26] and B3-PW91[23,43−47] functionals, while also considering the non-τ-dependent hybrid functionals EDF2,[48] mPW1PW91,[49] B1-LYP,[37,50] MPW1K,[51] B98,[23,52] B971,[33] B972,[53] PBE0,[30] BHandH,[19,54] BHandH-LYP,[19,54] and O3-LYP[55] as well as the τ-dependent hybrid functionals B1-B95,[37] M05,[56] M05-2X,[57] MPWB1K,[9] BMK,[58] and BB1K.[8]

We have chosen for the most part to combine these categories of methods with the Pople basis sets, 6-31G(d), 6-31+G(d,p), 6-31G(2df,p), 6-311+G(d,p), and 6-311+G(2df,p).[1,59,60] In a limited number of cases, we further examined basis set effects using additional basis sets: 6-31+G(d), 6-31G(d,p), 6-311G(d), 6-311+G(d), 6-311G(d,p), 6-311+G(2d,p), 6-311+G(3d,p), 6-311+G(3df,p), 6-311+G(3df,2p), 6-311+G(3df,3pd), 6-311++G(3df,3pd), cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ, aug-cc-pVTZ, aug-cc-pVQZ, and TZV2P.[1,59]

For the purpose of deriving our scale factors,[2,3] we define two primary sets of molecules for our analysis (listed in Tables S1 and S2 of the Supporting Information). The first, designated F1, is a set of 122 molecules with a total of 1066 vibrational frequencies (after counting degenerate modes) that we used previously,[2] and that are derived from the compilations listed by Schaefer and co-workers[15] and Shimanouchi.[61,62] The molecules in the F1 set were used in the calculations of scale factors suitable for scaling fundamentals. They contain no more than four heavy atoms of the first and second row and have no more than 10 atoms in total.

As in our previous paper,[2] the F1′ set was defined as a subset of F1 in which the four torsional modes relating to facile methyl rotations in CH_3COOH, CH_3COCH_3, and CH_3CCCH_3 were excluded, as the rms_{ov} error for the low-frequency vibrations were otherwise heavily dominated by these modes. The remaining frequencies (1062), comprising the F1′ set, were used to determine the scale factors and rms_{ov} values for the low-frequency vibrations and the thermal contributions to enthalpy and entropy. During the course of the present study, it was noted that certain molecules often gave excessively large errors with correlated wave function methods, especially for the low-frequency vibrations. Accordingly, a second subset of F1 was defined in which we excluded the molecules NO_2, O_3, ClCCCl, ClCCH, and HCCCCH (33 frequencies), which removes the worst offenders. The subset consisting of the remaining frequencies (1033) is referred to as F1″. Finally, it also became apparent that a third subset of F1 (and of F1″), namely F1‴, in which we remove three more molecules SiH_3CCH, CH_3COCH_3, and CH_3CCCH_3 (96 frequencies), was needed to obtain usable scale factors for MP2 with a number of basis sets.[63]

The second molecule set, designated Z1 (39 molecules and 89 frequencies), is comprised of the diatomic molecules from the G2 set[64] plus the compilation from Schaefer and co-workers.[15] The Z1 set was used to study zero-point vibrational energies, with the experimental ZPVE values for the molecules in the Z1 set calculated according to the standard formula (cf. eq 10 below).[65,66] The requisite experimental harmonic frequencies (ω_e) and anharmonic constants ($\omega_e x_e$) for the Z1 molecules were obtained from the compilation of Huber and Herzberg[67] and reports from Allen et al.,[68] Clabo et al.,[69] Martin et al.,[70] and Duncan and Law.[71] We have also examined the effect on B3-LYP scale factors of expanding the Z1 set to a set designated Z2 by adding nine additional ZPVEs reported in Martin's W4 study (making a total of 48 molecules and 125 frequencies).[72,73]

To determine our scale factors, we have followed the procedure used previously[2,3] that minimizes the residual separating experimental and theoretically predicted vibrational frequencies or thermodynamic quantities. The optimum scale factors for vibrational frequencies were determined by a least-squares procedure, minimizing the residual

$$\Delta = \sum_{i}^{\text{all}} (\lambda \omega_i^{\text{theor}} - \tilde{\nu}_i^{\text{expt}})^2 \tag{1}$$

where ω_i^{theor} and $\tilde{\nu}_i^{\text{expt}}$ are the ith theoretical harmonic frequency and ith experimental fundamental frequency (in cm^{-1}), respectively, which leads to

$$\lambda = \sum_{i}^{\text{all}} \omega_i^{\text{theor}} \tilde{\nu}_i^{\text{expt}} / \sum_{i}^{\text{all}} (\omega_i^{\text{theor}})^2 \tag{2}$$

TABLE 3: Scale Factors and $\mathrm{rms}_{\mathrm{ov}}$ Values Derived from a Least-Squares Fit of Theoretical Harmonic Frequencies to Observed Fundamentals for Various Geometry Convergence Criteria[a]

	default[b]		tight[c]		very tight[d]	
method	scale factor[e]	$\mathrm{rms}_{\mathrm{ov}}$[f]	scale factor[e]	$\mathrm{rms}_{\mathrm{ov}}$[f]	scale factor[e]	$\mathrm{rms}_{\mathrm{ov}}$[f]
HF/6-31G(d)	0.8953	50	0.8953	50	0.8953	50
HF/6-311+G(d,p)	0.9059	53	0.9059	53	0.9059	53
MP2/6-31G(d)	0.9434[g]	63[g]	0.9434[g]	64[g]	0.9432[h,i]	63[h,i]
MP2/6-311+G(d,p)	0.9513[g]	63[g]	0.9512[g]	63[g]	0.9510[h,j]	64[h,j]
B3-LYP/6-31G(d)	0.9613	33	0.9613	33	0.9613	34
B3-LYP/6-311+G(d,p)	0.9689	35	0.9688	35	0.9688	35
BMK/6-31G(d)	0.9475	39	0.9476	39	0.9474[k]	39[k]
BMK/6-311+G(d,p)	0.9566[l]	38[l]	0.9562[m]	38[m]	0.9562[n]	38[n]
MPWB1K/6-31G(d)	0.9297	37	0.9297	37	0.9297	37

[a] Using the F1 set of 1066 frequencies unless otherwise noted. The DFT calculations were carried out with an (ultrafine) pruned (99,590)p grid throughout. [b] Geometry convergence thresholds: maximum force, 4.5×10^{-4} au; rms force, 3.0×10^{-4} au; maximum displacement, 1.8×10^{-3} au; rms displacement, 1.2×10^{-3} au. [c] Geometry convergence thresholds: maximum force, 1.5×10^{-5} au; rms force, 1.0×10^{-5} au; maximum displacement, 6.0×10^{-5} au; rms displacement, 4.0×10^{-5} au. [d] Geometry convergence thresholds: maximum force, 2.0×10^{-6} au; rms force, 1.0×10^{-6} au; maximum displacement, 6.0×10^{-6} au; rms displacement, 4.0×10^{-6} au. [e] As defined by eq 2. [f] Overall root-mean-square error, as defined by eq 5, in units of cm^{-1}. [g] Values obtained with the first vibrational mode of ClCCCl removed; see text. [h] Values obtained with the first vibrational modes of ClCCCl and HCCCCH removed from the analysis; see text. [i] Values obtained with NCl_2F, $COCl_2$, and HCN removed from the analysis; see text. [j] Values obtained with ClF_3, ClNO, $SOCl_2$, H_2S, O=CHCH=O, CH_3CN, and CH_3NC removed from the analysis; see text. [k] Values obtained with NSF and H_2S_2 removed from the analysis; see text. [l] Values obtained with PH removed from the analysis; see text. [m] Values obtained with CH_2=C=CHCl, PH, H_2S_2, and $HCCCH_2Cl$ removed from the analysis; see text. [n] Values obtained with H_2S_2, PH, HNCO, CH_2CHCHO, $HCCCH_2Cl$, $HCCCH_2F$, and ClHC=C=CH_2 removed from the analysis; see text.

TABLE 4: Scale Factors and $\mathrm{rms}_{\mathrm{ov}}$ Values Derived from a Least-Squares Fit of Theoretical Harmonic Frequencies to Observed Fundamentals for Various Grids[a]

	B3-LYP/6-31G(d)		B3-LYP/6-311+G(d,p)		BMK/6-31G(d)		BMK/6-311+G(d,p)		MPWB1K/6-31G(d)	
grid	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]
(75,302)p[d]	0.9613	34	0.9688	35	0.9435	47	0.9527	47	0.9295	37
(99,590)p[e]	0.9613	33	0.9689	35	0.9475	39	0.9566	38	0.9297	37
(96,32,64)[f]	0.9613	33	0.9689	35	0.9484	39	0.9573	39	0.9296	37

	PBE/6-31G(d)		B972/6-31G(d)		BHandH/6-31G(d)		BLYP/6-31G(d)		HCTH407/6-31G(d)	
grid	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]
(75,302)p[d]	0.9875	40	0.9512	33	0.9270	45	0.9940	45	0.9698	41
(99,590)p[e]	0.9876	40	0.9512	33	0.9270	45	0.9941	45	0.9699	41

[a] Using the F1 set of 1066 frequencies. [b] As defined by eq 2. [c] Overall root-mean-square error, as defined by eq 5, in units of cm^{-1}. [d] Pruned grid with 75 radial shells per atom and 302 angular points per shell. [e] Pruned grid with 99 radial shells per atom and 590 angular points per shell. [f] Spherical product grid with 96 radial shells per atom and 32 θ points and 2×32 φ points per shell.

TABLE 5: Variation in Modified B3-LYP/6-31G(d) Scale Factors and $\mathrm{rms}_{\mathrm{ov}}$ Values as a Function of the Percentage of Exact Exchange

	ω[a]		$1/\omega$[b]	
percent exact exchange	scale factor[c]	$\mathrm{rms}_{\mathrm{ov}}$[d]	scale factor[e]	$\mathrm{rms}_{\mathrm{ov}}$[f]
0	0.9919	41	1.0452	17
10	0.9762	36	1.0204	15
20	0.9613	34	1.0007	13
30	0.9472	32	0.9828	13
40	0.9340	32	0.9674	13
50	0.9213	33	0.9539	13
60	0.9093	35	0.9410	13
70	0.8979	38	0.9287	14
80	0.8868	41	0.9196	15
90	0.8760	44	0.9129	16
100	0.8656	47	0.9093	18

[a] Using the F1 set of 1066 frequencies. [b] Using the F1′ set of 1062 frequencies. [c] As defined by eq 2. [d] Overall root-mean-square error, as defined by eq 5, in units of cm^{-1}. [e] As defined by eq 7. [f] Overall root-mean-square error in units of 10^{-5} cm.

The optimized scale factor λ was then used to calculate a minimized residual, $\Delta_{\min}$

$$\Delta_{\min} = (\lambda \omega_i^{\mathrm{theor}} - \tilde{\nu}_i^{\mathrm{expt}})^2 \qquad (3)$$

a molecular root-mean-square error, $\mathrm{rms}_{\mathrm{mol}}$

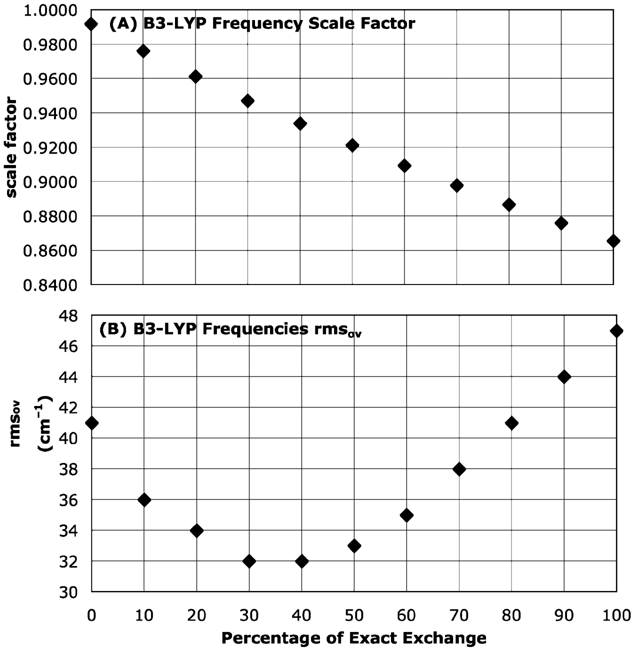

Figure 1. Plots showing the relationship between (A) frequency scale factors and (B) $\mathrm{rms}_{\mathrm{ov}}$ values and the proportion of exact exchange for modifications of the B3-LYP functional using the 6-31G(d) basis set.

$$\mathrm{rms}_{\mathrm{mol}} = \left(\sum_{1}^{n_{\mathrm{mol}}} \Delta_{\min}/n_{\mathrm{mol}}\right)^{1/2} \tag{4}$$

and an overall root-mean-square error, $\mathrm{rms}_{\mathrm{ov}}$

$$\mathrm{rms}_{\mathrm{ov}} = \left(\sum_{1}^{n_{\mathrm{all}}} \Delta_{\min}/n_{\mathrm{all}}\right)^{1/2} \tag{5}$$

where n_{mol} is the number of modes in a particular molecule and n_{all} is the total number of modes for all of the molecules considered.

To minimize the errors in frequencies at the low end of the frequency range, we have calculated an inverse frequency scale factor, which minimizes the residual

$$\Delta = \sum_{i}^{\mathrm{all}} \left(\frac{1}{\lambda\omega_i^{\mathrm{theor}}} - \frac{1}{\tilde{\nu}_i^{\mathrm{expt}}}\right)^2 \tag{6}$$

giving

$$\lambda = \sum_{i}^{\mathrm{all}} \left(\frac{1}{\omega_i^{\mathrm{theor}}}\right)^2 \Big/ \sum_{i}^{\mathrm{all}} \frac{1}{\omega_i^{\mathrm{theor}}\tilde{\nu}_i^{\mathrm{expt}}} \tag{7}$$

with the $\mathrm{rms}_{\mathrm{mol}}$ and $\mathrm{rms}_{\mathrm{ov}}$ values obtained from equations analogous to eqs 4 and 5.

ZPVE scale factors were developed by minimizing the residual

$$\Delta = \sum_{i}^{\mathrm{all}} (\lambda \mathrm{ZPVE}_i^{\mathrm{theor}} - \mathrm{ZPVE}_i^{\mathrm{expt}})^2 \tag{8}$$

for each of the molecules contained in the Z1 set. That is, we evaluated $\mathrm{ZPVE}^{\mathrm{theor}}$ using theoretical harmonic frequencies for each molecule via

$$\mathrm{ZPVE}/Nhc = {}^{1}/_{2} \sum_{i} \omega_i \tag{9}$$

and compare with $\mathrm{ZPVE}^{\mathrm{expt}}$ values obtained using experimental harmonic frequencies and their associated anharmonic corrections via (for diatomics)

$$\mathrm{ZPVE}/Nhc = G(0) = {}^{1}/_{2}\, \omega_{\mathrm{e}} - {}^{1}/_{4}\, \omega_{\mathrm{e}}x_{\mathrm{e}} \tag{10}$$

with an extension of eq 10 in the case of polyatomic molecules.[65] Again, the $\mathrm{rms}_{\mathrm{mol}}$ and $\mathrm{rms}_{\mathrm{ov}}$ values were obtained from equations analogous to eqs 4 and 5.

Knowledge of vibrational frequencies also plays a vital role in determining the thermal contributions to enthalpy ($\Delta H_{\mathrm{vib}}(T)$) and entropy ($S_{\mathrm{vib}}(T)$), which can be expressed as

$$\Delta H_{\mathrm{vib}}(T) = Nhc \sum_{i} \frac{\tilde{\nu}_i}{\mathrm{e}^{\mu_i} - 1} \tag{11}$$

$$S_{\mathrm{vib}}(T) = R \sum_{i} \left[\frac{\mu_i}{\mathrm{e}^{\mu_i} - 1} - \ln(1 - \mathrm{e}^{-\mu_i})\right] \tag{12}$$

where N is Avogadro's number and $\mu_i = hc\tilde{\nu}_i/kT$. We computed new frequency scale factors λ that will minimize the residuals

$$\Delta = \sum_{i}^{\mathrm{all}} [\Delta H_{\mathrm{vib}}^{\mathrm{theor}}(T)_i - \Delta H_{\mathrm{vib}}^{\mathrm{expt}}(T)_i]^2 \tag{13}$$

$$\Delta = \sum_{i}^{\mathrm{all}} [S_{\mathrm{vib}}^{\mathrm{theor}}(T)_i - S_{\mathrm{vib}}^{\mathrm{expt}}(T)_i]^2 \tag{14}$$

where (with energy conversion constants dropped for simplicity)

$$\Delta H_{\mathrm{vib}}^{\mathrm{theor}}(T)_i = \lambda\omega_i^{\mathrm{theor}}/(\mathrm{e}^{\mu_i^{\mathrm{theor}}} - 1) \tag{15}$$

$$S_{\mathrm{vib}}^{\mathrm{theor}}(T)_i = [\mu_i^{\mathrm{theor}}/(\mathrm{e}^{\mu_i^{\mathrm{theor}}} - 1)] - \ln(1 - \mathrm{e}^{-\mu_i^{\mathrm{theor}}}) \tag{16}$$

and $\mu_i^{\mathrm{theor}} = h\lambda\omega_i^{\mathrm{theor}}/kT$. Again, $\mathrm{rms}_{\mathrm{mol}}$ and $\mathrm{rms}_{\mathrm{ov}}$ values were obtained from equations analogous to eqs 4 and 5.

3. Results and Discussion

Only summary tables giving scale factors and overall root-mean-square errors ($\mathrm{rms}_{\mathrm{ov}}$) are presented within this article. However, a listing of molecules with the largest *molecular* root-mean-square errors ($\mathrm{rms}_{\mathrm{mol}}$) for individual methods is available in the Supporting Information (Tables S3−S7).[74,75] For the sake of completeness, the scale factors evaluated in our previous work[2,3] are included in Table 1.

3.1. Fundamental Frequencies. Harmonic vibrational frequency scale factors and their associated $\mathrm{rms}_{\mathrm{ov}}$ values, obtained for the F1 set of molecules, are presented in Table 2. These are discussed, together with the effect of geometry, integration grid density, extent of incorporation of exact exchange, and basis set, in the following sections.

3.1.1. Effect on Frequency Scale Factors and rms_{ov} Values of Geometry Convergence Criteria. The HF/6-31G(d), HF/6-311+G(d,p), MP2/6-31G(d), MP2/6-311+G(d,p), B3-LYP/6-31G(d), B3-LYP/6-311+G(d,p), BMK/6-31G(d), BMK/6-311+G(d,p), and MPWB1K/6-31G(d) levels of theory were used as a representative sample to examine the effect of the level of geometry convergence on calculated vibrational frequencies and subsequent scale factors (Table 3). The so-called "tight" and "very tight" geometry convergence criteria were compared with the default geometry convergence in Gaussian 03. Higher levels of self-consistent field (SCF) convergence criteria were employed in conjunction with the tight and very tight geometry optimization procedures as well as an ultrafine grid for all DFT calculations. As a result, some SCF convergence failures occurred, and molecules for which this was the case were removed from the F1 test set, as noted in Table 3. We observe that there is only minimal variation in both the optimum scale factors and the associated $\mathrm{rms}_{\mathrm{ov}}$ values when the geometry convergence criteria are tightened. We conclude that in general the default geometry convergence is suitable for our calculations.

3.1.2. Effect on Frequency Scale Factors and rms_{ov} Values of Integration Grid Density. The effect of integral quadrature granularity on the B3-LYP, BMK, MPWB1K, PBE, B972, BHandH, BLYP, and HCTH407 frequency scale factors and their $\mathrm{rms}_{\mathrm{ov}}$ values was evaluated in conjunction with the F1 set of molecules and the following three integration grids: pruned (75,302)p (default in Gaussian 03), pruned (99,590)p, and the spherical product grid (96,32,64). The results, which are summarized in Table 4, demonstrate that, with the exception of BMK, there is minimal variation in the scale factors and $\mathrm{rms}_{\mathrm{ov}}$ values associated with changes in grid density. BMK clearly does not perform optimally with respect to the default Gaussian 03 grid settings and benefits significantly with respect to

TABLE 6: Effect of Basis Set on Fundamental Vibrational Frequency Scale Factors and Corresponding rms_{ov} Values[a]

	B3-LYP		BMK		MP2[b,c]				HF	
basis set	scale factor[d]	rms_{ov}[e]	scale factor[d]	rms_{ov}[e]	scale factor[d]		rms_{ov}[e]		scale factor[d]	rms_{ov}[e]
6-31G(d)	0.9613	34	0.9475	39	0.9441	(0.9442)	47	(47)	0.8953	50
6-31+G(d)	0.9636	35	0.9495	38	0.9486	(0.9487)	52	(52)	0.8970	48
6-31G(d,p)	0.9627	33	0.9514	42	0.9377	(0.9377)	47	(47)	0.8992	53
6-31+G(d,p)	0.9648	35	0.9533	41	0.9418	(0.9418)	52	(52)	0.9007	51
6-31G(2df,p)	0.9652	32	0.9520	41	0.9462	(0.9460)	41	(42)	0.9035	55
6-311G(d)	0.9672	34	0.9531	38	0.9509	(0.9508)	44	(43)	0.9013	52
6-311+G(d)	0.9680	34	0.9539	37	0.9534	(0.9533)	48	(47)	0.9023	52
6-311G(d,p)	0.9682	33	0.9560	39	0.9504	(0.9503)	43	(43)	0.9051	54
6-311+G(d,p)	0.9688	35	0.9566	38	0.9523	(0.9522)	46	(46)	0.9059	53
6-311+G(2d,p)	0.9692	33	0.9554	35	0.9566	(0.9567)	44	(45)	0.9073	51
6-311+G(3d,p)	0.9689	32	0.9541	36	0.9573	(0.9573)	44	(45)	0.9070	52
6-311+G(2df,p)	0.9686	31	0.9551	36	0.9569	(0.9567)	40	(40)	0.9073	54
6-311+G(3df,p)	0.9683	31	0.9540	37	0.9575	(0.9574)	41	(42)	0.9066	54
6-311+G(3df,2p)	0.9682	31	0.9539	37	0.9570	(0.9569)	41	(42)	0.9068	55
6-311+G(3df,3pd)	0.9672	31	0.9540	37	0.9582	(0.9579)	42	(42)	0.9070	55
6-311++G(3df,3pd)	0.9673	31	0.9541	37	0.9583	(0.9581)	42	(42)	0.9070	55
cc-pVDZ	0.9717	38	0.9588	44	0.9538	(0.9538)	45	(46)	0.9052	50
cc-pVTZ	0.9682	31	0.9572	38	0.9561	(0.9559)	41	(41)	0.9072	54
cc-pVQZ	0.9684	30	0.9537	35	*f*	*f*	*f*	*f*	0.9072	54
aug-cc-pVDZ	0.9713[g]	41[g]	0.9588[g]	46[g]	0.9615	(0.9614)	53	(53)	0.9082	50
aug-cc-pVTZ	0.9687	32	0.9577	37	0.9598	(0.9599)	44	(45)	0.9076	53
aug-cc-pVQZ	0.9685	30	0.9537	35	*f*	*f*	*f*	*f*	0.9073	53
TZV2P	0.9669	32	0.9532	35	0.9528	(0.9527)	46	(47)	0.9058	50

[a] Using the F1 set of 1066 frequencies unless otherwise noted. [b] Using the F1″ set of 1033 frequencies unless otherwise noted. [c] Values in parentheses found using the F1‴ set of 970 frequencies. [d] As defined by eq 2. [e] Overall root-mean-square error, as defined by eq 5, in units of cm^{-1}. [f] Scale factors and rms_{ov} values not determined at these levels of theory. [g] HCCCCH has a bent structure at these levels of theory and is therefore removed from the analysis.

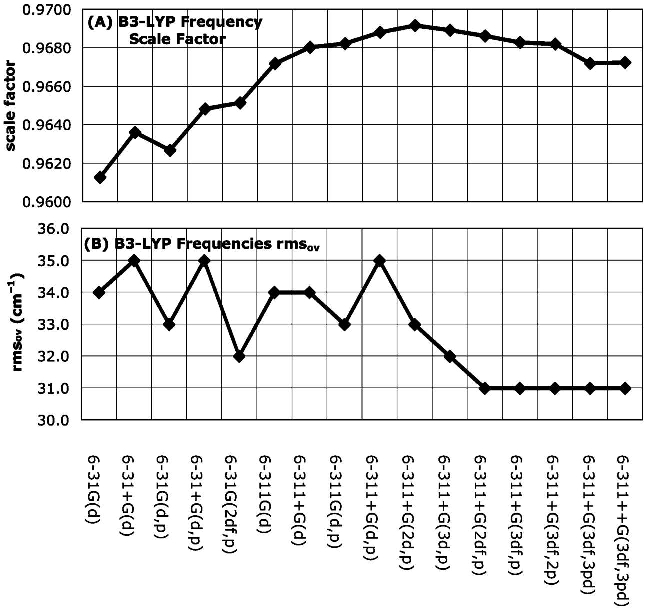

Figure 2. Plots showing the relationship between (A) frequency scale factors and (B) rms_{ov} values and basis set for fundamental frequencies calculated with B3-LYP.

precision from increased grid density. As a consequence, we have used the (99,590)p grid for BMK calculations in the remainder of this paper. However, for all of the other DFT methods in Table 4, we conclude that the default (75,302)p grid of Gaussian 03 gives an appropriate combination of accuracy and computational efficiency.

3.1.3. Comparisons With Results of Previous Studies. Scale factors for a number of the levels of theory contained in Table 2 have been previously reported in the literature. For those methods examined in our previous study,[2] we find that the different implementation of DFT procedures in Gaussian 03 compared with earlier versions does not lead to significant differences in the DFT scale factors. The truncation of the test sets used for MP2 and QCISD leads to slightly larger differences. This may be attributed to the worst-performing molecules being removed from the F1 test set for the correlated methods, resulting in a less skewed scale factor. Wong[4] used the F1 set to develop scale factors for MP2, B3-LYP, B3-P86, and B-LYP that all compare favorably with our values. Andersson and Uvdal[16] used a set of 125 molecules to derive a B3-LYP/6-311+G(d,p) scale factor of 0.9679, which is close to our value of 0.9688. Tantirungrotechai et al.[18] have recently obtained scale factors for HCTH407, B972, B98, O-LYP, O3-LYP, PBE0, and VSXC with the 6-31G(d) basis set using the F1 test set. Their reported scale factors are close to our values, although there are small differences in the rms_{ov} values for which we cannot account.

3.1.4. Problem Molecules. Molecules that give the poorest vibrational frequencies with the various theoretical procedures are listed in the Supporting Information (Table S3). We can see that virtually all of the theoretical procedures examined struggle to accurately predict the vibrational frequencies of singlet CH_2[76] with large rms_{mol} values that range in magnitude from 116 cm^{-1} (MP2/6-311+G(2df,p)) to 242 cm^{-1} (B-B95/6-31G(d)). In addition, large rms_{mol} values are consistently found for O_3,[76] while the density functional procedures do not perform well for H_2. Furthermore, the 6-31G(d) description of fluorine-containing molecules appears deficient because, regardless of the method used, consistently large rms_{mol} errors are generally found for HF and, to a lesser extent, F_2. Finally, the SCF failed to converge for Cl_2CS with EDF1/6-311+G(d,p), and this molecule has therefore been removed from the scale factor and rms error calculations for the fundamentals, low-frequency vibrations, and enthalpy and entropy for this level of theory.

3.1.5. Comparison of Methods. A careful analysis of the data in Table 2 reveals a number of significant points regarding the scale factors that we have derived for calculating fundamental

TABLE 7: Frequency Scale Factors Suitable for Low-Frequency Vibrations and Corresponding $\mathrm{rms}_{\mathrm{ov}}$ Values Derived from a Least-Squares Fit of Inverse Frequencies[a]

	6-31G(d)		6-31+G(d,p)		6-31G(2df,p)		6-311+G(d,p)		6-311+G(2df,p)	
method	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]	scale factor[b]	$\mathrm{rms}_{\mathrm{ov}}$[c]
HF	0.9062	15	0.9146	15	0.9048	15	0.9146	15	0.9075	15
MP2	1.0139[d]	21[d]	1.0333[d]	21[d]	0.9833[d]	14[d]	1.0157[d]	19[d]	0.9917[d]	13[d]
QCISD	1.0014[d]	17[d]	1.0203[d]	17[d]	*e*	*e*	1.0086[d]	17[d]	*e*	*e*
QCISD(T)	1.0375[d]	21[d]	1.0591[d]	22[d]	*e*	*e*	1.0429[d]	20[d]	*e*	*e*
CCSD	0.9971[d]	17[d]	1.0153[d]	17[d]	*e*	*e*	1.0034[d]	16[d]	*e*	*e*
CCSD(T)	1.0347[d]	21[d]	1.0567[d]	22[d]	*e*	*e*	1.0399[d]	20[d]	*e*	*e*
B-B95	1.0489	18	1.0617	18	1.0428	13	*e*	*e*	*e*	*e*
B-LYP	1.0627	18	1.0738	18	1.0540	16	1.0915	19	1.0615	14
B-P86	1.0497	17	1.0608	17	1.0480	15	1.0848	19	1.0498	13
G96-LYP	1.0605	18	1.0670	17	1.0552	17	1.0859	19	1.0574	13
HCTH147	1.0304	16	1.0421	16	1.0248	13	1.0531	17	1.0300	12
HCTH407	1.0239	15	1.0374	15	1.0205	13	1.0457	17	1.0275	13
HCTH93	1.0301	15	1.0424	16	1.0253	13	1.0519	17	1.0308	13
O-LYP	1.0355	16	1.0500	16	1.0302	13	1.0609	18	1.0378	13
PBE	1.0411	16	1.0539	16	1.0373	14	1.0714	18	1.0437	12
TPSS	1.0352	16	1.0459	16	1.0315	13	1.0568	17	1.0345	13
VSXC	1.0273	19	1.0353	18	1.0109	18	1.0380	21	1.0100	18
B1-B95	0.9804	14	0.9897	14	0.9838	13	*e*	*e*	*e*	*e*
B1-LYP	0.9930	13	1.0028	13	0.9915	13	1.0101	12	0.9971	12
B3-LYP	1.0007	13	1.0117	13	0.9998	13	1.0189	13	1.0053	12
B3-P86	0.9921	13	1.0012	12	0.9929	13	1.0081	12	0.9962	12
B3-PW91	0.9937	13	1.0032	12	0.9949	13	1.0086	12	0.9984	12
B971	0.9991	13	1.0083	13	0.9983	12	1.0162	13	1.0034	12
B972	0.9879	12	0.9976	12	0.9879	12	1.0027	12	0.9920	12
B98	0.9977	13	1.0069	13	0.9973	12	1.0132	13	1.0016	12
BB1K	0.9570	14	0.9654	14	*e*	*e*	*e*	*e*	*e*	*e*
BHandH	0.9370	13	0.9474	13	0.9389	14	0.9495	12	0.9426	13
BHandH-LYP	0.9484	13	0.9581	13	0.9482	13	0.9608	12	0.9528	13
BMK	0.9776	14	0.9844	13	0.9771	13	0.9879	12	0.9800	11
EDF1	1.0397	16	1.0522	16	*e*	*e*	1.0646[f]	17[f]	*e*	*e*
EDF2	0.9958	13	1.0067	13	*e*	*e*	1.0197	15	*e*	*e*
M05	0.9691	13	0.9786	13	0.9603	14	0.9757	13	0.9566	14
M05-2X	0.9364	18	0.9386	20	0.9194	20	0.9336	20	0.9168	22
MPW1K	0.9525	12	0.9621	12	0.9543	13	0.9648	12	0.9584	13
mPW1PW91	0.9828	12	0.9932	12	0.9848	13	0.9984	12	0.9888	12
MPWB1K	0.9536	14	0.9627	14	0.9610	14	*e*	*e*	*e*	*e*
O3-LYP	1.0042	13	1.0156	13	1.0043	12	1.0230	14	1.0099	12
PBE0	0.9821	12	0.9916	12	0.9834	12	0.9964	12	0.9873	12

[a] Using the F1′ set of 1062 frequencies unless otherwise noted. [b] As defined by eq 7. [c] Overall root-mean-square error in units of 10^{-5} cm. [d] Values obtained with the F″ set; see text. [e] Scale factors and $\mathrm{rms}_{\mathrm{ov}}$ values not determined at these levels of theory. [f] Values obtained with Cl_2CS removed from the analysis due to SCF convergence problems.

vibrations. Considering first the wave function procedures, we see that HF and MP2 lead to some of the highest $\mathrm{rms}_{\mathrm{ov}}$ values of any of the levels of theory included. In general, MP2, with the smaller F1″ set, performs better than HF, partly because molecules such as NO_2 and O_3 with particularly large $\mathrm{rms}_{\mathrm{mol}}$ values are excluded in the F1″ set. The largest $\mathrm{rms}_{\mathrm{ov}}$ error in Table 2 is found for HF/6-31G(2df,p) (55 cm^{-1}), which is followed closely by HF/6-311+G(2df,p) (54 cm^{-1}), HF/6-311+G(d,p) (53 cm^{-1}), and MP2/6-31+G(d,p) (52 cm^{-1}). QCISD and CCSD show considerable improvement in the $\mathrm{rms}_{\mathrm{ov}}$ values when compared with HF and MP2, though at significantly higher computational cost. CCSD/6-311+G(d,p) gives the lowest $\mathrm{rms}_{\mathrm{ov}}$ value (32 cm^{-1}) of any of the wave function methods in Table 2 and is closely followed by the related QCISD/6-311+G(d,p) (33 cm^{-1}). Note that both QCISD(T) and CCSD(T) have larger $\mathrm{rms}_{\mathrm{ov}}$ values than the respective values for QCISD and CCSD. The cause of this counterintuitive disparity between methods with and without perturbative triples correction is unclear and is presently under investigation.

The pure DFT functionals generally perform better than HF and MP2, giving $\mathrm{rms}_{\mathrm{ov}}$ values similar in magnitude to QCISD(T) or CCSD(T) at a significantly lower computational cost. As might be expected, we find that similar functionals generally give similar results. For example, this can be clearly seen for Handy's family of HCTH functionals.

Turning our attention to the hybrid DFT procedures, we see that the lowest $\mathrm{rms}_{\mathrm{ov}}$ values in Table 2 (30−32 cm^{-1})[77] are found for B1-LYP and B3-LYP with 6-31G(2df,p) and 6-311+G(2df,p), B971/6-311+G(2df,p), and B98/6-311+G(2df,p). As a general rule, the hybrid DFT procedures perform better than either the pure DFT procedures or the majority of wave function methods. For example, the hybrid PBE0 functional consistently gives lower $\mathrm{rms}_{\mathrm{ov}}$ values than the pure PBE functional. Similarly, the $\mathrm{rms}_{\mathrm{ov}}$ values for B3-LYP and O3-LYP show a systematic improvement compared with their respective B-LYP and O-LYP counterparts. Of course, not all of the vibrational frequencies for individual molecules are improved by employing hybrid DFT procedures. For instance, O3-LYP gives significantly larger $\mathrm{rms}_{\mathrm{mol}}$ values for O_3 than O-LYP. As found for the pure DFT methods, related hybrid DFT procedures give similar $\mathrm{rms}_{\mathrm{ov}}$ values. For example, B98, B971, and B972, all of which are refinements of B97, give almost identical results. Similarly, the B3-containing functionals (that differ only through the choice of the correlation component) give comparable results to one another. A pair of functionals related in a different way is BHandH and BHandH-LYP, and we see that some of the failings of BHandH are decreased with BHandH-LYP. For

TABLE 8: Effect of Basis Set on Low-Frequency Vibrational Frequency Scale Factors and Corresponding rms_{ov} Values[a]

	B3-LYP		BMK		MP2[b,c]				HF	
basis set	scale factor[d]	rms_{ov}[e]	scale factor[d]	rms_{ov}[e]	scale factor[d]		rms_{ov}[e]		scale factor[d]	rms_{ov}[e]
6-31G(d)	1.0007	13	0.9776	14	1.0139	(0.9974)	21	(18)	0.9062	15
6-31+G(d)	1.0078	13	0.9819	13	1.1396	(1.0322)	47	(22)	0.9131	15
6-31G(d,p)	1.0028	13	0.9803	14	1.0007	(0.9922)	17	(15)	0.9090	15
6-31+G(d,p)	1.0117	13	0.9844	13	1.0333	(1.0192)	21	(17)	0.9146	15
6-31G(2df,p)	0.9998	13	0.9771	13	0.9833	(0.9808)	14	(14)	0.9048	15
6-311G(d)	1.0109	13	0.9829	13	1.0124	(0.9919)	22	(18)	0.9105	15
6-311+G(d)	1.0184	13	0.9868	13	1.0766	(1.0204)	35	(22)	0.9137	15
6-311G(d,p)	1.0119	14	0.9848	13	0.9918	(0.9841)	16	(15)	0.9110	15
6-311+G(d,p)	1.0189	13	0.9879	12	1.0157	(1.0031)	19	(17)	0.9146	15
6-311+G(2d,p)	1.0157	12	0.9859	11	1.0065	(1.0054)	13	(13)	0.9150	14
6-311+G(3d,p)	1.0106	12	0.9812	12	1.0060	(1.0036)	14	(14)	0.9115	15
6-311+G(2df,p)	1.0053	12	0.9800	11	0.9917	(0.9907)	13	(13)	0.9075	15
6-311+G(3df,p)	1.0050	12	0.9780	12	0.9951	(0.9935)	13	(13)	0.9073	15
6-311+G(3df,2p)	1.0033	12	0.9771	12	0.9948	(0.9931)	13	(13)	0.9063	15
6-311+G(3df,3pd)	1.0016	12	0.9768	12	0.9976	(0.9957)	14	(14)	0.9052	15
6-311++G(3df,3pd)	1.0019	12	0.9770	12	0.9981	(0.9964)	14	(14)	0.9050	15
cc-PVDZ	1.0107	14	0.9878	13	0.9970	(0.9948)	15	(15)	0.9162	15
cc-PVTZ	1.0066	12	0.9861	12	0.9956	(0.9939)	12	(12)	0.9100	15
cc-PVQZ	1.0062	11	0.9830	12	*f*	*f*	*f*	*f*	0.9088	14
aug-cc-PVDZ	1.0364[g]	14[g]	1.0191[g]	17[g]	1.0418	(1.0338)	19	(17)	0.9293	15
aug-cc-PVTZ	1.0114	12	0.9872	13	1.0120	(1.0103)	13	(13)	0.9123	15
aug-cc-PVQZ	1.0085	11	0.9851	11	*f*	*f*	*f*	*f*	0.9096	14
TZV2P	1.0144	11	0.9876	11	1.0141	(1.0119)	14	(14)	0.9151	14

[a] Using the F1′ set of 1062 frequencies unless otherwise noted. [b] Using the F1″ set of 1033 frequencies unless otherwise noted. [c] Values in parentheses found using the F1‴ set of 970 frequencies. [d] As defined by eq 7. [e] Overall root-mean-square error in units of 10^{-5} cm. [f] Scale factors and rms_{ov} values not determined at these levels of theory. [g] HCCCCH has a bent structure at these levels of theory and is therefore removed from the analysis.

instance, the BHandH-LYP rms_{mol} values for F_2O (92−118 cm^{-1}), HOF (76−103 cm^{-1}), N_2 (66−84 cm^{-1}), and NO_2 (61−70 cm^{-1}) are consistently smaller than the respective BHandH results (with rms_{mol} values of 139−167, 109−134, 94−115, and 120−129 cm^{-1}, respectively).

A final interesting observation that may be made from an inspection of Table 2 is that there appears to be a connection between the magnitude of the DFT scale factors and the extent of incorporation of exact Hartree−Fock exchange. This is exemplified by comparing the scale factors for HF/6-31G(d) (0.8953), containing 100% exact exchange, BHandH/6-31G(d) (0.9270), containing 50% exact exchange, B3-LYP/6-31G(d) (0.9613), containing 20% exact exchange, and B-LYP/6-31G(d) (0.9940), containing no exact exchange. The calculated scale factor increases monotonically with decreasing incorporation of exact exchange. This is examined in more detail in the following section.

3.1.6. Investigation of the Effect of Variation in the Extent of Incorporation of Exact Exchange on the Calculated Scale Factor. In the light of the apparent relationship between the magnitude of the scale factor and the proportion of exact HF exchange, we have evaluated scale factors for theoretical vibrational frequencies using the 6-31G(d) basis set and a modified B3-LYP functional that includes a variable amount of exact exchange. This is possible with Gaussian 03, which includes a user-defined exchange-correlation model of the general form

$$AE_x^{\text{Slater}} + (1 - A)E_x^{\text{HF}} + B\Delta E_x^{\text{Becke88}} + E_c^{\text{VWN}} + C\Delta E_c^{\text{LYP}} \qquad (17)$$

where *A*, *B*, and *C* are empirically derived coefficients obtained by Becke.[78] We have varied the *A* parameter corresponding to varying the proportions of exact HF exchange, while keeping the other parameters constant. Specifically, the proportions of exact HF exchange have been varied over the range from 0% to 100% in 10% increments for molecules in the F1 set. Our results, which are summarized in Table 5 and Figure 1, show that there is an approximately linear relationship between the magnitude of the scale factor and the proportion of exact exchange with larger proportions of exact exchange leading to smaller scale factors.

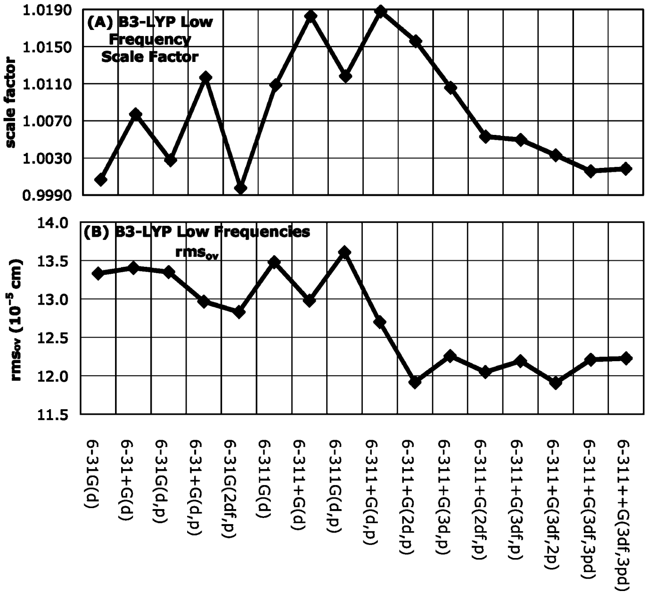

Figure 3. Plots showing the relationship between (A) low-frequency scale factors and (B) rms_{ov} values and basis set for fundamental frequencies calculated with B3-LYP.

In contrast, plotting rms_{ov} against the proportion of exact exchange produces a curve with a minimum somewhere in the region between 30% and 40% exact exchange (Figure 1). It is interesting to note that B3-LYP incorporates 20% exact exchange, which is close to but not precisely at this minimum rms_{ov} value. The optimum values of 30−40% for the proportion of exact exchange lead to rms_{ov} values compar-

TABLE 9: Frequency Scale Factors and rms$_{ov}$ Values Derived from a Least-Squares Fit of ZPVEs[a]

	6-31G(d)		6-31+G(d,p)		6-31G(2df,p)		6-311+G(d,p)		6-311+G(2df,p)	
method	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]
HF	0.9135	0.71	0.9200	0.72	0.9222	0.79	0.9255	0.77	0.9268	0.77
MP2	0.9670[d]	0.91[d]	0.9657[d]	0.82[d]	0.9678[d]	0.52[d]	0.9768[d]	0.55[d]	0.9777[d]	0.46[d]
QCISD	0.9777	0.60	0.9703	0.51	0.9707	0.26	0.9812	0.28	0.9803	0.21
QCISD(T)	0.9859	0.77	0.9786	0.71	*e*	*e*	0.9907	0.43	*e*	*e*
CCSD	0.9758	0.58	0.9686	0.46	0.9691	0.21	0.9795	0.25	0.9786	0.18
CCSD(T)	0.9851	0.76	0.9779	0.68	*e*	*e*	0.9897	0.44	*e*	*e*
B-B95	1.0129	0.53	1.0162[f]	0.36[f]	1.0152	0.39	*e*	*e*	*e*	*e*
B-LYP	1.0135	0.61	1.0169	0.42	1.0158	0.44	1.0189	0.43	1.0186	0.38
B-P86	1.0121	0.48	1.0155	0.32	1.0150	0.36	1.0183	0.33	1.0185	0.30
G96-LYP	1.0121	0.56	1.0148	0.40	1.0143	0.41	1.0168[g]	0.47[g]	1.0166	0.36
HCTH147	0.9964	0.43	0.9999	0.28	0.9998	0.32	1.0028	0.30	1.0037	0.27
HCTH407	0.9911	0.44	0.9950	0.29	0.9951	0.33	0.9981	0.30	0.9993	0.28
HCTH93	0.9957	0.42	0.9991	0.29	0.9992	0.33	1.0022	0.31	1.0033	0.28
O-LYP	0.9985	0.48	1.0022	0.31	1.0024	0.35	1.0056	0.31	1.0070	0.28
PBE	1.0085	0.47	1.0123	0.30	1.0120	0.35	1.0154	0.32	1.0161	0.29
TPSS	0.9925	0.57	0.9957	0.41	0.9971	0.39	0.9999	0.39	1.0007	0.35
VSXC	0.9877	0.46	0.9904	0.31	0.9896	0.34	0.9937	0.34	0.9947	0.29
B1-B95	0.9716[f]	0.37[f]	0.9760	0.31	0.9762	0.41	*e*	*e*	*e*	*e*
B1-LYP	0.9760	0.42	0.9805	0.30	0.9802	0.38	0.9838	0.37	0.9840	0.33
B3-LYP	0.9813	0.42	0.9857	0.30	0.9853	0.37	0.9887	0.36	0.9889	0.32
B3-P86	0.9768	0.35	0.9809	0.27	0.9814	0.37	0.9845	0.34	0.9852	0.32
B3-PW91	0.9780	0.35	0.9819	0.27	0.9825	0.37	0.9858	0.34	0.9865	0.32
B971	0.9817	0.35	0.9859	0.27	0.9859	0.35	0.9893	0.33	0.9899	0.30
B972	0.9719	0.35	0.9760	0.28	0.9768	0.36	0.9799	0.33	0.9809	0.32
B98	0.9809	0.35	0.9850	0.28	0.9849	0.37	0.9884	0.35	0.9886	0.31
BB1K	0.9539	0.41	0.9587	0.40	0.9595	0.49	*e*	*e*	*e*	*e*
BHandH	0.9500	0.56	0.9562	0.57	0.9568	0.68	0.9607	0.65	0.9620	0.65
BHandH-LYP	0.9446	0.44	0.9498	0.42	0.9506	0.51	0.9540	0.49	0.9547	0.48
BMK	0.9709	0.49	0.9773	0.52	0.9752	0.57	0.9794	0.58	0.9787	0.48
EDF1	1.0006	0.48	1.0037	0.32	*e*	*e*	1.0066	0.33	*e*	*e*
EDF2	0.9805	0.39	0.9847	0.29	*e*	*e*	0.9879	0.37	*e*	*e*
M05	0.9736	0.39	0.9787	0.32	0.9809	0.42	0.9841	0.43	0.9851	0.43
M05-2X	0.9580	0.51	0.9631	0.45	0.9657	0.49	0.9658	0.50	0.9663	0.47
MPW1K	0.9489	0.41	0.9537	0.41	0.9552	0.51	0.9584	0.49	0.9596	0.48
mPW1PW91	0.9708	0.35	0.9751	0.29	0.9759	0.39	0.9793	0.37	0.9804	0.35
MPWB1K	0.9513	0.42	0.9563	0.41	0.9569	0.50	*e*	*e*	*e*	*e*
O3-LYP	0.9826	0.39	0.9867	0.26	0.9872	0.32	0.9904	0.30	0.9918	0.28
PBE0	0.9726	0.36	0.9771	0.30	0.9779	0.40	0.9812	0.37	0.9824	0.36

[a] Using the Z1 set of 39 molecules unless otherwise noted. [b] As defined by eq 8. [c] Overall rms error in ZPVEs in kJ mol^{-1}. [d] Values obtained with NO and CN removed from the analysis; see text. [e] Scale factors and rms$_{ov}$ values not determined at these levels of theory. [f] Values obtained with LiH removed from the analysis due to SCF convergence problems. [g] Values obtained with Li$_2$ removed from the analysis due to SCF convergence problems.

TABLE 10: Sensitivity to Test Set of ZPVE Scale Factors and rms$_{ov}$ Values

	Z1[a]		Z2[b]	
method	scale factor[c]	rms$_{ov}$[d]	scale factor[c]	rms$_{ov}$[d]
B3-LYP/6-31G(d)	0.9813	0.42	0.9826	0.44
B3-LYP/6-31G(2df,p)	0.9861	0.37	0.9861	0.39
B3-LYP/6-311+G(2df,p)	0.9889	0.33	0.9895	0.33
B3-LYP/6-311+G(3df,2p)	0.9876	0.31	0.9884	0.33

[a] Using the Z1 test set of 39 molecules. [b] Using the Z2 test set of 48 molecules. [c] As defined by eq 8. [d] Overall rms error in ZPVEs in kJ mol^{-1}.

able to those from the most precise procedures listed in Table 2. This suggests that a hypothetical hybrid functional of the B3-LYP form containing ~35% exact exchange should produce quite accurate scaled theoretical frequencies.

3.1.7. Effect of Basis Set. Somewhat surprisingly, the rms$_{ov}$ values in Table 2 tend in some instances to increase with increasing basis set size. To examine this effect further, we obtained HF, MP2, B3-LYP, and BMK vibrational frequency scale factors with a wider range of basis sets (Table 6). The vibrational frequency scale factors and corresponding rms$_{ov}$ values for B3-LYP are displayed in Figure 2.

Considering first the optimum fundamental scale factors calculated for B3-LYP in conjunction with a range of Pople basis sets of increasing size, we see that the frequency scale factors "converge" at about 6-311+G(d) with an average value of 0.9682 from this point on (Figure 2). Andersson and Uvdal[16] also investigated the effect of basis set on B3-LYP scale factors, albeit with a smaller test set than our F1 set. Using the 6-311G basis set and various combinations of diffuse and/or polarization functions, they concluded that the magnitude of the scale factor converged by the 6-311G(d,p) stage. Thus, despite the different test sets, there is general agreement between our independent determinations of the convergence of B3-LYP scale factors as a function of basis set size. In contrast to the convergence of scale factors, rms$_{ov}$ values converge less rapidly. Thus, for B3-LYP the lowest rms$_{ov}$ value of 31 cm^{-1} (Figure 2) is not achieved until 6-311+G(3df,p). The highest rms$_{ov}$ values are found for 6-31+G(d), 6-31+G(d,p), and 6-311+G(d,p), suggesting that the inclusion of diffuse functions in the smaller basis sets has an adverse effect in B3-LYP frequency calculations.

Considering the BMK scale factors next (Table 6), we see similar behavior to B3-LYP for the larger basis sets. The scale factors "converge" by 6-311+G(2d,p) with an average

TABLE 11: Frequency Scale Factors and rms$_{ov}$ Values Derived from a Least-Squares Fit of Theoretical and Experimental $\Delta H_{vib}(T)$ Values at 298.15 K[a]

	298.15 K									
	6-31G(d)		6-31+G(d,p)		6-31G(2df,p)		6-311+G(d,p)		6-311+G(2df,p)	
method	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]
HF	0.8902	0.044	0.8955	0.044	0.8878	0.044	0.8967	0.043	0.8885	0.045
MP2	1.0059[d]	0.055[d]	1.0198[d]	0.053[d]	0.9823	0.033	1.0071[d]	0.044[d]	0.9826	0.030
QCISD	0.9986[d]	0.044[d]	1.0100[d]	0.042[d]	*e*	*e*	0.9970[d]	0.037[d]	*e*	*e*
QCISD(T)	1.0273[d]	0.058[d]	1.0419[d]	0.056[d]	*e*	*e*	1.0274[d]	0.044[d]	*e*	*e*
CCSD	0.9936[d]	0.044[d]	1.0043[d]	0.042[d]	*e*	*e*	0.9918[d]	0.037[d]	*e*	*e*
CCSD(T)	1.0247[d]	0.057[d]	1.0391[d]	0.055[d]	*e*	*e*	1.0244[d]	0.044[d]	*e*	*e*
B-B95	1.0552	0.047	1.0602	0.046	1.0413	0.037	*e*	*e*	*e*	*e*
B-LYP	1.0648	0.048	1.0703	0.048	1.0504	0.039	1.0766	0.050	1.0538	0.035
B-P86	1.0502	0.046	1.0546	0.045	1.0368	0.036	1.0603	0.046	1.0387	0.032
G96-LYP	1.0600	0.047	1.0642	0.046	1.0457	0.037	1.0698	0.049	1.0484	0.034
HCTH147	1.0325	0.043	1.0372	0.043	1.0193	0.035	1.0404	0.045	1.0199	0.032
HCTH407	1.0240	0.042	1.0292	0.041	1.0118	0.036	1.0322	0.044	1.0124	0.033
HCTH93	1.0311	0.043	1.0357	0.043	1.0182	0.034	1.0383	0.045	1.0185	0.032
O-LYP	1.0378	0.044	1.0426	0.043	1.0249	0.035	1.0455	0.045	1.0262	0.032
PBE	1.0435	0.044	1.0485	0.043	1.0308	0.036	1.0534	0.045	1.0328	0.032
TPSS	1.0382	0.044	1.0424	0.043	1.0264	0.035	1.0463	0.045	1.0263	0.033
VSXC	1.0359	0.047	1.0393	0.045	1.0164	0.042	1.0406	0.049	1.0174	0.039
B1-B95	0.9788	0.035	0.9838	0.035	0.9714	0.034	*e*	*e*	*e*	*e*
B1-LYP	0.9920	0.034	0.9977	0.035	0.9830	0.032	1.0017	0.034	0.9860	0.031
B3-LYP	1.0004	0.035	1.0062	0.035	0.9909	0.032	1.0102	0.036	0.9938	0.031
B3-P86	0.9881	0.035	0.9927	0.035	0.9795	0.033	0.9963	0.035	0.9811	0.031
B3-PW91	0.9899	0.035	0.9947	0.035	0.9815	0.032	0.9978	0.035	0.9830	0.031
B971	0.9989	0.035	1.0037	0.035	0.9899	0.031	1.0072	0.035	0.9922	0.029
B972	0.9847	0.034	0.9895	0.034	0.9763	0.032	0.9922	0.034	0.9773	0.031
B98	0.9967	0.035	1.0016	0.035	0.9879	0.031	1.0046	0.035	0.9899	0.029
BB1K	0.9503	0.035	0.9551	0.035	*e*	*e*	*e*	*e*	*e*	*e*
BHandH	0.9276	0.038	0.9335	0.038	0.9234	0.040	0.9352	0.036	0.9247	0.039
BHandH-LYP	0.9400	0.035	0.9453	0.035	0.9341	0.035	0.9478	0.034	0.9361	0.035
BMK	0.9679	0.037	0.9728	0.037	0.9610	0.034	0.9740	0.034	0.9644	0.031
EDF1	1.0402	0.044	1.0448	0.043	*e*	*e*	1.0486[f]	0.045[f]	*e*	*e*
EDF2	0.9947	0.035	1.0000	0.036	*e*	*e*	1.0069	0.041	*e*	*e*
M05	0.9712	0.036	0.9761	0.037	0.9558	0.036	0.9752	0.035	0.9571	0.035
M05-2X	0.9470	0.040	0.9504	0.041	0.9321	0.042	0.9467	0.042	0.9297	0.043
MPW1K	0.9424	0.035	0.9473	0.035	0.9373	0.036	0.9494	0.034	0.9382	0.036
mPW1PW91	0.9781	0.034	0.9831	0.034	0.9705	0.033	0.9861	0.034	0.9721	0.032
MPWB1K	0.9462	0.036	0.9511	0.036	0.9411	0.037	*e*	*e*	*e*	*e*
O3-LYP	1.0048	0.036	1.0098	0.036	0.9950	0.032	1.0123	0.037	0.9965	0.030
PBE0	0.9777	0.034	0.9827	0.034	0.9703	0.033	0.9856	0.034	0.9720	0.032

[a] Using the F1′ set of 1062 frequencies. [b] As defined by eq 13. [c] Overall root-mean-square error in $\Delta H_{vib}(T)$ in units of kJ mol^{-1}. [d] Values obtained with the F″ set; see text. [e] Scale factors and rms$_{ov}$ values not determined at these levels of theory. [f] Values obtained with Cl_2CS removed from the analysis due to SCF convergence problems.

value of 0.9543 from this point on. The range of rms$_{ov}$ values is slightly larger than that for B3-LYP with a minimum of 35 cm^{-1} (6-311+G(2d,p)) and a maximum of 42 cm^{-1} (6-31G(d,p)).

Of all the methods examined for scale factor convergence as a function of basis set size, the HF procedure gives the most unusual results (Table 6). The scale factors for HF converge by 6-311+G(d,p) with an average value from this point on of 0.9068. Intriguingly, the lowest rms$_{ov}$ value is found for the relatively small 6-31+G(d) basis set, while the largest rms$_{ov}$ values are given by the three largest basis sets considered (6-311+G(3df,2p), 6-311+G(3df,3pd), and 6-311++G(3df,3pd)).

The MP2 scale factors converge by 6-311+G(2d,p) with an average value of 0.9575 from this position on. We note that the largest basis sets give the lowest rms$_{ov}$ values (40−42 cm^{-1}), suggesting that moving to a large basis set (6-311+G(2df,p) or larger) for MP2 does improve results. As noted above also for B3-LYP, diffuse functions appear to significantly increase the MP2 rms$_{ov}$ values to the extent that both 6-31+G(d) and 6-31+G(d,p) give poorer results for MP2 than for the corresponding HF calculations. Note that two different molecular test sets, F1″ and the even smaller set F1‴, have been employed (Table 6). The changes in test set can be seen for the most part to make little difference, so most of our conclusions are likely to hold more generally.

We have also briefly considered a range of correlation-consistent Dunning basis sets and a single Ahlrichs (TZV2P) basis set (Table 6). Wilson and co-workers[13] have previously reported scale factors for HF, B3-LYP, and MP2 with the range of Dunning sets that we have considered but with different (smaller) test sets. We have redetermined the scale factors with our standard test set so as to provide a consistent set of scale factors obtained with a uniform test set (Table 6). Looking first at the HF results, we find that the rms$_{ov}$ value becomes slightly worse as the basis set size is increased, as found also with the Pople basis sets. Furthermore, we note that the HF scale factors with the Dunning sets remain relatively constant and are close to those obtained with the larger Pople sets. For B3-LYP, BMK, and MP2, we observe a significant drop in rms$_{ov}$ when the basis set is increased from DZ to TZ, for both the cc-pVnZ series and the aug-cc-pVnZ series. The subsequent improvement in going from TZ to QZ is somewhat smaller (especially for B3-LYP). Thus, with our larger test set we do not find the large changes in scale factors for B3-LYP between the TZ and QZ basis sets that was evident in the

TABLE 12: Frequency Scale Factors Derived from a Least-Squares Fit of Theoretical and Experimental $\Delta H_{\mathrm{vib}}(T)$ Values at 450 K[a]

	450 K				
	6-31G(d)	6-31+G(d,p)	6-31G(2df,p)	6-311+G(d,p)	6-311+G(2df,p)
method	scale factor[b]	scale factor[b]	scale factor[b]	scale factor[b]	scale factor[b]
HF	0.8844	0.8910	0.8858	0.8931	0.8875
MP2	0.9824[c]	0.9960[c]	0.9738[c]	0.9913[c]	0.9825[c]
QCISD	0.9808[c]	0.9902[c]	*d*	0.9844[c]	*d*
QCSID(T)	1.0018[c]	1.0138[c]	*d*	1.0091[c]	*d*
CCSD	0.9765[c]	0.9852[c]	*d*	0.9798[c]	*d*
CCSD(T)	0.9998[c]	1.0115[c]	*d*	1.0066[c]	*d*
B-B95	1.0390	1.0481	1.0330	*d*	*d*
B-LYP	1.0455	1.0553	1.0387	1.0591	1.0447
B-P86	1.0343	1.0427	1.0288	1.0467	1.0333
G96-LYP	1.0413	1.0497	1.0348	1.0532	1.0396
HCTH147	1.0177	1.0262	1.0124	1.0285	1.0157
HCTH407	1.0107	1.0196	1.0061	1.0220	1.0096
HCTH93	1.0165	1.0247	1.0115	1.0269	1.0145
O-LYP	1.0220	1.0309	1.0170	1.0333	1.0214
PBE	1.0290	1.0380	1.0241	1.0416	1.0288
TPSS	1.0191	1.0267	1.0145	1.0300	1.0176
VSXC	1.0193	1.0275	1.0103	1.0293	1.0148
B1-B95	0.9710	0.9786	0.9688	*d*	*d*
B1-LYP	0.9816	0.9899	0.9781	0.9928	0.9822
B3-LYP	0.9895	0.9979	0.9857	1.0008	0.9899
B3-P86	0.9791	0.9864	0.9764	0.9895	0.9794
B3-PW91	0.9808	0.9883	0.9782	0.9911	0.9814
B971	0.9883	0.9960	0.9852	0.9988	0.9890
B972	0.9755	0.9829	0.9730	0.9854	0.9757
B98	0.9862	0.9938	0.9830	0.9963	0.9867
BB1K	0.9545	0.9599	*d*	*d*	*d*
BHandH	0.9252	0.9330	0.9255	0.9352	0.9280
BHandH-LYP	0.9332	0.9404	0.9319	0.9428	0.9348
BMK	0.9601	0.9675	0.9578	0.9683	0.9622
EDF1	1.0242	1.0326	*d*	1.0351[e]	*d*
EDF2	0.9852	0.9933	*d*	0.9976	*d*
M05	0.9677	0.9757	0.9606	0.9761	0.9648
M05-2X	0.9464	0.9527	0.9403	0.9511	0.9402
MPW1K	0.9367	0.9435	0.9364	0.9460	0.9386
mPW1PW91	0.9700	0.9775	0.9680	0.9803	0.9711
MPWB1K	0.9405	0.9522	0.9398	*d*	*d*
O3-LYP	0.9936	1.0018	0.9903	1.0041	0.9940
PBE0	0.9702	0.9778	0.9685	0.9806	0.9717

[a] Using the F1′ set of 1062 frequencies. [b] As defined by eq 13. [c] Values obtained with the F″ set; see text. [d] Scale factors not determined at these levels of theory. [e] Values obtained with Cl_2CS removed from the analysis due to SCF convergence problems.

work of Wilson and co-workers.[13] Interestingly, the addition of diffuse functions to the DZ basis set significantly increases the $\mathrm{rms}_{\mathrm{ov}}$ values. For the TZ2VP set, we see that, with the exception of MP2, this set gives consistently low $\mathrm{rms}_{\mathrm{ov}}$ values.

3.1.8. Summary. In our previous paper,[2] we recommended B3-LYP/6-31G(d) and B3-PW91/6-31G(d) for the calculation of scaled fundamental frequencies. In the present work, it is clear that a number of other levels of theory provide comparable $\mathrm{rms}_{\mathrm{ov}}$ values; i.e., they are comparable in accuracy. However, none of the methods examined performs significantly better. Hence, it is our suggestion that B3-LYP/6-31G(d) and B3-PW91/6-31G(d) continue to be used to predict fundamental vibrational frequencies. B1-LYP and B3-LYP (with 6-31G-(2df,p) and 6-311+G(2df,p)), B971/6-311+G(2df,p), and B98/6-311+G(2df,p), among other hybrid procedures, also give very good results.

3.2. Low-Frequency Vibrations. There are thermochemical quantities for which the evaluation is dominated by low frequencies with the contribution from high frequencies being minimal. It is important in such circumstances to examine whether more appropriate scale factors might be derived for low-frequency vibrations than those derived in section 3.1 by the standard least-squares procedure, which are weighted to the high end of the frequency range. Therefore scale factors for low-frequency vibrations have been evaluated (Table 7).

3.2.1. Comparison with Results of Previous Studies. A low-frequency scale factor of 1.0100 for B3-LYP/6-311+G(d,p) has been previously reported by Andersson and Uvdal[16] using a 125 molecule set, which is close to our value of 1.0189.

3.2.2. Problem Molecules. Table S4 in the Supporting Information gives a comprehensive list of the largest $\mathrm{rms}_{\mathrm{mol}}$ values obtained for each of the theoretical procedures considered. The poorest results for low-frequency vibrations are consistently found for $CSCl_2$ ($40-76 \times 10^{-5}$ cm) and to a lesser extent ClCCCl (up to 158×10^{-5} cm).

3.2.3. Comparison of Methods. Analysis of the data in Table 7 leads to a number of important observations. For instance, we find that the HF method shows remarkably low $\mathrm{rms}_{\mathrm{ov}}$ values (15×10^{-5} cm) and, with the exception of MP2/6-31G-(2df,p) and MP2/6-311+G(2df,p), performs better than the other wave function methods. Indeed, MP2 and, surprisingly, CCSD-(T) and QCISD(T) give some of the largest $\mathrm{rms}_{\mathrm{ov}}$ values in Table 7.

The pure DFT procedures generally give similar $\mathrm{rms}_{\mathrm{ov}}$ values to CCSD and QCISD, while not performing as well as HF.

TABLE 13: Frequency Scale Factors Derived from a Least-Squares Fit of Theoretical and Experimental $\Delta H_{vib}(T)$ Values at 600 K[a]

	600 K				
	6-31G(d)	6-31+G(d,p)	6-31G(2df,p)	6-311+G(d,p)	6-311+G(2df,p)
method	scale factor[b]	scale factor[b]	scale factor[b]	scale factor[b]	scale factor[b]
HF	0.8827	0.8902	0.8864	0.8928	0.8887
MP2	0.9707[c]	0.9836[c]	0.9695[c]	0.9834[c]	0.9795[c]
QCISD	0.9713[c]	0.9793[c]	*d*	0.9777[c]	*d*
QCSID(T)	0.9883[c]	0.9986[c]	*d*	0.9987[c]	*d*
CCSD	0.9674[c]	0.9749[c]	*d*	0.9737[c]	*d*
CCSD(T)	0.9866[c]	0.9966[c]	*d*	0.9966[c]	*d*
B-B95	1.0281	1.0397	1.0275	*d*	*d*
B-LYP	1.0320	1.0443	1.0303	1.0475	1.0371
B-P86	1.0239	1.0349	1.0237	1.0386	1.0291
G96-LYP	1.0284	1.0393	1.0270	1.0424	1.0325
HCTH147	1.0077	1.0185	1.0075	1.0210	1.0121
HCTH407	1.0016	1.0129	1.0021	1.0154	1.0070
HCTH93	1.0065	1.0171	1.0067	1.0195	1.0110
O-LYP	1.0114	1.0229	1.0117	1.0255	1.0175
PBE	1.0195	1.0311	1.0198	1.0346	1.0257
TPSS	1.0067	1.0165	1.0070	1.0199	1.0114
VSXC	1.0078	1.0187	1.0052	1.0209	1.0110
B1-B95	0.9664	0.9758	0.9680	*d*	*d*
B1-LYP	0.9746	0.9848	0.9750	0.9876	0.9798
B3-LYP	0.9821	0.9925	0.9824	0.9953	0.9872
B3-P86	0.9737	0.9829	0.9751	0.9861	0.9788
B3-PW91	0.9752	0.9846	0.9767	0.9877	0.9807
B971	0.9813	0.9911	0.9823	0.9940	0.9869
B972	0.9698	0.9790	0.9713	0.9818	0.9750
B98	0.9793	0.9889	0.9801	0.9916	0.9845
BB1K	0.9414	0.9501	*d*	*d*	*d*
BHandH	0.9249	0.9342	0.9283	0.9368	0.9315
BHandH-LYP	0.9297	0.9384	0.9316	0.9409	0.9349
BMK	0.9559	0.9651	0.9570	0.9661	0.9616
EDF1	1.0136	1.0244	*d*	1.0269[e]	*d*
EDF2	0.9789	0.9890	*d*	0.9927	*d*
M05	0.9653	0.9753	0.9633	0.9767	0.9690
M05-2X	0.9453	0.9533	0.9440	0.9528	0.9451
MPW1K	0.9341	0.9425	0.9371	0.9454	0.9401
mPW1PW91	0.9652	0.9746	0.9671	0.9777	0.9711
MPWB1K	0.9378	0.9465	0.9404	*d*	*d*
O3-LYP	0.9861	0.9966	0.9873	0.9991	0.9921
PBE0	0.9659	0.9754	0.9681	0.9786	0.9722

[a] Using the F1′ set of 1062 frequencies. [b] As defined by eq 13. [c] Values obtained with the F″ set; see text. [d] Scale factors not determined at these levels of theory. [e] Values obtained with Cl_2CS removed from the analysis due to SCF convergence problems.

VSXC/6-311+G(d,p) gives a relatively large rms$_{ov}$ (21 × 10^{-5} cm). As with the fundamentals, related methods perform similarly.

Once again hybrid DFT procedures give the best results, with BMK/6-311+G(2df,p) giving the lowest rms$_{ov}$ value (11 × 10^{-5} cm), closely followed by a large number of other (mainly hybrid) DFT procedures. As for the fundamentals, we find that closely related functionals generally give similar results with respect to their rms$_{ov}$ values. In contrast to the fundamentals, however, there is no improvement seen in going from BHandH to BHandH-LYP.

3.2.4. Effect of Proportion of Exact Exchange. When the percentage of exact exchange is varied, the effect on low-frequency scale factors (Table 5) is very similar to that observed for standard fundamental frequencies, and the reader is directed to section 3.1.6 for the relevant discussion.

3.2.5. Effect of Basis Set. We have carried out an extensive basis set study for the low-frequency scale factors using B3-LYP, BMK, HF, and MP2 (Table 8). Scale factor convergence at the B3-LYP level can be seen to be occurring much more slowly (Figure 3) than with the standard frequency scale factors (Figure 2). In addition, unlike the situation for the fundamental frequency scale factors, where we observed that specific basis sets generally gave the lowest rms$_{ov}$ values for the full range of methods, we generally do not see such a trend in the results for the low-frequency scale factors.

The MP2 rms$_{ov}$ values provide some useful insights concerning basis set performance. Employing the F1″ set, we see that the 6-31+G(d) and 6-311+G(d) basis sets perform particularly poorly for a number of molecules (which seriously distorts their scale factor). Although less extreme, the MP2 rms$_{ov}$ values obtained with the smaller F1‴ set confirm these findings with rms$_{ov}$ values that increase as diffuse functions are added to smaller basis sets. This implies that for MP2 in particular the 6-31+G(d) and 6-311+G(d) basis sets are unsuitable for low-frequency vibrational frequency calculations, as found also for the standard frequency calculations.

Considering now the Dunning basis sets, we note that the scale factors and rms$_{ov}$ values reported for the HF level by Wilson and co-workers[13] appear to have been calculated using a standard (rather than inverse) least-squares procedure and thus are not directly comparable with our results. The comparatively large rms$_{ov}$ values found for MP2 by Wilson and co-workers[13] may be attributed to a single mode, the B_2 deformation of diazomethane (CH_2N_2), which is poorly predicted by MP2 and produces greatly distorted scale factors and rms$_{ov}$ values. We again note that the inclusion of diffuse functions in DZ basis sets for B3-LYP, BMK, and MP2

TABLE 14: Frequency Scale Factors and rms$_{ov}$ Values Derived from a Least-Squares Fit of Theoretical and Experimental $S_{vib}(T)$ Values at 298.15 K[a]

	298.15 K									
	6-31G(d)		6-31+G(d,p)		6-31G(2df,p)		6-311+G(d,p)		6-311+G(2df,p)	
method	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	rms$_{ov}$[c]
HF	0.8978	0.28	0.9035	0.28	0.8949	0.28	0.9041	0.28	0.8959	0.28
MP2	1.0178[d]	0.39[d]	1.0334[d]	0.38[d]	0.9858	0.23	1.0158[d]	0.32[d]	0.9908	0.22
QCISD	1.0058[d]	0.30[d]	1.0202[d]	0.30[d]	*e*	*e*	1.0049[d]	0.27[d]	*e*	*e*
QCISD(T)	1.0405[d]	0.40[d]	1.0583[d]	0.40[d]	*e*	*e*	1.0382[d]	0.33[d]	*e*	*e*
CCSD	1.0009[d]	0.30[d]	1.0145[d]	0.30[d]	*e*	*e*	0.9998[d]	0.27[d]	*e*	*e*
CCSD(T)	1.0376[d]	0.40[d]	1.0555[d]	0.39[d]	*e*	*e*	1.0351[d]	0.33[d]	*e*	*e*
B-B95	1.0577	0.33	1.0644	0.32	1.0438	0.25	*e*	*e*	*e*	*e*
B-LYP	1.0683	0.33	1.0749	0.33	1.0527	0.27	1.0870	0.35	1.0571	0.24
B-P86	1.0544	0.32	1.0602	0.31	1.0409	0.25	1.0726	0.34	1.0430	0.22
G96-LYP	1.0643	0.33	1.0685	0.32	1.0492	0.26	1.0798	0.34	1.0522	0.24
HCTH147	1.0357	0.30	1.0420	0.30	1.0220	0.24	1.0486	0.32	1.0233	0.22
HCTH407	1.0273	0.28	1.0342	0.28	1.0149	0.24	1.0399	0.31	1.0168	0.23
HCTH93	1.0347	0.29	1.0410	0.30	1.0214	0.23	1.0466	0.32	1.0224	0.22
O-LYP	1.0415	0.30	1.0483	0.31	1.0280	0.24	1.0546	0.32	1.0300	0.22
PBE	1.0468	0.30	1.0535	0.30	1.0340	0.24	1.0637	0.33	1.0367	0.22
TPSS	1.0425	0.30	1.0481	0.30	1.0308	0.24	1.0554	0.32	1.0308	0.23
VSXC	1.0374	0.33	1.0413	0.32	1.0156	0.31	1.0435	0.36	1.0151	0.29
B1-B95	0.9816	0.24	0.9874	0.24	0.9767	0.23	*e*	*e*	*e*	*e*
B1-LYP	0.9947	0.23	1.0011	0.23	0.9869	0.22	1.0074	0.23	0.9906	0.21
B3-LYP	1.0029	0.24	1.0099	0.24	0.9946	0.22	1.0161	0.24	0.9984	0.21
B3-P86	0.9919	0.24	0.9974	0.23	0.9846	0.22	1.0030	0.23	0.9867	0.21
B3-PW91	0.9937	0.23	0.9994	0.23	0.9866	0.22	1.0040	0.23	0.9886	0.21
B971	1.0017	0.24	1.0074	0.24	0.9939	0.22	1.0134	0.24	0.9968	0.20
B972	0.9883	0.23	0.9943	0.23	0.9810	0.22	0.9983	0.23	0.9827	0.21
B98	0.9997	0.24	1.0055	0.24	0.9921	0.22	1.0106	0.24	0.9947	0.20
BB1K	0.9545	0.24	0.9599	0.24	*e*	*e*	*e*	*e*	*e*	*e*
BHandH	0.9322	0.25	0.9391	0.25	0.9291	0.26	0.9412	0.23	0.9310	0.25
BHandH-LYP	0.9449	0.23	0.9510	0.23	0.9399	0.23	0.9541	0.22	0.9425	0.23
BMK	0.9731	0.25	0.9781	0.24	0.9680	0.23	0.9813	0.23	0.9709	0.21
EDF1	1.0440	0.30	1.0503	0.30	*e*	*e*	1.0586[f]	0.31[f]	*e*	*e*
EDF2	0.9972	0.24	1.0037	0.24	*e*	*e*	1.0149	0.28	*e*	*e*
M05	0.9715	0.24	0.9771	0.25	0.9555	0.25	0.9757	0.24	0.9548	0.24
M05-2X	0.9425	0.30	0.9445	0.32	0.9239	0.32	0.9398	0.32	0.9206	0.34
MPW1K	0.9480	0.23	0.9539	0.23	0.9442	0.24	0.9564	0.22	0.9456	0.24
mPW1PW91	0.9821	0.23	0.9883	0.23	0.9761	0.22	0.9927	0.23	0.9783	0.22
MPWB1K	0.9508	0.24	0.9562	0.24	0.9485	0.25	*e*	*e*	*e*	*e*
O3-LYP	1.0075	0.24	1.0139	0.25	0.9989	0.22	1.0186	0.26	1.0010	0.21
PBE0	0.9814	0.23	0.9875	0.23	0.9755	0.23	0.9915	0.23	0.9776	0.22

[a] Using the F1′ set of 1062 frequencies. [b] As defined by eq 14. [c] Overall root-mean-square error in $S_{vib}(T)$ in units of J K^{-1} mol^{-1}. [d] Values obtained with the F″ set; see text. [e] Scale factors and rms$_{ov}$ values not determined at these levels of theory. [f] Values obtained with Cl_2CS removed from the analysis due to SCF convergence problems.

significantly increases the rms$_{ov}$ values. Finally the TZV2P basis set again performs well in terms of rms$_{ov}$ values, especially for B3-LYP and BMK.

3.2.6. Summary. In our previous paper,[2] we found that B3-type DFT functionals gave the best results. As noted for the fundamentals, we suggest that these functionals continue to be used to predict low-frequency vibrations due to their well-established nature and the fact that none of the functionals examined perform significantly better. However, due to the low rms$_{ov}$ value found for BMK/6-311+G(2df,p), this level of theory (among others) can also be considered for low-frequency vibrational frequency calculations.

3.3. Zero-Point Vibrational Energies. We now turn our attention to scaled thermodynamic quantities, beginning with the scale factors for zero-point vibrational energies and their associated rms$_{ov}$ values (Table 9). It might be expected that the performance of various methods for predicting accurate scaled ZPVEs should parallel that for standard vibrational frequencies, and this is generally observed. We therefore comment only briefly on the individual ZPVE results.[79] However, we note some differences between the two sets of predictions that can be largely attributed to the different test sets that are used.

3.3.1. Comparison with Results of Previous Studies. As with the fundamental scale factors, some ZPVE scale factors presented in Table 9 have previously been reported in the literature. Using a 24 molecule set and the 6-31G(d) basis set, Wong[4] developed scale factors for MP2, B-LYP, B3-P86, and B3-LYP that are comparable to our results. Curtiss et al.[11] developed a single scale factor for B3-LYP/6-31G(2df,p), which matches our result. As with the fundamentals, Tantirungrotechai et al.[18] have reported ZPVE scale factors for HCTH407, B972, B98, O-LYP, O3-LYP, PBE0, and VSXC in conjunction with the 6-31G(d) basis set. With the exception of PBE0, where their value inexplicably differs from our scale factor by 0.0085, we generally observe good agreement between their results and our scale factors and rms$_{ov}$ values. ZPVE scale factors have also been reported by Truhlar and co-workers[6−9] for HF, MP2, B1-B95, BB1K, MPW1K, and MPWB1K in conjunction with the 6-31+G(d,p) basis set. Again, there is good agreement between the two sets of values.

3.3.2. Problem Molecules. As noted in our earlier paper,[2] both NO and CO produce large rms$_{mol}$ values with MP2; hence they have been removed from all of the MP2 analyses. In addition, the SCF failed to converge for LiH and Li_2 at a number of levels

TABLE 15: Frequency Scale Factors Derived from a Least-Squares Fit of Theoretical and Experimental $S_{\mathrm{vib}}(T)$ Values at 450 K[a]

	450 K				
	6-31G(d)	6-31+G(d,p)	6-31G(2df,p)	6-311+G(d,p)	6-311+G(2df,p)
method	scale factor[b]	scale factor[b]	scale factor[b]	scale factor[b]	scale factor[b]
HF	0.8915	0.8976	0.8906	0.8990	0.8920
MP2	1.0017[c]	1.0164[c]	0.9802[c]	1.0045[c]	0.9869[c]
QCISD	0.9944[c]	1.0065[c]	*d*	0.9955[c]	*d*
QCSID(T)	1.0229[c]	1.0382[c]	*d*	1.0249[c]	*d*
CCSD	0.9897[c]	1.0012[c]	*d*	0.9906[c]	*d*
CCSD(T)	1.0204[c]	1.0356[c]	*d*	1.0221[c]	*d*
B-B95	1.0493	1.0571	1.0389	*d*	*d*
B-LYP	1.0582	1.0662	1.0465	1.0745	1.0516
B-P86	1.0454	1.0523	1.0354	1.0608	1.0386
G96-LYP	1.0541	1.0602	1.0428	1.0679	1.0466
HCTH147	1.0277	1.0349	1.0177	1.0396	1.0199
HCTH407	1.0199	1.0277	1.0110	1.0318	1.0136
HCTH93	1.0265	1.0337	1.0170	1.0377	1.0188
O-LYP	1.0328	1.0405	1.0230	1.0450	1.0262
PBE	1.0388	1.0465	1.0295	1.0537	1.0332
TPSS	1.0321	1.0385	1.0234	1.0439	1.0249
VSXC	1.0293	1.0351	1.0132	1.0371	1.0151
B1-B95	0.9768	0.9834	0.9731	*d*	*d*
B1-LYP	0.9888	0.9960	0.9829	1.0007	0.9868
B3-LYP	0.9969	1.0045	0.9906	1.0092	0.9946
B3-P86	0.9861	0.9924	0.9809	0.9968	0.9834
B3-PW91	0.9878	0.9943	0.9828	0.9980	0.9853
B971	0.9956	1.0022	0.9900	1.0067	0.9933
B972	0.9825	0.9891	0.9773	0.9924	0.9795
B98	0.9936	1.0002	0.9880	1.0041	0.9911
BB1K	0.9498	0.9559	*d*	*d*	*d*
BHandH	0.9289	0.9362	0.9274	0.9383	0.9296
BHandH-LYP	0.9396	0.9461	0.9362	0.9489	0.9389
BMK	0.9671	0.9732	0.9633	0.9753	0.9669
EDF1	1.0352	1.0423	*d*	1.0479[e]	*d*
EDF2	0.9918	0.9989	*d*	1.0070	*d*
M05	0.9698	0.9765	0.9579	0.9759	0.9594
M05-2X	0.9443	0.9482	0.9315	0.9450	0.9296
MPW1K	0.9427	0.9491	0.9405	0.9516	0.9423
mPW1PW91	0.9766	0.9833	0.9724	0.9869	0.9750
MPWB1K	0.9460	0.9476	0.9444	*d*	*d*
O3-LYP	1.0013	1.0084	0.9950	1.0120	0.9979
PBE0	0.9763	0.9830	0.9722	0.9865	0.9749

[a] Using the F1′ set of 1062 frequencies. [b] As defined by eq 14. [c] Values obtained with the F″ set; see text. [d] Scale factors not determined at these levels of theory. [e] Values obtained with Cl_2CS removed from the analysis due to SCF convergence problems.

of theory, and these molecules have therefore been excluded from the ZPVE scale factor and rms error calculations for such procedures.

3.3.3. Comparison of Methods. For the HF method, the $\mathrm{rms_{ov}}$ values increase as the basis set size is increased, with 6-31G(d) giving the lowest error (0.71 kJ mol^{-1}) (Table 9). In contrast, the MP2 $\mathrm{rms_{ov}}$ values decrease significantly with increases in basis set size, with the lowest value obtained with 6-311+G(2df,p) (0.46 kJ mol^{-1}). As previously found for the fundamentals and low-frequency vibrations, adding perturbative triples to CCSD and QCISD actually increases the error. Comparative calculations in ACESII,[21] which, unlike Gaussian, has analytical gradients for QCISD(T) and CCSD(T), gave comparable errors, indicating that it is not a numerical problem. Changing to Dunning-type basis sets did not alter the situation. For example, with the cc-pVTZ basis set, CCSD leads to an $\mathrm{rms_{ov}}$ value of 0.18 kJ mol^{-1} whereas CCSD(T) gives a larger value of 0.28 kJ mol^{-1} (Table S14 in the Supporting Information). For both QCISD and QCISD(T), increases in basis set size correlate with significant decreases in their respective $\mathrm{rms_{ov}}$ values, with 6-311+G(2df,p) giving the lowest values overall. The behavior as a function of basis set of the CCSD and CCSD(T) scale factors and $\mathrm{rms_{ov}}$ values closely mirrors that of QCISD and QCSID(T). The lowest $\mathrm{rms_{ov}}$ values are found for CCSD/6-311+G(2df,p) (0.18 kJ mol^{-1}) and QCISD/6-311+G(2df,p) (0.21 kJ mol^{-1}).

As a general rule, hybrid DFT procedures have scale factors that are smaller in magnitude and show better performance than pure DFT procedures. In general, the lowest $\mathrm{rms_{ov}}$ values are given with the 6-31+G(d,p) and 6-311+G(2df,p) basis sets, with the exception of PBE0 for which the 6-311+G(d,p) basis gives the lowest $\mathrm{rms_{ov}}$ value and BHandH where the 6-31G(d) basis set gives the best result. The best DFT results are obtained with O3-LYP/6-31+G(d,p) (0.26 kJ mol^{-1}). Other DFT functionals that perform well include HCTH147, B971, B972, B98, B3-P86, and B3-PW91.

3.3.4. Comparison of Trends in Scale Factors for Fundamental Frequencies and ZPVEs. From a comparison of sections 3.1.5 and 3.3.3, it is apparent that the basis sets that give lower $\mathrm{rms_{ov}}$ values for fundamentals and ZPVEs are not the same. This is a surprising result and can be ascribed to the different test sets used for the two situations. The Z1 set used for the ZPVEs is far smaller than the F1 set used for the fundamentals, and this can lead to distorted statistics. For example, Z1 has proportionately more atoms than the F1 set of Cl and F, for which the descriptions are improved through the addition of diffuse functions. This leads to lower $\mathrm{rms_{ov}}$ values for the basis sets that contain such functions. However, because the F1 set

TABLE 16: Frequency Scale Factors Derived from a Least-Squares Fit of Theoretical and Experimental $S_{\mathrm{vib}}(T)$ Values at 600 K[a]

	600 K				
	6-31G(d)	6-31+G(d,p)	6-31G(2df,p)	6-311+G(d,p)	6-311+G(2df,p)
method	scale factor[b]	scale factor[b]	scale factor[b]	scale factor[b]	scale factor[b]
HF	0.8888	0.8954	0.8894	0.8971	0.8911
MP2	0.9914[c]	1.0056[c]	0.9767[c]	0.9975[c]	0.9845[c]
QCISD	0.9867[c]	0.9975[c]	*d*	0.9896[c]	*d*
QCSID(T)	1.0115[c]	1.0251[c]	*d*	1.0163[c]	*d*
CCSD	0.9823[c]	0.9925[c]	*d*	0.9850[c]	*d*
CCSD(T)	1.0093[c]	1.0227[c]	*d*	1.0137[c]	*d*
B-B95	1.0423	1.0513	1.0351	*d*	*d*
B-LYP	1.0495	1.0590	1.0411	1.0657	1.0468
B-P86	1.0382	1.0466	1.0316	1.0537	1.0355
G96-LYP	1.0456	1.0532	1.0375	1.0596	1.0419
HCTH147	1.0210	1.0295	1.0143	1.0335	1.0174
HCTH407	1.0138	1.0228	1.0081	1.0265	1.0115
HCTH93	1.0199	1.0282	1.0136	1.0318	1.0163
O-LYP	1.0257	1.0347	1.0193	1.0387	1.0233
PBE	1.0324	1.0415	1.0263	1.0475	1.0308
TPSS	1.0237	1.0313	1.0180	1.0361	1.0205
VSXC	1.0221	1.0297	1.0105	1.0317	1.0136
B1-B95	0.9734	0.9809	0.9715	*d*	*d*
B1-LYP	0.9841	0.9923	0.9803	0.9965	0.9846
B3-LYP	0.9920	1.0005	0.9879	1.0046	0.9922
B3-P86	0.9820	0.9893	0.9791	0.9934	0.9820
B3-PW91	0.9837	0.9912	0.9809	0.9947	0.9839
B971	0.9909	0.9986	0.9875	1.0026	0.9913
B972	0.9783	0.9858	0.9754	0.9890	0.9781
B98	0.9888	0.9965	0.9854	1.0000	0.9890
BB1K	0.9471	0.9541	*d*	*d*	*d*
BHandH	0.9277	0.9357	0.9279	0.9381	0.9305
BHandH-LYP	0.9364	0.9437	0.9348	0.9464	0.9378
BMK	0.9635	0.9706	0.9614	0.9724	0.9653
EDF1	1.0280	1.0364	*d*	1.0411[e]	*d*
EDF2	0.9875	0.9957	*d*	1.0024	*d*
M05	0.9683	0.9761	0.9597	0.9762	0.9626
M05-2X	0.9445	0.9497	0.9355	0.9474	0.9345
MPW1K	0.9400	0.9471	0.9396	0.9497	0.9418
mPW1PW91	0.9729	0.9805	0.9708	0.9840	0.9739
MPWB1K	0.9434	0.9505	0.9433	*d*	*d*
O3-LYP	0.9962	1.0046	0.9925	1.0078	0.9961
PBE0	0.9729	0.9806	0.9710	0.9840	0.9741

[a] Using the F1′ set of 1062 frequencies. [b] As defined by eq 14. [c] Values obtained with the F″ set; see text. [d] Scale factors not determined at these levels of theory. [e] Values obtained with Cl_2CS removed from the analysis due to SCF convergence problems.

is a more representative set of molecules, the performance indicated by the rms$_{\mathrm{ov}}$ values for the fundamental frequencies should be considered more significant than the corresponding results for the ZPVEs.

To assess the sensitivity of the optimum scale factors to the test set used, we carried out additional B3-LYP calculations with several basis sets on the expanded Z2 test set. This consists of the 39 Z1 molecules together with an additional nine molecules from the W4 set, making a total of 48 molecules (125 frequencies). It can be seen (Table 10) that the scale factors for the Z1 and Z2 test sets are quite similar, demonstrating some robustness with respect to choice of test set. Because the Z2 set is larger, we recommend a value of 0.9826 for the ubiquitous B3-LYP/6-31G(d) scale factor, which is not significantly different[80] to our previous value[2] of 0.9806 or the current Z1 value in Table 2 of 0.9813. Thus expansion of the test set by 25% has only a very minor effect on the optimized scale factors.

3.3.5. Summary. ZPVE scale factors and associated rms$_{\mathrm{ov}}$ values are presented in Table 9. Our results suggest that O3-LYP/6-31+G(d,p) provides a reliable and inexpensive (compared with CCSD/6-311+G(d,p)) level of theory for calculating ZPVEs. It is worth noting that the B3-containing functionals that we previously recommended[2] also perform comparatively well and can continue to be used. Because the Z1 test set is relatively small and is dominated by diatomic molecules, it is a less representative molecular set than F1, and the conclusions regarding more subtle details, reached on the basis of the results obtained with the F1 set, are therefore more significant. However, redetermination of a selection of B3-LYP ZPVE scale factors with the expanded Z2 test set is found to lead to only very minor changes in the optimum values. Our new recommended scale factor of 0.9826 for B3-LYP/6-31G(d) ZPVEs is only slightly different from our previous value[2] of 0.9806.

3.4. Enthalpies. We now turn our attention to a second thermodynamic quantity derived from vibrational frequencies, specifically the vibrational component of the thermal contribution to enthalpy, $\Delta H_{\mathrm{vib}}(T)$ (Tables 11−13). Due to the fact that $\Delta H_{\mathrm{vib}}(T)$ is particularly sensitive to low-frequency vibrations, it may be expected that the performance of the various methods with respect to $\Delta H_{\mathrm{vib}}(T)$ will mirror the results found for the low-frequency scale factors. This is indeed the case. Our discussion of $\Delta H_{\mathrm{vib}}(T)$ will therefore be brief. Values of the scale factors at temperatures of 298.15, 450, and 600 K are presented in Tables 11, 12, and 13, respectively. These data allow interpolation to any desired temperature within the 298−600 K range.

3.4.1. Problem Molecules. It could be expected that due to the sensitivity of $\Delta H_{\mathrm{vib}}(T)$ to low frequencies the largest rms$_{\mathrm{mol}}$

values should be found for the same molecules as previously discussed in the low-frequency section 3.2.2. This is indeed generally the case (Table S6) with $CSCl_2$ and ClCCCl again consistently giving particularly large rms_{mol} values. Comparably large rms_{mol} values are observed for $CH_2{=}C{=}CHCl$ and HCCCCH for some of the methods.

3.4.2. Comparison of Methods. Considering the wave function methods first, we see that MP2, QCISD(T), and CCSD(T) give comparable and large rms_{ov} values, while HF gives comparatively low rms_{ov} values. QCISD and CCSD give rms_{ov} values that show a slight improvement compared with the HF values, except when the 6-31G(d) basis set is used, where they are very close to HF. Pure DFT procedures provides rms_{ov} values comparable to QCISD and CCSD. For the hybrid DFT procedures, we see that the lowest rms_{ov} values are found for B98/6-311+G(2df,p) and B971/6-311+G(2df,p) (0.029 kJ mol^{-1}). The rms_{ov} values found for all of the functionals show for the most part little variation with respect to change in basis set size. The results are broadly consistent with observations based on scaling inverse frequencies (Table 7).

3.4.3. Summary. B98/6-311+G(2df,p) and B971/6-311+G-(2df,p) give the best results for the thermal contributions to enthalpy. However, a large number of levels of hybrid DFT theory give only marginally higher rms_{ov} values. These include the B3-containing functionals that we previously recommended and that we continue to recommend.

3.5. Entropies. We finally turn our attention to another thermodynamic quantity that is derived from vibrational frequencies, specifically the vibrational component of the thermal contribution to entropy (Tables 14−16). As with $\Delta H_{vib}(T)$, it is clear from eq 16 that the low-frequency vibrations contribute more to $S_{vib}(T)$ than do high-frequency vibrations, and we only discuss the results briefly.

3.5.1. Problem Molecules. Because $S_{vib}(T)$ is dependent on low frequencies, it is not surprising that the most poorly predicted molecules are again $CSCl_2$ and ClCCCl (Table S7 of the Supporting Information).

3.5.2. Comparison of Methods. Of the wave function methods considered, HF and, at a considerably higher cost, CCSD and QCISD give the lowest rms_{ov} values. As with the enthalpies, we note that MP2, QCISD(T), and CCSD(T) give similar and large rms_{ov} values while the pure DFT procedures provide rms_{ov} values comparable to CCSD and QCISD. The lowest rms_{ov} values are found for the hybrid procedures B98/6-311+G(2df,p) and B971/6-311+G(2df,p) (0.20 J K^{-1} mol^{-1}) with comparable rms_{ov} values for a large number of other hybrid DFT procedures. As with the other properties that are largely dependent on low frequencies, there is little variation in the magnitude of the scale factors and no systematic effects in rms_{ov} values associated with increasing the size of the basis sets.

3.5.3. Summary. The B3-containing functionals can continue to be used as no method gives markedly better performance.[2] However, due to the low rms_{ov} values found for B98/6-311+G-(2df,p) and B971/6-311+G(2df,p), these levels of theory (among others) can also be considered for calculations of the thermal contribution to entropy.

4. Conclusions

The purpose of the present study has been to evaluate frequency scale factors suitable for the prediction of fundamental vibrational frequencies, low-frequency vibrational frequencies, zero-point vibrational energies, and the thermal contributions to enthalpy and entropy from calculated harmonic vibrational frequencies. We have achieved this for more than 100 levels of theory. In addition, we have examined the effect on the scale factors of the proportion of incorporated exact HF exchange for hybrid DFT methods. We have also investigated the effect of variation in basis set size on the calculated scale factors and associated rms_{ov} values for an extensive range of Pople-type basis sets as well as for a small number of Dunning correlation-consistent basis sets and a single Ahlrichs basis set. We make the following observations and recommendations.

4.1. Fundamentals. We see in the first instance that hybrid DFT procedures generally perform well. In particular, we recommend Becke's three- and one-parameter hybrid functionals (e.g., B3-LYP and B1-LYP) and the modifications to Becke's B-97 hybrid functional (e.g., B972). CCSD/6-311+G(d,p) and QCISD/6-311+G(d,p) both give particularly low rms_{ov} values. However, due to their higher computational cost, these methods are restricted in their application.

When examining the effect of the size of the basis set, we see that for the majority of DFT procedures the 6-31G(d) basis set often results in lower rms_{ov} values than does 6-31+G(d,p) or 6-311+G(d,p), and it is not until basis sets the size of 6-311+G(2df,p) are employed that systematic improvements begin to appear. For the Hartree−Fock method, no consistent reduction in rms_{ov} values is observed as the basis set is increased. The size of the basis set by which convergence in the magnitude of the scale factor appears to have occurred varies with theoretical method and is found to be B3-LYP/6-311G(d), BMK/6-311+G(d), HF/6-311G(d,p), and MP2/6-311+G(2df,p).

Finally, we observe that for a modified B3-LYP procedure scale factors decrease almost linearly with increases in the percentage of exact HF-exchange, while the rms_{ov} error shows a minimum at 30−40% exact exchange.

4.2. Low-Frequency Vibrations, Enthalpy, and Entropy. Low-frequency vibrational frequencies and the quantities $\Delta H_{vib}(T)$ and $S_{vib}(T)$ that are sensitive to low-frequency vibrations show similar behavior with respect to rms_{ov} values. In general, the hybrid DFT procedures routinely perform well and are therefore recommended for calculating low-frequency vibrations as well as $\Delta H_{vib}(T)$ and $S_{vib}(T)$.

Convergence of scale factors with respect to basis set is slow for low frequencies computed with the HF, MP2, BMK, and B3-LYP procedures. MP2 appears to not perform well with respect to predicting low frequencies when smaller basis sets that include diffuse functions, e.g., 6-31+G(d) and 6-311+G-(d), are used. The effect of varying the percentage of exact exchange shows behavior analogous to that found for normal fundamental frequencies.

4.3. Zero-Point Vibrational Energies. As with the fundamental vibrational frequency scale factors, both CCSD/6-311+G(d,p) and QCISD/6-311+G(d,p) perform well. However, we again note that a number of hybrid DFT procedures give comparable rms_{ov} values for considerably less computational cost and therefore provide a good tradeoff between accuracy and expense for the calculation of ZPVEs. These include, among others, the B3-type functionals that we have previously recommended.[2] We now recommend a slightly modified B3-LYP/6-31G(d) ZPVE scale factor of 0.9826.

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Supporting Information Available: Frequencies for molecules in the F1 data set and ZPVEs for molecules in the Z1 and Z2 data sets (Tables S1 and S2, respectively), the largest $\mathrm{rms}_{\mathrm{mol}}$ values for the individual methods for fundamental frequencies (Table S3), low-frequency vibrational modes (Table S4), ZPVEs (Table S5), $\Delta H_{\mathrm{vib}}(T)$ (Table S6), and $S_{\mathrm{vib}}(T)$ (Table S7), results for the HFB and HFS methods (Tables S8 and S9), the detailed basis set dependence of scale factors and $\mathrm{rms}_{\mathrm{ov}}$ values for ZPVEs (Table S10), $\Delta H_{\mathrm{vib}}(T)$ (Table S11), and $S_{\mathrm{vib}}(T)$ (Table S12), the variation in scale factors as a function of the percentage of exact exchange (Table S13), and finally the effect of Dunning-type basis sets on ZPVE scale factors and corresponding $\mathrm{rms}_{\mathrm{ov}}$ values (Table S14). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(2) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(3) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(4) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(5) Fast, P. L.; Corchado, J.; Sanchez, M. L.; Truhlar, D. G. *J. Phys. Chem. A* **1999**, *103*, 3139.

(6) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936.

(7) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 4786.

(8) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2715.

(9) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 6908.

(10) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 4388.

(11) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108.

(12) Halls, M. D.; Velkovski, J.; Schlegel, H. B. *Theor. Chem. Acc.* **2001**, *105*, 413.

(13) Sinha, P.; Boesch, S. E.; Gu, C. M.; Wheeler, R. A.; Wilson, A. K. *J. Phys. Chem. A* **2004**, *108*, 9213.

(14) Healy, E. F.; Holder, A. *J. Mol. Struct.: THEOCHEM* **1993**, *281*, 141.

(15) Grev, R. S.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1991**, *95*, 5128.

(16) Andersson, M. P.; Uvdal, P. *J. Phys. Chem. A* **2005**, *109*, 2937.

(17) Csonka, G. I.; Ruszinsky, A.; Perdew, J. P. *J. Phys. Chem. A* **2005**, *109*, 6779.

(18) Tantirungrotechai, Y.; Phanasant, K.; Roddecha, S.; Surawatanawong, P.; Sutthikhum, V.; Limtrakul, J. *J. Mol. Struct: THEOCHEM* **2006**, *760*, 189.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(20) Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; DiStasio, R. A.; Lochan, R. C.; Wang, T.; Beran, G. J. O.; Besley, N. A.; Herbert, J. M.; Lin, C. Y.; Van Voorhis, T.; Chien, S. H.; Sodt, A.; Steele, R. P.; Rassolov, V. A.; Maslen, P. E.; Korambath, P. P.; Adamson, R. D.; Austin, B.; Baker, J.; Byrd, E. F. C.; Dachsel, H.; Doerksen, R. J.; Dreuw, A.; Dunietz, B. D.; Dutoi, A. D.; Furlani, T. R.; Gwaltney, S. R.; Heyden, A.; Hirata, S.; Hsu, C. P.; Kedziora, G.; Khalliulin, R. Z.; Klunzinger, P.; Lee, A. M.; Lee, M. S.; Liang, W.; Lotan, I.; Nair, N.; Peters, B.; Proynov, E. I.; Pieniazek, P. A.; Rhee, Y. M.; Ritchie, J.; Rosta, E.; Sherrill, C. D.; Simmonett, A. C.; Subotnik, J. E.; Woodcock, H. L.; Zhang, W.; Bell, A. T.; Chakraborty, A. K.; Chipman, D. M.; Keil, F. J.; Warshel, A.; Hehre, W. J.; Schaefer, H. F.; Kong, J.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3172.

(21) Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Kucharski, S. A.; Gwaltney, S. R.; Beck, S.; Balková, A.; Bernholdt, D. E.; Baeck, K. K.; Rozyczko, P.; Sekino, H.; Hober, C.; and Bartlett, R. J. *ACES II*; Quantum Theory Project, University of Florida: Gainesville, FL. (Integral packages included are VMOL (Almlöf, J.; Taylor, P. R.), VPROPS (Taylor, P. R.), and ABACUS (Helgaker, T.; Jensen, H. J. A.; Jørgensen, P.; Olsen, J.; Taylor, P. R.).

(22) (a) Bylaska, E. J.; de Jong, W. A.; Kowalski, K.; Straatsma, T. P.; Valiev, M.; Wang, D.; Aprà, E.; Windus, T. L.; Hirata, S.; Hackler, M. T.; Zhao, Y.; Fan, P.-D.; Harrison, R. J.; Dupuis, M.; Smith, D. M. A.; Nieplocha, J.; Tipparaju, V.; Krishnan, M.; Auer, A. A.; Nooijen, M.; Brown, E.; Cisneros, G.; Fann, G. I.; Früchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J. A.; Tsemekhman, K.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; Elwood, D.; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nakajima, T.; Niu, S.; Pollack, L.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G.; van Lenthe, J.; Wong, A.; Zhang, Z. *NWChem, A Computational Chemistry Package for Parallel Computers*, version 5.0; Pacific Northwest National Laboratory: Richland, WA, 2006. (b) Kendall, R. A.; Apra, E.; Bernholdt, D. E.; Bylaska, E. J.; Dupuis, M.; Fann, G. I.; Harrison, R. J.; Ju, J. L.; Nichols, J. A.; Nieplocha, J.; Straatsma, T. P.; Windus, T. L.; Wong, A. T. *Comput. Phys. Commun.* **2000**, *128*, 260.

(23) Schmider, H. L.; Becke, A. D. *J. Chem. Phys.* **1998**, *108*, 9624.

(24) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(25) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 2000.

(26) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(27) Gill, P. M. W. *Mol. Phys.* **1996**, *89*, 433.

(28) Adamo, C.; Barone, V. *J. Comput. Chem.* **1998**, *19*, 418.

(29) Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403.

(30) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(31) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.

(32) Adamson, R. D.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1998**, *284*, 6.

(33) Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264.

(34) Boese, A. D.; Doltsinis, N. L.; Handy, N. C.; Sprik, M. *J. Chem. Phys.* **2000**, *112*, 1670.

(35) Boese, A. D.; Handy, N. C. *J. Chem. Phys.* **2001**, *114*, 5497.

(36) Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.1.

(37) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.

(38) Van Voorhis, T.; Scuseria, G. E. *J. Chem. Phys.* **1998**, *109*, 400.

(39) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.

(40) Kohn, W.; Sham, L. J. *Phys. Rev. B* **1965**, *140*, 1133.

(41) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4.

(42) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(43) Burke, K.; Perdew, J. P.; Wang, Y. Derivation of a generalized gradient approximation: The PW91 density functional. In *Electronic Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum Press: New York, 1998.

(44) Perdew, J. P. *Electronic Structure of Solids*; Akademie Verlag: Berlin, 1991; Vol. 11.

(45) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(46) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1993**, *48*, 4978.

(47) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533.

(48) Lin, C. Y.; George, M. W.; Gill, P. M. W. *Aust. J. Chem.* **2004**, *57*, 365.

(49) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(50) Adamo, C.; Barone, V. *Chem. Phys. Lett.* **1997**, *274*, 242.

(51) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.

(52) Becke, A. D. *J. Chem. Phys.* **1997**, *107*, 8554.

(53) Wilson, P. J.; Bradley, T. J.; Tozer, D. J. *J. Chem. Phys.* **2001**, *115*, 9233.

(54) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

(55) Cohen, A. J.; Handy, N. C. *Mol. Phys.* **2001**, *99*, 607.

(56) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.* **2005**, *123*.

(57) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.

(58) Boese, A. D.; Martin, J. M. L. *J. Chem. Phys.* **2004**, *121*, 3405.

(59) See, for example: Jensen, F. *Introduction to Computational Chemistry*, 2nd ed.; Wiley: Chichester, U. K., 2007.

(60) The basis sets are used with the default types of basis functions (pure or Cartesian) found in Gaussian 03 with the exception of 6-31G-(2df,p) in NWChem, which is used with Cartesian functions only.

(61) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 993.

(62) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies*; NSRDS-NBS 39; National Bureau of Standards: Washington, DC, 1972.

(63) We note that removing half of the molecules from the F1 test set at random for B3-LYP/6-31G(d) leads to a scale factor of 0.9598, which is not very different from the scale factor of 0.9613 for the full F1 set. Thus we feel that removing a small number of problem molecules will not have adverse consequences on the calculated scale factor, but it naturally will lead to smaller $\mathrm{rms}_{\mathrm{ov}}$ values. In contrast, leaving such molecules in the analysis is likely to lead to significantly skewed scale factors.

(64) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(65) Hollas, J. M. *Modern Spectroscopy*; Wiley: Chichester, U. K., 1987.

(66) Herzberg, G. *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950.

(67) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(68) Allen, W. D.; Yamaguchi, Y.; Csaszar, A. G.; Clabo, D. A.; Remington, R. B.; Schaefer, H. F. *Chem. Phys.* **1990**, *145*, 427.

(69) Clabo, D. A.; Allen, W. D.; Remington, R. B.; Yamaguchi, Y.; Schaefer, H. F. *Chem. Phys.* **1988**, *123*, 187.

(70) Martin, J. M. L.; Lee, T. J.; Taylor, P. R.; Francois, J. P. *J. Chem. Phys.* **1995**, *103*, 2589.

(71) Duncan, J. L.; Law, M. M. *J. Mol. Spectrosc.* **1990**, *140*, 13.

(72) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

(73) In this expanded set, we excluded O_3 and PH_3, both of which are not described well by B3-LYP, with $\mathrm{rms}_{\mathrm{mol}}$ values in the range of 1.65−1.94 (O_3) and 1.35−1.98 (PH_3) kJ mol^{-1}. Their inclusion would have distorted the values of the optimum scale factors.

(74) In a small number of cases, we were unable to obtain SCF convergence, and such cases were omitted from the statistical analysis, as noted in footnotes to the relevant tables.

(75) Also omitted from the main text but included as Tables S8 and S9 of the Supporting Information are results for the HFS and HFB methods, which do not include electron correlation. We find that these methods give rise to large errors and are therefore not suitable for vibrational frequency calculations.

(76) Koch, W.; Holthausen, M. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2000.

(77) Where a range of $\mathrm{rms}_{\mathrm{mol}}$ or $\mathrm{rms}_{\mathrm{ov}}$ values is given for a particular theoretical procedure, this refers to the range of results from the 6-31G(d), 6-31+G(d,p), 6-31G(2df,p), 6-311+G(d,p), and 6-311+G(2df,p) basis sets.

(78) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(79) Note that because ZPVEs have a linear relationship with ω_i a separate detailed discussion of the effect of basis set on frequency scale factors for ZPVEs has not been included. ZPVE scale factor and $\mathrm{rms}_{\mathrm{ov}}$ values are, however, included in Table S10.

(80) Irikura, K. K.; Johnson, R. D., III.; Kacker, R. N. *J. Phys. Chem. A* **2005**, *109*, 8430.