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Harmonic frequency scaling factors for Hartree-Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2 with the Sadlej pVTZ electric property basis set

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Abstract. Scaling factors for obtaining fundamental vibrational frequencies from harmonic frequencies calculated at six of the most commonly used levels of theory have been determined from regression analysis for the polarized-valence triple-zeta (pVTZ) Sadlej electric property basis set. The Sadlej harmonic frequency scaling factors for first- and second-row molecules were derived from a comparison of a total of 900 individual vibrations for 111 molecules with available experimental frequencies. Overall, the best performers were the hybrid density functional theory (DFT) methods, Becke's three-parameter exchange functional with the Lee–Yang–Parr fit for the correlation functional (B3-LYP) and Becke's three-parameter exchange functional with Perdew and Wang's gradient-corrected correlation functional (B3-PW91). The uniform scaling factors for use with the Sadlej pVTZ basis set are 0.9066, 0.9946, 1.0047, 0.9726, 0.9674 and 0.9649 for Hartree–Fock, the Slater–Dirac exchange functional with the Vosko–Wilk–Nusair fit for the correlation functional (S-VWN), Becke's gradient-corrected exchange functional with the Lee–Yang–Parr fit for the correlation functional (B-LYP), B3-LYP, B3-PW91 and second-order Møller–Plesset theory with frozen core (MP2(fc)), respectively. In addition to uniform frequency scaling factors, dual scaling factors were determined to improve the agreement between computed and observed frequencies. The scaling factors for the wavenumber regions below 1800 cm^{-1} and above 1800 cm^{-1} are 0.8981 and 0.9097, 1.0216 and 0.9857, 1.0352 and 0.9948, 0.9927 and 0.9659, 0.9873 and 0.9607, 0.9844 and 0.9584 for Hartree–Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2(fc), respectively. Hybrid DFT methods along with the Sadlej pVTZ basis set provides reliable theoretical vibrational spectra in a cost-effective manner.

Key words: Vibrational frequencies – Scaling factors – Density functional theory – Sadlej basis set

1 Introduction

Theoretical calculations of the vibrational frequencies and spectral intensities for polyatomic species have become an invaluable chemical tool over the past decade. This can be largely attributed to the increased availability and efficiency of robust energy derivative programs, in which the first and second derivatives are computed analytically [1], and the increased power of affordable computers. These advances have pushed the applicability of first-principle investigation of molecular vibrational properties from the small-molecule domain to the treatment of reasonably large systems [2–6]. Compared to conventional ab initio methods that include electron correlation, the superior performance and cost-effectiveness of density functional theory (DFT) is particularly desirable for larger molecules [7–9] and transition-metal complexes [10, 11]. The interpretation of experimental vibrational spectra for large molecules is greatly assisted by quantum chemical predictions, particularly in the region below 1800 cm^{-1}, where the high density of states results in spectral congestion.

Observed bands can be assigned on the basis of agreement between computed harmonic frequencies and experimental frequencies; however, more reliable interpretations can be made by making use of theoretical intensities as well, which can resolve the assignment of closely spaced bands. Therefore, it is desirable for a theoretical method to provide both reliable intensities and vibrational frequencies.

Previous work comparing theoretical harmonic frequencies with observed fundamentals have shown that the calculated frequencies generally overestimate fundamental frequencies, because of the incomplete treatment of electron correlation, neglect of mechanical anharmonicity and basis set truncation effects. To improve the agreement between the predicted and observed frequencies, the computed harmonic frequencies are usually

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scaled for comparison. In the first use of scaling, separate factors were applied to stretching and bending force constants [12]. A systematic procedure with multiple scale factors was employed by Blom and Altona [13]. Various scaling strategies have been devised since these initial efforts [14–19]. The most sophisticated schemes developed by Rauhut and Pulay [18] and Baker et al. [19] use about a dozen parameters to scale force constants in internal coordinates. Simple uniform scaling achieves comparable accuracy (about 50% larger root-mean-square error), avoids any ambiguities related to the choice of internal coordinate system and can be applied to systems with partial bonding, such as transition states and clusters. This strategy is adopted in the present work.

A uniform scaling factor of 0.89 was found by Pople et al. [20] in a comparison of harmonic frequencies computed at the Hartree–Fock/3-21G level of theory to observed fundamentals. Subsequent studies comparing Hartree–Fock frequencies computed using the larger 6-31G(d) basis set and experimental fundamentals suggest very similar uniform scaling factors of 0.8929 and 0.8953 [21, 22]. DFT consistently predicts harmonic vibrational frequencies in better agreement with observed fundamentals than conventional ab initio methods. In comparisons of observed fundamentals with computed harmonics using the 6-31G(d) basis set, Scott and Radom [23] and Wong [24] obtained scaling factors of 0.9833 for the Slater–Dirac exchange functional with the Vosko–Wilk–Nusair fit for the correlation functional (S-VWN), 0.9945 for Becke's gradient-corrected exchange functional with the Lee–Yang–Parr fit for the correlation functional (B-LYP) and 0.9614 for Becke's three-parameter exchange functional with the Lee–Yang–Parr fit for the correlation functional (B3-LYP), and for conventional ab initio methods they found scale factors of 0.9427 and 0.9537 for second-order Møller–Plesset (MP2) and quadratic configuration interaction with single and doubles excitations (QCISD), respectively.

The theoretical prediction of vibrational intensities is a computationally demanding task, because of the need to represent the tail region of the molecular wavefunction [25, 26], which requires medium- to large-sized basis sets with an adequate complement of polarization and diffuse functions, and because of the need to include electron correlation. Inclusion of electron correlation was found to be essential for obtaining quantitative IR intensities [27–29]. Work in our laboratory has shown that IR intensities furnished by the hybrid DFT methods (B3-LYP and Becke's three-parameter exchange functional with Perdew and Wang's gradient-corrected correlation functional, B3-PW91) were in closest agreement with intensities obtained using a highly correlated ab initio method, QCISD [30]. Good IR intensities were achieved using medium-sized polarized basis sets augmented with a set of diffuse functions. Overall the quality of IR intensities obtained by various methods were resolved into the following order: hybrid DFT > MP2 > local DFT ≈ gradient-corrected DFT > Hartree–Fock.

The prediction of quantitative Raman intensities is more costly than the prediction of IR intensities (which require second derivatives) because they depend on the square of the polarizability derivative, which requires calculation of the third derivative of the system energy with respect to geometric coordinates and the external electric field ($\partial\alpha/\partial Q_k = \partial^3 E/\partial Q_k \partial F_i \partial F_k$). Other work in our laboratory has found that the basis set dependence of predicted Raman intensities was quite large, requiring significantly larger basis sets to obtain quantitative results than needed for IR intensities [31]. Raman vibrational intensities were found to be relatively insensitive to correlation effects at levels of theory applicable to large molecules, in marked contrast to the observed behavior of theoretical IR intensities. The quality of the basis set employed was found to be the dominant consideration in obtaining quantitative Raman intensities. We found, however, that the medium-sized Sadlej polarized-valence triple-zeta (pVTZ) electric property basis set [32–34],[1] which was fit to reproduce polarizabilities, provided excellent quantitative Raman intensities comparable to those obtained using the much larger Dunning correlation consistent aug-cc-pVTZ basis set [35–37].

Harmonic vibrational scaling factors for the most widely used theoretical methods using the Sadlej basis would be highly beneficial because of the excellent quantitative vibrational intensities provided by the Sadlej pVTZ basis set and the substantial savings it affords in computational cost. In the present work, harmonic vibrational frequencies were computed for a set of 900 individual vibrations for a diverse set of 111 first- and second-row molecules and were compared to experimental fundamental frequencies [38].[2] In this work we report harmonic frequency scaling factors computed by regression analysis, for the conventional ab initio methods, Hartree–Fock and MP2 and the local, gradient-corrected and hybrid density functional methods, S-VWN, B-LYP, B3-LYP and B3-PW91 using the Sadlej polarized basis set.

2 Methods

The calculations in this study were performed using the Gaussian 98 suite of programs [39]. Following full geometry optimizations at each level of theory, harmonic frequencies were computed analytically for Hartree–Fock, MP2 (fc) [40, 41] and the various DFT methods employed in this study. The vibrational properties were computed for the test molecules in their ground state, enforcing their respective point group symmetry. The DFT methods employed here consisted of the S-VWN local functional [42, 43], the B-LYP gradient-corrected functional [44, 45] and two hybrid functionals: B3-LYP [46] and B3-PW91 [47]. The calculations were carried out with Sadlej's pVTZ basis set, optimized for electric properties [5s,3p,2d/7s,5p,2d/3s,2p] [32–34]. Complete tables of numerical data are available on the World Wide Web [48].

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[1] Sadlej's polarized electric property basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 1.0. Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA.

[2] F1 set of molecules used previously by Pople et al. [22], Scott and Radom [23] and Wong [24] minus $AlCl_3$, BF_3, B_2H_6, BH_3CO, CH, NH, OH, SH, SiH, PH and LiF.

3 Discussion and results

When predicting molecular properties using quantum chemical methods, researchers are often faced with a trade-off between the computational cost and the quality of results furnished by the method employed. The development and the use of scaling factors for theoretical harmonic frequencies have greatly extended the practical utility of results obtained from computationally inexpensive methods. The majority of previous studies related to the present work have focused on scaling factors for a number of theoretical methods using the reasonably small Pople split-valence double-zeta basis set with one set of polarization functions on heavy atoms, 6-31G(d) [49–51]. Experience has shown that this basis set is an economical choice yielding reliable molecular geometries and harmonic frequencies that, after scaling, provide good agreement with observed fundamentals. In addition to vibrational frequencies, the theoretical prediction of complete vibrational spectra requires reliable intensities as well. Studies investigating the basis set dependence of theoretical vibrational intensities, both IR and Raman, have shown that intensities computed using the 6-31G(d) and comparably sized basis sets provide only qualitative agreement with experimental observations [26]. Recently we have shown the moderately sized Sadlej polarized electric property basis set to be an outstanding cost-effective performer in the prediction of quantitative vibrational intensities [31]. In order to increase the utility of the Sadlej basis set we determined uniform scaling factors and low- and high-frequency scaling factors for the most often used theoretical methods. The molecules comprising the test set for the work described here are shown, along with their respective point-group symmetries in Table 1. Together, they provide a set of 900 experimentally well established fundamental frequencies against which the theoretical harmonic frequencies can be tested.

3.1 Hartree–Fock

Harmonic frequencies computed at the Hartree-Fock level are known to systematically overestimate fundamental frequencies by 10–15%. There is good agreement in the literature defining a uniform harmonic frequency scaling factor for the Hartree–Fock/6-31G(d) level of theory of 0.8929–0.8953. The Sadlej pVTZ electric property basis set is roughly twice the size of the Pople 6-31G(d) basis set. The basis set dependence of theoretical harmonic frequencies is known to be modest in comparison to that of IR and Raman intensities [52]. In previous work, the Sadlej basis was shown to furnish vibrational intensities comparable to those obtained at around 10 times the computational cost, making the Sadlej basis an excellent compromise between cost and performance [31].

Table 1. Set of molecules and respective symmetry used in this study

Molecule	Symmetry	Molecule	Symmetry	Molecule	Symmetry	Molecule	Symmetry
$NClF_2$	C_s	CH_3F	C_{3v}	H_2O	C_{2v}	CH_3CH_2F	C_s
ClF_3	C_{2v}	CH_4	T_d	H_2O_2	C_2	c-C_2H_4NH	C_s
$HOCl$	C_s	CH_3OH	C_s	H_2S	C_{2v}	CH_3CH_3	D_{3d}
SiH_3Cl	C_{3v}	CH_3NH_2	C_s	H_2S_2	C_2	CH_3NNCH_3	C_{2h}
$ClNO$	C_s	CH_3SiH_3	C_{3v}	NH_3	C_{3v}	CH_3OCH_3	C_{2v}
$ClNO_2$	C_{2v}	C_2Cl_2	D_{*h}	PH_3	C_{3v}	CH_2CCHCl	C_1
$ClNS$	C_s	C_2N_2	D_{*h}	SiH_4	T_d	$HCCCH_2Cl$	C_s
NCl_2F	C_s	$HCCCl$	C_{*v}	NO_2	C_{2v}	$HCCCH_2F$	C_s
SiH_2Cl_2	C_{2v}	$HCCF$	C_{*v}	N_2O	C_{*v}	CH_2CCH_2	D_{2d}
Cl_2O	C_{2v}	$HCCH$	D_{*h}	SO_2	C_{2v}	CH_3CCH	C_{3v}
$SOCl_2$	C_s	Trans CHClCHCl	C_{2h}	O_3	C_{2v}	CH_2CHCHO	C_s
SCl_2	C_{2v}	Cis CHClCHCl	C_{2v}	SO_3	D_{3h}	CH_3CH_2CN	C_s
$SiHCl_3$	C_{3v}	CH_2CCl_2	C_{2v}	$COClF$	C_s	c-C_3H_6	D_{3h}
PCl_3	C_{3v}	Cis CHFCHF	C_{2v}	$ClCN$	C_{*v}	CH_3COCH_3	C_{2v}
HOF	C_s	Trans CHFCHF	C_{2h}	$COCl_2$	C_{2v}	$HCCCCH$	D_{*h}
SiH_3F	C_{3v}	$OCHCHO$	C_{2h}	$CSCl_2$	C_{3v}	$CH_2CHCHCH_2$	C_{2h}
ONF	C_s	CH_3CN	C_{3v}	FCN	C_{*v}	CH_3CCH_3	D_{3h}
NSF	C_s	CH_3NC	C_{3v}	COF_2	C_{2v}	H_2	D_{*h}
F_2NH	C_s	CH_3COF	C_s	CSF_2	C_{2v}	HF	C_{*v}
N_2F_2	C_{2h}	CH_2CH_2	D_{2h}	COS	C_{*v}	N_2	D_{*h}
F_2O	C_{2v}	Trans CH_2ClCH_2Cl	C_{2h}	CO_2	D_{*h}	O_2	D_{*h}
F_2SO	C_s	Gauche CH_2ClCH_2Cl	C_2	CS_2	D_{*h}	F_2	D_{*h}
S_2F_2	C_2	c-C_2H_4O	C_{2v}	$CHCl_3$	C_{3v}	$CH_2(^1A_1)$	C_{2v}
$SiHF_3$	C_{3v}	CH_3CHO	C_s	CHF_3	C_{3v}	$CH_2(^3B_1)$	C_{2v}
NF_3	C_{3v}	$HCOOCH_3$	C_s	HCN	C_{*v}	HCO	C_s
PF_3	C_{3v}	CH_3COOH	C_s	$HNCO$	C_s	$HCOOH$	C_s
HNO_3	C_s	SiH_3CCH	C_{3v}	CH_2Cl_2	C_{2v}	CH_3Cl	C_{3v}
HN_3	C_s	CH_3CH_2Cl	C_s	H_2CO	C_{2v}		

The average difference, the average absolute difference and the standard deviation from experimental data are presented in Table 2. Not surprisingly, the Hartree–Fock frequencies are in worse agreement with experimental fundamentals than the other theoretical methods considered here. This is expected, because of the neglect of electron correlation in the Hartree–Fock calculations. An important observation for the results presented in Table 2 is that the average difference and the average absolute difference are almost identical (within 3 cm^{-1}) giving excellent motivation to develop a uniform scaling factor for this level of theory. Least-squares regression analysis gives a suggested Hartree–Fock frequency scaling factor of 0.9066. This scaling factor is a little larger than the scaling factors determined for the 6-31G(d) basis set, but is comparable to scaling factors determined for larger basis sets such as 6-311G(d,p) and 6-311G(2d,p) of 0.9051 and 0.9054, respectively [23]. After scaling, the Hartree–Fock/Sadlej frequencies are in much better agreement, showing a marked decrease in the average difference, the average absolute difference and the standard deviation of around 145, 112 and 54 cm^{-1}, respectively. The effect of uniform scaling on the error in the Hartree–Fock frequencies is shown in Fig. 1. The agreement for unscaled frequencies is severely biased toward overestimation. Upon uniform scaling the distribution of errors becomes much more satisfactory, peaking around zero difference. Some of the problematic molecules for which the scaled Hartree–Fock/Sadlej frequencies were in worst agreement are NSF, F_2O, F_2 and O_3. Scott and Radom [23] have previously noted severe disagreement between Hartree–Fock frequencies and experimental fundamentals for these systems.

Given the overestimation of vibrational frequencies at the Hartree–Fock level, the inclusion of electron correlation, even at minimal levels, should improve the agreement between computed harmonic frequencies and experimental fundamentals. It has been noted that the effect of electron correlation on molecular geometries is to slightly elongate bonds, leading to a systematic decrease in force constants and, therefore, lower vibrational frequencies [53–55].

3.2 Local and gradient-corrected DFT

Over the past decade, DFT has become an extremely popular alternative to conventional correlated ab initio methods. DFT methods provide molecular properties and energetics in similar or better agreement with experimental data than methods such as MP2. Previous studies examining the performance of local and gradient-corrected DFT in computing vibrational frequencies have shown that they provide good agreement with observed fundamental frequencies. The uniform scaling factors for the S-VWN and B-LYP levels of theory with the 6-31G(d) basis set have been determined to be 0.9833 and 0.9945–0.995, respectively [23, 24, 56]. Both scaling factors are significantly closer to unity than that of Hartree–Fock, suggesting that the theoretical harmonic frequencies obtained by these methods may be used without scaling. The differences and the standard deviation for the S-VWN/Sadlej and the B-LYP/Sadlej levels of theory are shown in Table 2. In contrast to Hartree–Fock, comparisons of the average difference and the average absolute difference for these methods show that the predicted harmonic frequencies are distributed around the experimental fundamental frequencies, with S-VWN overestimating the frequencies more than B-LYP. Also both S-VWN and B-LYP have standard deviations roughly half that of Hartree–Fock. Regression analysis gives uniform scaling factors of 0.9946 and 1.0047 for S-VWN/Sadlej and B-LYP/Sadlej, respectively. As with Hartree–Fock, the scaling factors determined for the Sadlej basis set for S-VWN and B-LYP are slightly larger than those for the 6-31G(d) basis set. Scaling factors for S-VWN frequencies obtained using a larger basis set than 6-31G(d) have not been reported; however, for the B-LYP/cc-pVDZ level of theory, a uniform scaling factor of 1.00 has been suggested [57], in agreement with work presented here. After uniform scaling the predicted frequencies are better distributed around the experimental values; however, the effect is small, as expected with scaling factors so close to unity. Histograms of the errors in the S-VWN/Sadlej and the B-LYP/Sadlej frequencies are shown in Figs. 2 and 3, respectively. An immediate observation is that compared

Table 2. Scaling factors and average difference, average absolute difference and standard deviation from experimental fundamentals with the Sadlej polarized-valence triple-zeta basis set (cm^{-1})

	Hartree–Fock	S-VWN	B-LYP	B3-LYP	B3-PW91	MP2(fc)
Raw frequencies						
Average difference	146.66	−6.45	−26.61	25.87	34.64	33.09
Average absolute difference	149.39	44.17	42.37	44.69	49.12	55.77
Standard deviation	109.27	54.66	47.85	59.53	63.68	88.79
Uniform scaling						
Uniform scaling factor	0.9066	0.9946	1.0047	0.9726	0.9674	0.9649
Average difference	1.99	−14.05	−20.08	−13.27	−12.30	−17.25
Average absolute difference	36.96	43.10	41.49	33.04	33.67	41.73
Standard deviation	55.71	52.40	50.31	42.01	42.91	70.03
Dual scaling						
$< 1800\ \mathrm{cm}^{-1}$ scaling factor	0.8981	1.0216	1.0352	0.9927	0.9873	0.9844
$> 1800\ \mathrm{cm}^{-1}$ scaling factor	0.9097	0.9857	0.9948	0.9659	0.9607	0.9584
Average difference	−2.01	−2.61	−7.47	−4.60	−3.63	−8.84
Average absolute difference	37.45	35.21	30.97	25.23	26.29	31.84
Standard deviation	54.88	47.32	44.95	38.84	39.64	68.82

with Hartree–Fock/Sadlej the distribution of errors is much broader, but with fewer large errors, limiting the improvement that can be obtained by uniform scaling. S-VWN seems to underestimate vibrational frequencies as often and in similar magnitude as overestimate them and the effect of uniform scaling is very small. B-LYP tends to underestimate vibrational frequencies and uniform scaling has some effect in shifting the error distribution closer to zero. Some of the problematic molecules for which the scaled S-VWN/Sadlej and B-LYP/Sadlej frequencies were in poor agreement are NSF and NSCl.

3.3 Hybrid DFT

Previous results obtained using hybrid DFT methods and the 6-31G(d) basis set have suggested that the hybrid DFT methods are the most successful procedures for predicting vibrational frequencies in agreement with experimental fundamentals. In addition to providing harmonic frequencies that can be easily scaled for reliable prediction of fundamentals, hybrid DFT has been shown to outperform Hartree–Fock, local and gradient-corrected DFT and MP2 in predict-

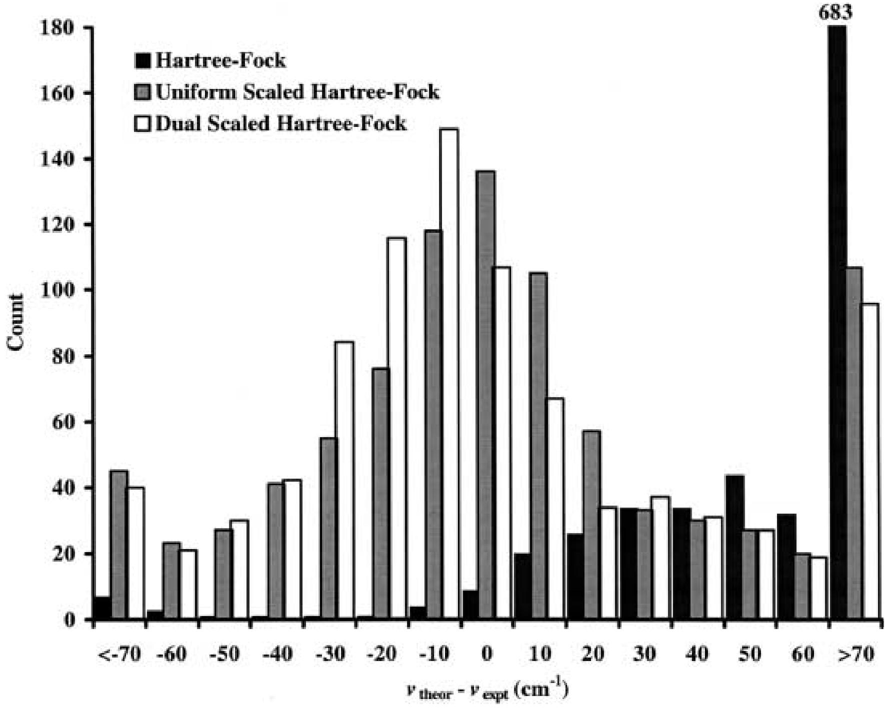

Fig. 1. Histogram of frequency differences between computed harmonics and observed fundamentals for the unscaled and scaled Hartree–Fock/Sadlej pVTZ level of theory

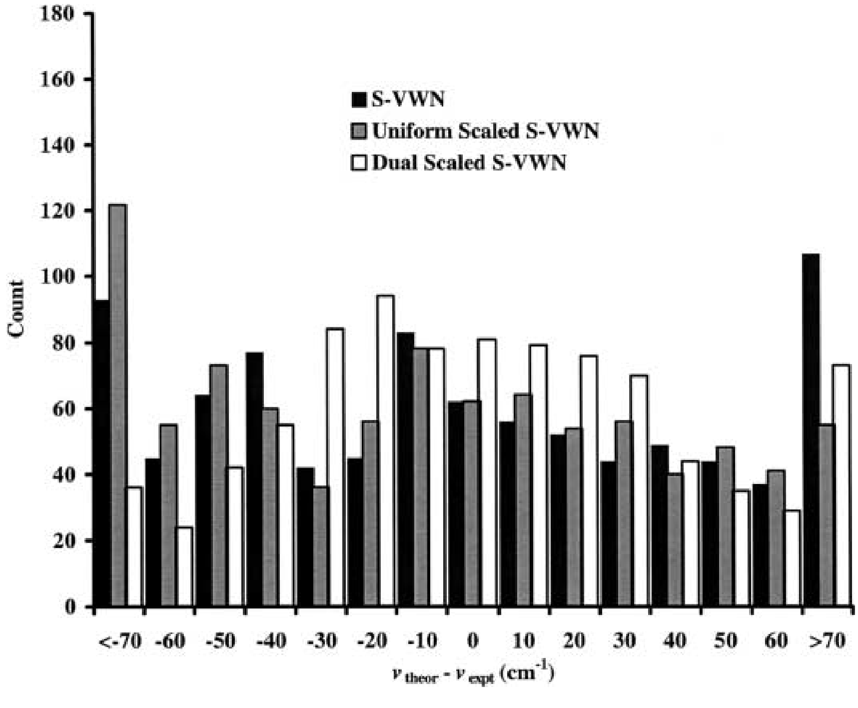

Fig. 2. Histogram of frequency differences between computed harmonics and observed fundamentals for the unscaled and scaled S-VWN/Sadlej pVTZ level of theory

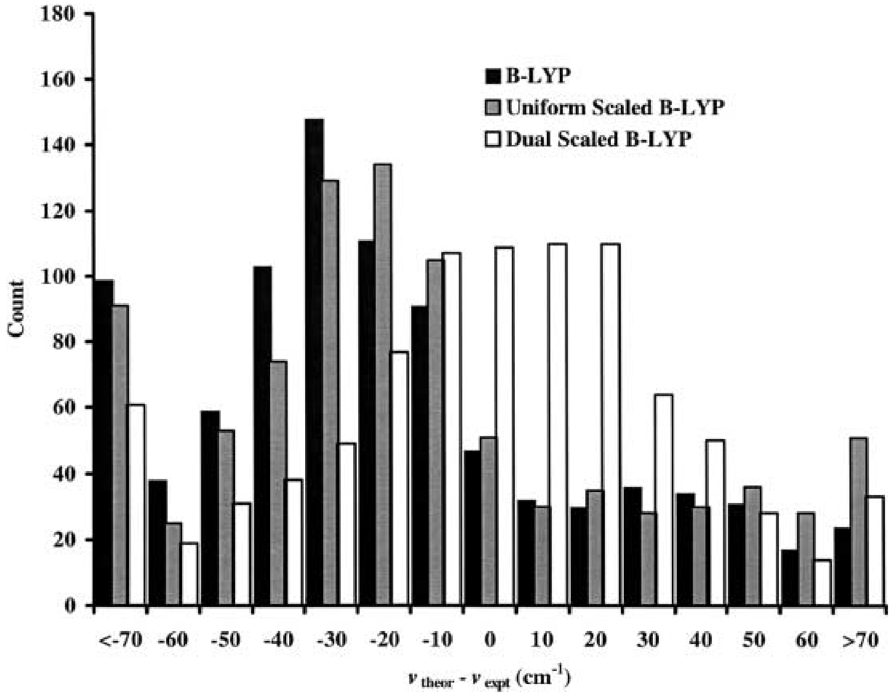

Fig. 3. Histogram of frequency differences between computed harmonics and observed fundamentals for the unscaled and scaled B-LYP/Sadlej pVTZ level of theory

ing IR and Raman intensities [30, 31]. The uniform scaling factors for the B3-LYP/6-31G(d) and B3-PW91/6-31G(d) levels of theory have been determined to be 0.9614 and 0.9573, respectively [23]. The average difference, the average absolute difference and the standard deviation for the B3-LYP and B3-PW91 methods are shown in Table 2. Comparing the average difference and the average absolute difference for these methods suggests that the predicted harmonic frequencies are distributed around the experimental numbers, with some tendency for overestimation, behavior intermediate between that observed for Hartree–Fock and the pure DFT methods. The uniform scaling factors for B3-LYP/Sadlej and B3-PW91/Sadlej have been determined to be 0.9726 and 0.9674, respectively, similar to, but a little larger than, those reported with the 6-31G(d) basis set. This new scaling factor for B3-LYP/Sadlej replaces our earlier estimate of 0.9663, computed for a much smaller set of test molecules [31]. Uniform scaling significantly decreases the average differences, the average absolute differences and the standard deviation for both methods. The effect of uniform scaling on the error distribution for the B3-LYP/Sadlej and B3-PW91/Sadlej frequencies can be seen in Figs. 4 and 5, respectively. The raw hybrid DFT frequencies have many large overestimation errors, similar to that observed for Hartree–Fock. Uniform scaling does an excellent job in diminishing the number of extreme outliers; however, the scaled distribution peaks just under zero, showing a tendency of the uniformly scaled frequencies to slightly underestimate fundamentals. As with the Hartree–Fock and the pure DFT methods, hybrid DFT calculations on the molecules NSF and NSCl showed some of the largest differences between theory and experiment.

3.4 Second-order Møller–Plesset theory

MP2 is the only conventional correlated ab initio method for which calculations on larger-sized chemical systems are feasible. Previous studies assessing the agreement between experiment and MP2 frequencies using the 6-31G(d), 6-31G(d,p) and 6-311G(d,p) basis sets have suggested uniform scaling factors of 0.9427–0.9434, 0.9370 and 0.9496, respectively [21–23]. The average difference, the average absolute difference and the standard deviation from experimental fundamentals are listed for MP2 in Table 2. The MP2 differences are very similar to those obtained using the hybrid DFT methods; however, the standard deviation is larger than for those methods. Regression analysis yields a uniform scaling factor of 0.9649 for the MP2/Sadlej level of theory, also comparable to the scaling factors determined for the hybrid DFT methods and a little closer to unity than scaling factors determined for MP2 using the smaller Pople basis sets. In previous studies using the 6-31G(d) basis set [21–23], similar behavior was observed for MP2 frequencies. The effect of scaling on the error distribution for MP2/Sadlej frequencies is shown in Fig. 6. The distribution of errors shown there resembles those for the hybrid methods described previously, with uniform scaling diminishing the number of extreme outliers and the scaled distribution peaks just under zero, showing a tendency of a uniformly scaled frequencies to slightly underestimate fundamentals. Even after uniform scaling the MP2 standard deviation seems suspiciously high in comparison to the DFT methods considered here. The apparent discrepancy in the inflated standard deviation is resolved by noting the effect of a few severe outliers. Pople and coworkers [22, 58] have pointed out that MP2 theory fails to adequately

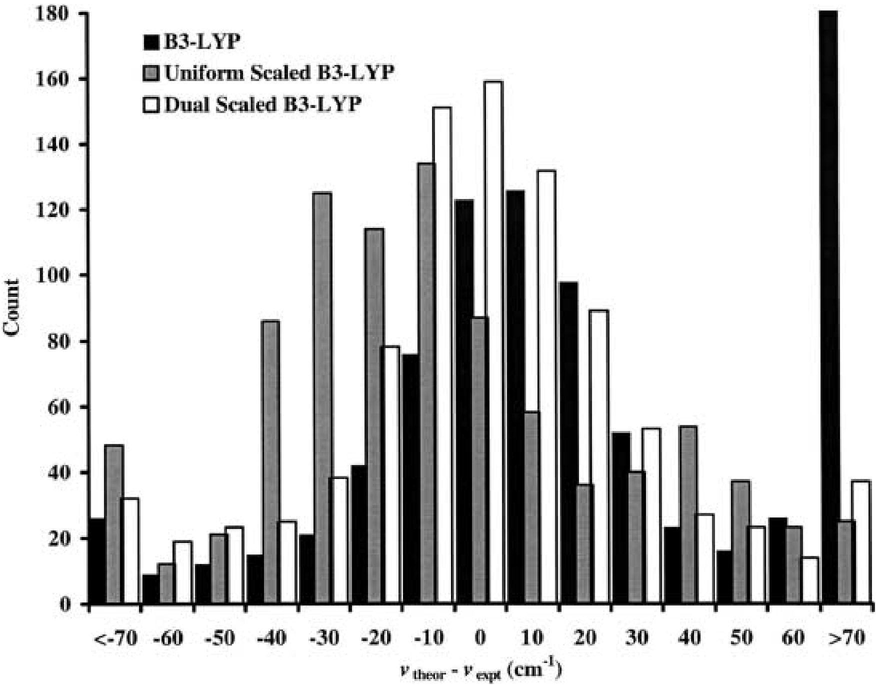

Fig. 4. Histogram of frequency differences between computed harmonics and observed fundamentals for the unscaled and scaled B3-LYP/Sadlej pVTZ level of theory

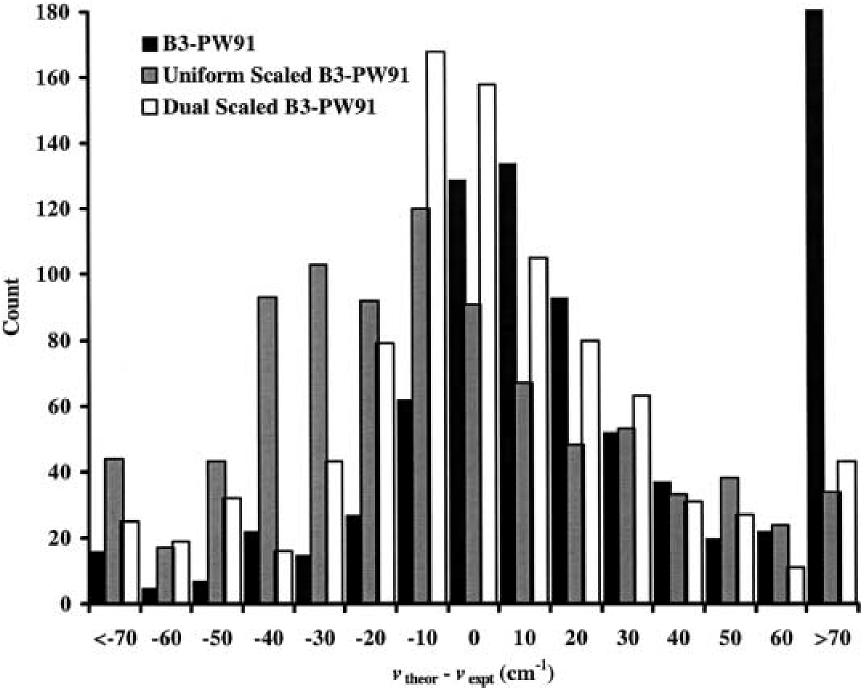

Fig. 5. Histogram of frequency differences between computed harmonics and observed fundamentals for the unscaled and scaled B3-PW91/Sadlej pVTZ level of theory

describe O_3 and NO_2 asymmetric stretching frequencies. If the most severe outliers (O_3, NO_2, NSF and NSCl) for the MP2/Sadlej frequencies are neglected, the uniform scaling factors are practically unchanged, whereas the standard deviation decreases from around 70 to 49 cm^{-1}.[3]

3.5 Dual scaling

Experimental vibrational spectra are usually discussed in terms of different wavenumber regions known to generally correspond to different types of vibrations. The upper wavenumber region, above 1800 cm^{-1}, contains vibrations composed largely of localized hydrogen stretches, whereas the mid wavenumber region contains heavy atom in-plane stretches and bends, and the low wavenumber region, the out-of-plane and torsional modes. It is in the latter two regions, below

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[3] MP2(fc) calculations on C_2Cl_2 with the Sadlej basis set resulted in one imaginary frequency. Subsequent calculations using the 6-31G(d) basis set also gave one imaginary frequency, suggesting an inherent weakness in MP2 theory to adequately describe this molecule.

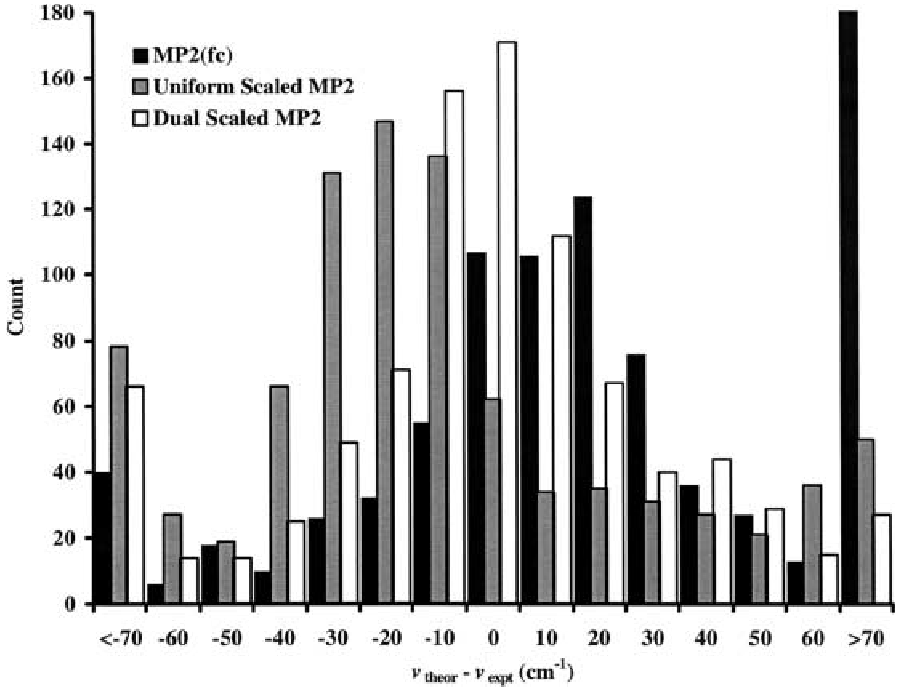

Fig. 6. Histogram of frequency differences between computed harmonics and observed fundamentals for the unscaled and scaled MP2/Sadlej pVTZ level of theory

1800 cm^{-1} (the fingerprint region), where quantum chemical prediction can be the most useful in making vibrational band assignments that may not be otherwise interpretable. Also, high-energy modes can be expected to be more anharmonic, leading to greater errors because of the harmonic approximation. To investigate the utility of separate scaling factors (dual scaling) for the two ranges < 1800 cm^{-1} and > 1800 cm^{-1}, we reanalyzed the agreement between the theoretical harmonic frequencies and the experimental fundamentals for these two ranges. The dual scaling factors for the levels of theory considered here using the Sadlej pVTZ basis set are listed in Table 2. An interesting first observation is in comparing dual scaling factors: the two pure DFT methods, S-VWN and B-LYP, tend to underestimate the low-frequency vibrations and tend to overestimate the high-frequency vibrations. The difference between the < 1800 cm^{-1} and the > 1800 cm^{-1} scale factors are approx. $+3\%$ for correlated methods and approx -1% for Hartree–Fock. The dual scaling procedure does an excellent job in improving the error distribution between the scaled theoretical frequencies and experimental fundamental frequencies. The dual scaled error distributions are peaked around zero and the distributions are more symmetric, compared with the raw and uniform scaled frequency errors. The Hartree–Fock agreement is the least affected by dual scaling, whereas the DFT methods and MP2 share increased agreement with experiment. The effect of dual scaling on the error distributions is evident from Figs. 1–6. All methods show an improved error distribution from the raw and uniform scaled data. In particular, the histograms for the hybrid DFT methods, B3-LYP and B3-PW91, and MP2 show a marked improvement using dual scaling.

4 Conclusions

The purpose of this work was to determine harmonic frequency scaling factors for use with the Sadlej electric property basis set, which is known to provide excellent vibrational intensities in a cost-effective fashion. Uniform scaling factors were determined through least-squares analysis for the Hartree–Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2 levels of theory. In addition to uniform scaling factors, dual scaling factors were determined which were shown to favorably increase the agreement between computed harmonic frequencies and experimental fundamentals. The hybrid DFT methods, B3-LYP and B3-PW91, were found to be most reliable for the prediction of vibrational frequencies, outperforming MP2 at significantly less cost. For the prediction of vibrational spectra the use of hybrid DFT methods along with the Sadlej pVTZ basis set is cost-effective and yields excellent results for both frequencies and intensities.

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