Harmonic Vibrational Frequencies: Scaling Factors for HF, B3LYP, and MP2 Methods in Combination with Correlation Consistent Basis Sets

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A least-squares approach has been used to determine multiplicative scaling factors for harmonic vibrational frequencies to facilitate comparison with experimentally observed frequencies. The harmonic frequencies were calculated using several of the most popular quantum chemical methods (HF, MP2, and B3LYP) and the correlation consistent family of basis sets (cc-pV*x*Z and aug-cc-pV*x*Z, where $x = \mathrm{D}(2)$, T(3), or Q(4)). Calculations were performed on 41 organic molecules for which fundamental frequencies are well established. When the derived scaling factors are applied, the percentage of calculated frequencies that deviate less than 3% from the experimental frequencies is 93−97% for B3LYP and 88−92% for MP2 when quadruple-ζ level basis sets are used. Similarly, scaling factors were determined for computing the vibrational components of the thermal contributions to enthalpy and entropy. An additional set of molecules was used in calculating scaling factors for the zero-point vibrational energy.

I. Introduction

Computational chemistry has become an important tool to aid in molecular identification by vibrational spectroscopy. Calculation of vibrational frequencies by ab initio molecular orbital (MO) or density functional methods can help in the interpretation of experimental spectra and is particularly useful for reliable assignments of the fundamental vibrational frequencies.

Unfortunately, calculated vibrational frequencies usually overestimate the experimental fundamentals. This overestimation is due to three factors: (1) the overall neglect of anharmonicity, (2) an incomplete description of electron correlation due to the use of an incomplete basis set, and (3) an approximate method used to solve the Schrödinger equation. The second factor arises because the computational cost for methods including electron correlation increases rapidly as the number of basis functions increases, preventing an advanced theoretical treatment for all but the very smallest of molecules.

Earlier work has demonstrated the uniformity of the overestimation of the vibrational frequencies and has shown the usefulness of global, multiplicative scaling factors for a large range of ab initio method and basis set combinations. One of the earliest global scaling factors was determined by Pople et al. for HF/3-21G where a 12% difference between calculated and experimental frequencies was observed.[1] The scaling factor was determined to be 0.8929 (the reciprocal of 1.12) and is used in practice as 0.89. In later work, Hehre et al.[2] determined a scaling factor for HF/6-31G(d) that was close to the value found by Pople et al.[1] More recently, in density functional theory (DFT) studies, Rauhut and Pulay determined the scaling factor for B3LYP/6-31G(d) to be 0.990.[3] Scott and Radom have done an extensive study of semiempirical, ab initio, and DFT methods with a series of Pople type basis sets.[4] They found the smallest overall error for their method and basis set combinations for BLYP/6-311G(*df,p*) frequencies, with a scaling factor of 0.9986. In 2001, Schlegel et al.[5] found scaling factors for DFT and ab initio methods with the Sadlej pVTZ basis set. They found a substantial deviation between the computed frequencies at the Hartree−Fock level (which required a scaling factor of 0.8951) and the fundamental frequencies. When these scaling factors are applied to calculated vibrational frequencies, the error relative to the experimental fundamental frequencies is significantly reduced compared to the errors arising from the raw (unscaled) theoretical data.

Despite the availability of scaling factors for a large number of method and basis set combinations, no global scaling factors are available for methods in combination with the correlation consistent basis sets. The correlation consistent basis sets are currently one of the most widely used family of basis sets due to their convergent behavior for a range of properties with respect to increasing basis set size.[6−11] The behavior is systematic to the degree that a number of formulas have evolved which enable property descriptions to be extrapolated toward the complete basis set (CBS) limit,[12] the limit at which no further improvement in basis set is possible, and any remaining error is due to the method choice alone. Though numerous properties are regularly convergent, limited testing implied that calculated vibrational frequencies are not among them. Computer time requirements generally preclude calculations with basis sets

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larger than the cc-pVDZ or cc-pVTZ sets for systems such as organic molecules with approximately 10−20 heavy atoms. At this level, there can still be significant deviations from experimental frequencies.

In this work, we investigate the deviation of vibrational frequencies computed with several quantum chemical methods (HF, B3LYP, and MP2) in combination with the correlation consistent basis sets from experimental fundamental frequencies for a set of 41 common organic molecules. This set of molecules was chosen from earlier work by Healy and Holder where frequency scaling factors were developed for AM1.[13] We develop global frequency scaling factors, as well as scaling factors for calculating the vibrational components of the thermal contributions to enthalpy and entropy and for the zero-point vibrational energy.

II. Computational Methods

All calculations were done with the Gaussian 98 software package.[14] Three levels of theory were used including HF, B3LYP, and MP2 in combination with two families of correlation consistent basis sets, the standard polarized valence basis sets, cc-pV*x*Z, and the polarized valence basis sets augmented with diffuse functions, aug-cc-pV*x*Z, where $x = \mathrm{D}(2)$, T(3), or Q(4).

III. Theoretical Procedures

A. Frequencies. As done in earlier work by Scott and Radom,[4] frequency scaling factors were determined using a least-squares method. The residuals, Δ, were minimized as

$$\Delta = \sum_{i}^{\text{all}} (\lambda\omega_i^{\text{calc}} - \nu_i^{\text{expt}})^2 \tag{1}$$

where ω_i^{calc} is the *i*th harmonic frequency resulting from calculation, ν_i^{expt} is the corresponding experimental fundamental frequency, and the frequencies are given in units of cm^{-1}. λ represents the optimum global scaling factor obtained from the modification of eq 1 as

$$\lambda = \sum_{i}^{\text{all}} \omega_i^{\text{calc}}\, \nu_i^{\text{expt}} / \sum_{i}^{\text{all}} (\omega_i^{\text{calc}})^2 \tag{2}$$

To determine the overall root-mean-square (rms) error, a minimized residual must first be determined for each mode where

$$\Delta_{\text{min}} = (\lambda\omega_i^{\text{calc}} - \nu_i^{\text{expt}})^2 \tag{3}$$

The overall rms error is then determined by

$$\text{rms} = \Big(\sum_{1}^{n_{\text{mol}}} \Delta_{\text{min}}/n_{\text{all}}\Big)^{1/2} \tag{4}$$

where n_{all} represents the total number of modes of all molecules considered in this study.

The procedure, as outlined above, works well for higher frequencies. For some thermochemical properties, however, the contribution of lower frequencies dominates. As shown in earlier work, an inverse scaling factor determination is more suitable. The process is similar to the above description and is summarized below. Again, this is an approach used by Scott and Radom for lower frequencies. Inverse frequency scaling factors were obtained by first determining the residual Δ

$$\Delta = \sum_{i}^{\text{all}} \left(\frac{1}{\lambda\omega_i^{\text{calc}}} - \frac{1}{\upsilon_i^{\text{expt}}}\right)^2 \tag{5}$$

and then solving

$$\lambda = \sum_{i}^{\text{all}} \left(\frac{1}{\omega_i^{\text{calc}}}\right)^2 / \sum_{i}^{\text{all}} \frac{1}{\omega_i^{\text{calc}}\, \upsilon_i^{\text{expt}}} \tag{6}$$

The root-mean-square error has been determined as illustrated in eqs 3 and 4.

B. Thermodynamic Properties: Enthalpy and Entropy. Enthalpic and entropic thermal contributions to thermodynamic properties depend on vibrational frequencies as shown in eqs 7 and 8, respectively.

$$\Delta H_{\text{vib}}(T) = Nhc \sum_{i} \frac{\tilde{\nu}_i}{e^{\mu_i} - 1} \tag{7}$$

$$S_{\text{vib}}(T) = R \sum \left[\frac{\mu_i}{e^{\mu_i} - 1} - \ln(1 - e^{-\mu_i})\right] \tag{8}$$

where *N* is Advogadro's number, *h* is Planck's constant, *c* is the speed of light, *R* is the gas constant, and

$$\mu_i = \frac{hc\tilde{\nu}_i}{kT} \tag{9}$$

In eq 9, *k* is Boltzmann's constant, *T* is temperature, and $\tilde{\nu}_i$ is the *i*th fundamental frequency in cm^{-1}.

As vibrational frequencies are closely linked to thermodynamic properties, there is a need to correct for the corresponding differences in vibrational enthalpy and entropy. Again, a least-squares approach was used to determine a scaling factor for the enthalpic contribution by minimizing the residual

$$\Delta = \sum_{i}^{\text{all}} [\Delta H_{\text{vib}}^{\text{calc}}(T)_i - \Delta H_{\text{vib}}^{\text{expt}}(T)_i]^2 \tag{10}$$

The scaling factor is brought into the equation in the following term:

$$\Delta H_{\text{vib}}^{\text{calc}}(T) = \frac{\lambda\omega_i^{\text{calc}}}{e^{\mu_i^{\text{calc}}} - 1} \tag{11}$$

where

$$\mu_i^{\text{calc}} = \frac{h\lambda\omega_i^{\text{calc}}}{kT} \tag{12}$$

and units for the enthalpic contribution are kJ/mol.

The entropy of vibration can be found using a similar procedure.

$$\Delta = \sum_{i}^{\text{all}} [S_{\text{vib}}^{\text{calc}}(T)_i - S_{\text{vib}}^{\text{expt}}(T)_i]^2 \tag{13}$$

where

$$S_{\text{vib}}^{\text{calc}}(T) = \frac{\lambda\omega_i^{\text{calc}}}{e^{\mu_i^{\text{calc}}} - 1} - \ln(1 - e^{-\mu_i^{\text{calc}}}) \tag{14}$$

and the entropy is in J/(mol K).

TABLE 1: High-Frequency Scaling Factors and Overall Root-Mean-Square Errors (rms)[a]

level of theory	basis set	scaling factor[b]	rms (cm^{-1})
HF	cc-pVDZ	0.9084	44
	cc-pVTZ	0.9115	47
	cc-pVQZ	0.9111	49
	aug-cc-pVDZ	0.9110	43
	aug-cc-pVTZ	0.9119	46
	aug-cc-pVQZ	0.9114	47
B3LYP	cc-pVDZ	0.9709	45
	cc-pVTZ	0.9691	35
	cc-pVQZ	0.9751	36
	aug-cc-pVDZ	0.9698	49
	aug-cc-pVTZ	0.9676	37
	aug-cc-pVQZ	0.9705	34
MP2	cc-pVDZ	0.9543	52
	cc-pVTZ	0.9575	43
	cc-pVQZ	0.9624	44
	aug-cc-pVDZ	0.9604	56
	aug-cc-pVTZ	0.9557	50
	aug-cc-pVQZ	0.9601	63

[a] From the original 42 molecule set used in this study and derived from ref 13, only 41 molecules have been used. Acetone was eliminated from this study because of the particularly poor agreement between the calculated and fundamental low frequencies. [b] Though it has become common to report frequency scaling factors to four places past the decimal, due to the accuracy of frequencies, practical use of the scaling factors should include three places past the decimal, at most.

C. Thermodynamic Properties: Zero-Point Vibrational Energy. It has been well-established that different scaling factors are needed for zero-point vibrational energies (ZPVEs) than for vibrational frequencies. In its simplest formulation, the ZPVE can be given by

$$E(\text{ZPVE}) = \frac{1}{2}\sum h\omega_i^{\text{expt}} \tag{15}$$

so using the same scaling factor for ZPVEs and frequencies might seem logical, but the above expression is not rigorous, as it does not include the effects of anharmonicities. Using ZPVEs determined by this process can result in dramatic errors in the determination of bond energies or atomization energies. Schaefer, for example, showed that errors in ZPVEs for systems such as C_2H_6 can be as large as the target accuracy.[15]

Considering the effects of anharmonicities would result in improved ZPVEs. Unfortunately, for large molecules such as those described previously, the determination of accurate force fields is extremely difficult for both spectroscopists and quantum chemists. Therefore, to determine appropriate scaling factors for ZPVEs, we use a set of 24 small molecules studied by Schaefer and co-workers in 1991,[15] because the force fields of these molecules are believed to be relatively accurate.

Again, a linear least-squares fit is used to compare experimentally derived ZPVEs with those determined from the ab initio and DFT calculations.

IV. Results and Discussion

To determine appropriate frequency scaling factors, a distinction between high and low frequencies was made. Several truncation points between "high" and "low" frequencies were examined including 1000, 1200, 1500, and 1800 cm^{-1}. Scaling factors and overall root-mean-square errors were determined for each method and basis set combination, and it was discovered that a cutoff value of 1000 cm^{-1} presented the lowest overall error.

In Table 1, frequency scaling factors and overall root-mean-square errors are reported for frequencies over 1000 cm^{-1}. The HF scaling factors differ very little upon increasing basis set size and are also similar to values obtained in earlier studies for basis sets of comparable size.[2−4] This is not surprising because the correlation consistent basis sets were developed specifically for methods that use electron correlation, whereas the HF method, of course, includes no contribution from electron correlation. Overall, a scaling factor of 0.91 is recommended for HF. For B3LYP and MP2, there is a slight fluctuation in the optimal scaling factors as basis set size increases. The B3LYP scaling factor (0.97) is larger than the MP2 scaling factor (0.96), indicating a slightly higher overestimation of raw frequencies by MP2 than for B3LYP as compared with experiment.

TABLE 2: Percent Error of Calculated High Frequencies after Scaling within a Given Error Range for HF

% error	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	cc-pVQZ	aug-cc-pVQZ
0−1	38.9	38.7	31.8	32.5	31.8	30.7
1−2	22.2	24.3	28.8	27.6	28.5	30.7
2−3	11.8	10.8	9.2	11.1	10.6	10.1
3−4	6.8	7.8	8.3	6.6	7.3	6.6
4−5	6.1	6.1	5.4	6.1	5.9	6.8
5−6	4.7	3.5	5.7	5.0	4.0	4.5
6−7	2.1	2.1	2.6	2.6	3.3	2.6
7−8	1.7	2.1	2.1	2.1	2.4	1.9
8−9	1.4	1.2	1.9	1.9	2.1	1.4
9−10	0.7	0.5	0.7	0.7	0.5	1.2
>10	3.5	2.8	3.5	3.8	3.5	3.5

TABLE 3: Percent Error of Calculated High Frequencies after Scaling within a Given Error Range for B3LYP

% error	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	cc-pVQZ	aug-cc-pVQZ
0−1	50.4	51.7	53.2	58.1	68.1	79.4
1−2	16.8	22.4	39.1	34.1	20.6	11.3
2−3	15.6	14.0	3.5	3.2	8.5	2.3
3−4	10.2	4.2	1.4	1.9	1.4	1.4
4−5	0.7	4.2	1.4	1.4	0.0	0.7
5−6	0.7	0.0	0.0	0.0	0.0	2.1
6−7	2.1	0.7	0.0	0.0	0.7	1.4
7−8	0.0	0.7	0.7	0.7	0.0	0.7
8−9	0.7	0.0	0.0	0.7	0.0	0.0
9−10	0.7	0.7	0.7	0.0	0.7	0.7
>10	2.1	1.4	0.0	0.0	0.0	0.0

TABLE 4: Percent Error of Calculated High Frequencies after Scaling within a Given Error Range for MP2

% error	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	cc-pVQZ	aug-cc-pVQZ
0−1	27.9	30.6	35.5	43.8	64.4	69.1
1−2	22.6	28.8	19.2	17.6	22.8	14.5
2−3	18.6	19.4	14.1	15.6	4.8	4.8
3−4	15.0	10.7	14.1	10.8	2.4	4.7
4−5	4.9	3.5	10.8	10.1	0.0	0.7
5−6	2.7	1.4	3.5	0.0	0.7	2.7
6−7	2.7	0.0	1.4	1.4	1.4	1.4
7−8	1.4	1.4	0.7	0.0	2.1	0.7
8−9	1.4	1.4	0.0	0.0	0.7	0.0
9−10	0.7	1.4	0.0	0.0	0.0	0.7
>10	2.1	1.4	0.7	0.7	0.7	0.7

Tables 2−4 report the percentage of calculated frequencies within a given error range of experiment after the scaling factors have been applied to the computed results for the HF, B3LYP, and MP2 methods, respectively. For MP2/cc-pVQZ and MP2/aug-cc-pVQZ, 88−92% of the high-end frequencies are within 3% of experiment after scaling. For B3LYP, this value is slightly higher, with 93−97% of the high-end frequencies in this range when either quadruple-ζ level basis set is used.

In Table 5, low-frequency scaling factors and overall root-mean-square errors are reported. The scaling factor of 0.89 works best for HF when combined with the cc-pV*x*Z and aug-

TABLE 5: Low-Frequency Scaling Factors and Overall Root-Mean-Square Errors (rms) in 10^{-5} cm

level of theory	basis set	scaling factor	rms
HF	cc-pVDZ	0.8956	33
	cc-pVTZ	0.8925	35
	cc-pVQZ	0.8924	35
	aug-cc-pVDZ	0.9034	31
	aug-cc-pVTZ	0.8934	35
	aug-cc-pVQZ	0.8926	35
B3LYP	cc-pVDZ	0.9807	12
	cc-pVTZ	0.9876	9
	cc-pVQZ	0.9873	8
	aug-cc-pVDZ	1.0022	9
	aug-cc-pVTZ	0.9891	9
	aug-cc-pVQZ	0.9852	8
MP2	cc-pVDZ	1.0752	54
	cc-pVTZ	1.0638	53
	cc-pVQZ	1.0500	50
	aug-cc-pVDZ	1.0999	52
	aug-cc-pVTZ	1.0634	52
	aug-cc-pVQZ	1.0698	47

TABLE 6: Scaling Factors for the Computation of Thermal Contributions to Enthalpy at 298.15 K and Overall Root-Mean-Square Errors (rms) in kJ/mol

level of theory	basis set	scaling factor	rms
HF	cc-pVDZ	1.1254	0.039
	cc-pVTZ	1.1278	0.043
	cc-pVQZ	1.1284	0.042
	aug-cc-pVDZ	1.1169	0.038
	aug-cc-pVTZ	1.1259	0.042
	aug-cc-pVQZ	1.1272	0.042
B3LYP	cc-pVDZ	0.9784	0.058
	cc-pVTZ	0.9854	0.054
	cc-pVQZ	0.9872	0.053
	aug-cc-pVDZ	0.9789	0.057
	aug-cc-pVTZ	0.9867	0.055
	aug-cc-pVQZ	0.9859	0.052
MP2	cc-pVDZ	0.9796	0.058
	cc-pVTZ	0.9907	0.056
	cc-pVQZ	0.9957	0.055
	aug-cc-pVDZ	0.9473	0.058
	aug-cc-pVTZ	0.9901	0.056
	aug-cc-pVQZ	0.9658	0.056

cc-pV*x*Z basis sets, where $x = \mathrm{T}(3)$ and Q(4). A slightly higher value, 0.90, is recommended for the double-ζ basis sets. Scaling factor values from 0.98 to 1.00 are recommended for B3LYP. For MP2, all of the scaling factors are over 1.00, ranging from 1.05 to 1.10.

Thermodynamic scaling factors for the contributions to enthalpy and entropy are reported in Tables 6 and 7, respectively. For HF, the enthalpy contributions are underestimated for all basis sets. There is slight fluctuation in the scaling factors needed for B3LYP and MP2 enthalpy contributions with the cc-pV*x*Z basis sets. A factor of 0.98 is needed at the double-ζ level, whereas 0.99 should be used at the triple- and quadruple-ζ levels. The fluctuation in scaling factors is more significant for MP2 when the aug-cc-pV*x*Z basis sets are used. For the entropy contributions, the B3LYP scaling factors are slightly larger than the MP2 scaling factors.

In Table 8, scaling factors for zero-point vibrational energies and corresponding rms errors are reported. The MP2 and B3LYP scaling factors are quite similar; they range from 0.97 to 0.99 and are closer to 1.00 for the larger basis sets. As expected, the scaling factors are slightly above the scaling factors obtained for frequencies.

TABLE 7: Scaling Factors for the Computation of Thermal Contributions to Entropy at 298.15 K and Overall Root-Mean-Square Errors (rms) in kJ/mol

level of theory	basis set	scaling factor	rms
HF	cc-pVDZ	1.1370	0.21
	cc-pVTZ	1.1363	0.21
	cc-pVQZ	1.1370	0.22
	aug-cc-pVDZ	1.1254	0.21
	aug-cc-pVTZ	1.1342	0.22
	aug-cc-pVQZ	1.1352	0.22
B3LYP	cc-pVDZ	0.9475	0.34
	cc-pVTZ	0.9576	0.32
	cc-pVQZ	0.9586	0.32
	aug-cc-pVDZ	0.9486	0.33
	aug-cc-pVTZ	0.9538	0.32
	aug-cc-pVQZ	0.9673	0.31
MP2	cc-pVDZ	0.9379	0.24
	cc-pVTZ	0.9477	0.23
	cc-pVQZ	0.9575	0.22
	aug-cc-pVDZ	0.9049	0.23
	aug-cc-pVTZ	0.9467	0.23
	aug-cc-pVQZ	0.9264	0.22

TABLE 8: Scaling Factors for Zero-Point Vibrational Energy (ZPVE) and Overall Root-Mean-Square Errors (rms) in kcal/mol

level of theory	basis set	scaling factor	rms
HF	cc-pVDZ	0.9204	0.34
	cc-pVTZ	0.9213	0.43
	cc-pVQZ	0.9202	0.34
	aug-cc-pVDZ	0.9232	0.35
	aug-cc-pVTZ	0.9216	0.34
	aug-cc-pVQZ	0.9211	0.35
B3LYP	cc-pVDZ	0.9689	0.34
	cc-pVTZ	0.9764	0.28
	cc-pVQZ	0.9854	0.25
	aug-cc-pVDZ	0.9787	0.32
	aug-cc-pVTZ	0.9867	0.30
	aug-cc-pVQZ	0.9884	0.27
MP2	cc-pVDZ	0.9784	0.36
	cc-pVTZ	0.9832	0.31
	cc-pVQZ	0.9943	0.28
	aug-cc-pVDZ	0.9675	0.34
	aug-cc-pVTZ	0.9830	0.29
	aug-cc-pVQZ	0.9959	0.27

V. Conclusions

Multiplicative scaling factors for vibrational frequencies and thermodynamics properties were determined for the correlation consistent basis sets (cc-pV*x*Z and aug-cc-pV*x*Z where $x = \mathrm{D}$, T, or Q) with the HF, B3LYP, and MP2 methods by using least-squares fitting methods. Frequency scaling factors for the HF method are independent of the basis set to two decimal places, whereas scaling factors for B3LYP and MP2 are slightly more sensitive to basis set selection. Over 97% of scaled B3LYP frequencies over 1000 cm^{-1} resulted in a percent error less than 3%, whereas approximately 92% of the scaled MP2 frequencies have a percent error less than 3% at the quadruple-ζ level of basis set.

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Supporting Information Available: Harmonic frequencies calculated using HF (Table 1S), B3LYP (Table 2S), and MP2 (Table 3S) with the correlation consistent basis sets and their respective mode assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

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