Harmonic Vibrational Frequencies: An Evaluation of Hartree−Fock, Møller−Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors

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Scaling factors for obtaining fundamental vibrational frequencies, low-frequency vibrations, zero-point vibrational energies (ZPVE), and thermal contributions to enthalpy and entropy from harmonic frequencies determined at 19 levels of theory have been derived through a least-squares approach. Semiempirical methods (AM1 and PM3), conventional uncorrelated and correlated ab initio molecular orbital procedures [Hartree−Fock (HF), Møller−Plesset (MP2), and quadratic configuration interaction including single and double substitutions (QCISD)], and several variants of density functional theory (DFT: B-LYP, B-P86, B3-LYP, B3-P86, and B3-PW91) have been examined in conjunction with the 3-21G, 6-31G(d), 6-31+G(d), 6-31G-(d,p), 6-311G(d,p), and 6-311G(df,p) basis sets. The scaling factors for the theoretical harmonic vibrational frequencies were determined by a comparison with the corresponding experimental fundamentals utilizing a total of 1066 individual vibrations. Scaling factors suitable for low-frequency vibrations were obtained from least-squares fits of inverse frequencies. ZPVE scaling factors were obtained from a comparison of the computed ZPVEs (derived from theoretically determined harmonic vibrational frequencies) with ZPVEs determined from experimental harmonic frequencies and anharmonicity corrections for a set of 39 molecules. Finally, scaling factors for theoretical frequencies that are applicable for the computation of thermal contributions to enthalpy and entropy have been derived. A complete set of recommended scale factors is presented. The most successful procedures overall are B3-PW91/6-31G(d), B3-LYP/6-31G(d), and HF/6-31G(d).

1. Introduction

The determination of vibrational frequencies by ab initio computational methods is becoming increasingly important in many areas of chemistry. One such area is the identification of experimentally observed reactive intermediates for which the theoretically predicted frequencies can serve as fingerprints. Another important area is the derivation of thermochemical and kinetic information through statistical thermodynamics.

Ab initio 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. Thus, for example, Hartree−Fock (HF) theory tends to overestimate vibrational frequencies because of improper dissociation behavior, a shortcoming that can be partially compensated for by the explicit inclusion of electron correlation.

The overestimation of ab initio harmonic vibrational frequencies is, however, found to be relatively uniform, and as a result generic frequency scaling factors are often applied. Good overall agreement between the scaled theoretical harmonic frequencies and the anharmonic experimental frequencies can then usually be obtained. The determination of appropriate scale factors for estimating experimental fundamental frequencies from theoretical harmonic frequencies has received considerable attention in the literature.[2−11]

Semiempirical methods, such as AM1[12] and PM3,[13] are potentially attractive for the computation of vibrational frequencies because of their inherent low computational cost. However, there has been little systematic work reported on the performance of such methods for the prediction of vibrational frequencies. The most comprehensive study to date is an AM1 investigation by Healy and Holder[2] on 42 common organic molecules in which the computed harmonic frequencies were found to differ from experiment by an average of 10.4%. We are unaware of any such study for the PM3 method.

Pople et al.[3] found that the harmonic vibrational frequencies calculated at HF/3-21G for a set of 38 molecules (477 frequencies) had a mean ω(3-21G)/$\tilde{\nu}$(expt) ratio of 1.123, which suggested that this level of theory overestimates frequencies by about 12%. A scaling factor of 0.89 for theoretical HF/3-21G harmonic frequencies was proposed as being appropriate for predictive purposes. Hehre et al.[4] determined from an HF/6-31G(d) study of 36 molecules a mean percentage deviation of theoretical harmonic frequencies from experimental fundamentals of about 13%, similar to the findings of Pople et al.[3] for HF/3-21G. An HF/6-31G(d) theoretical frequency scaling factor of 0.8929 has been widely used in theoretical thermochemical studies.[14]

Hehre et al.[4] also determined that the MP2-fu/6-31G(d) method gave mean percentage deviations of theoretical harmonic frequencies from experimental fundamentals of about 7%. Such an error indicates that an appropriate scale factor for MP2-fu/6-31G(d) theoretical frequencies would be 0.921. In a later study, DeFrees and McLean[5] found somewhat larger scale factors (of 0.96 for first-row molecules and 0.94 for second-row molecules) by determining an average of the experimental/theoretical frequency ratios for individual modes.

Recently, we determined the scale factors for the HF/6-31G-(d) and MP2-fu/6-31G(d) methods using a set of 122 molecules (1066 frequencies) and a least-squares approach.[6] We computed an optimum HF/6-31G(d) frequency scale factor of 0.8953, very

Harmonic Vibration Frequencies

J. Phys. Chem., Vol. 100, No. 41, 1996 **16503**

similar to the previous standard value of 0.8929, and recommended that the standard value remain unchanged. A scale factor appropriate for frequencies computed at the MP2-fu/6-31G(d) level of theory (0.9427) was also determined, which lies between the values proposed by Hehre[4] and DeFrees.[5] We also found that, even after removing some exceptionally poorly predicted frequencies for O_3 and NO_2, the overall root-mean-square (rms) error for the MP2-fu/6-31G(d) method was only slightly smaller than the overall rms error for the HF/6-31G(d) level of theory.

Some work has been presented in the literature on harmonic vibrational frequencies determined with more sophisticated correlated methods.[15−18] These studies have, however, been generally limited to small polyatomic molecules. Procedures such as QCISD, CCSD, and CCSD(T) have been shown by several researchers to provide excellent agreement with experimental harmonic frequencies when used in conjunction with a variety of basis sets (double zeta plus polarization and larger).[15−18] While the computational cost of such procedures is very expensive relative to that for HF or MP2, recent and continuing improvements in raw computer speed together with more efficient programs make these methods increasingly feasible.

The advent of density functional theory (DFT) has provided an alternative means of including electron correlation in the study of the vibrational frequencies of moderately large molecules.[19] Of the myriad of DFT functionals that are available today, perhaps the most prominent are B-LYP and B3-LYP. B-LYP uses a combination of the Becke exchange functional[20] (B) coupled with the correlational functional of Lee, Yang, and Parr (LYP),[21] while the hybrid B3-LYP procedure uses Becke's three-parameter exchange functional (B3),[22] as slightly modified by Stephens et al.,[23] in combination with the LYP correlation functional.

Pople et al.[24] have shown that B-LYP/6-31G(d) *harmonic* vibrational frequencies reproduce observed *fundamentals* with surprising accuracy. They found, for example, an average error of only 13 cm^{-1} for a small set of molecules with up to three heavy atoms. The same set of molecules gave average errors of 243, 138, and 95 cm^{-1} for the (unscaled) HF/6-31G(d), MP2-fu/6-31G(d), and QCISD/6-31G(d) methods, respectively. However, if the theoretically determined frequencies are compared with experimental *harmonic* frequencies, the average error for the B-LYP method is increased while that for the conventional ab initio methods decreases.[24] Such a finding indicates that the good agreement between B-LYP harmonic frequencies and experimentally observed anharmonic frequencies is partly fortuitous.

In another study, Rauhut and Pulay[8] developed scaling factors for the B-LYP/6-31G(d) method based on a set of 20 small molecules with a wide range of functional groups. Their overall frequency scaling factor for the B-LYP/6-31G(d) method was determined to be 0.990 with an rms deviation of 26 cm^{-1}. Rauhut and Pulay, in the same study,[8] also developed a scaling factor for the B3-LYP/6-31G(d) method (0.963) that resulted in a slightly lower overall rms deviation of 19 cm^{-1}. This result is in accord with the findings of Finley and Stephens.[10]

Use of the B and B3 exchange functionals with other correlation functionals such as P86[25] and PW91[26] to compute vibrational frequencies has received less attention in the recent literature. Hertwig and Koch[27] systematically studied vibrational frequencies for the main group homonuclear diatomics and found that the B-P86 method was superior to B-LYP [in conjunction with the 6-311G(d) basis]. Finley and Stephens[10] found that, as with B3-LYP, the B3-P86 method performed better than B-LYP (with the TZ2P basis) in the prediction of experimental harmonic frequencies. Other less extensive stud-

ies[28] have suggested that the choice of exchange functional is a more important consideration than the choice of correlation functional in achieving reliable theoretical frequencies from DFT methods.

Apart from an interest in vibrational frequencies in their own right, one important use of theoretically determined vibrational frequencies is in the computation of zero-point vibrational energies (ZPVEs). ZPVE values determined from theoretical harmonic frequencies are used widely and, in particular, in very high level composite ab initio procedures such as the G1 and G2 theories of Pople and co-workers[14] and the complete basis set methodologies of Petersson et al.[29]

In the simplest approximation, the ZPVE of a molecule is evaluated theoretically as

$$\text{ZPVE}/Nhc = \frac{1}{2}\sum_i \omega_i \qquad (1)$$

where ω_i is the ith harmonic vibrational frequency expressed in cm^{-1} (more rigorously called the harmonic vibrational wavenumber) and Nhc is the appropriate energy conversion constant. This expression is not precise since it does not take into account the effects of anharmonicity.

The effect on ZPVEs of anharmonicity can be illustrated by considering a simple diatomic molecule for which the vibrational term values are given by

$$G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \ldots \quad (2)$$

where ω_e is the harmonic vibrational frequency, $\omega_e x_e$ and $\omega_e y_e$ are anharmonicity constants, all in cm^{-1}, and v is the vibrational quantum number.[30] This series is often truncated at the second term because the subsequent terms are generally quite small, e.g. $\omega_e y_e \ll \omega_e x_e$.

The ZPVE is then given by

$$\text{ZPVE}/Nhc = G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e \qquad (3)$$

and the fundamental frequency ($\tilde{\nu}$) is given by

$$\tilde{\nu} = G(0 \rightarrow 1) = \omega_e - 2\omega_e x_e \qquad (4)$$

Extension to polyatomic molecules is straightforward.[30]

Simply using harmonic frequencies (i.e. ignoring anharmonicities) to calculate the ZPVE (ZPVE$^{\text{harm}}$) results in an error in ZPVE (err$^{\text{harm}}$) given by

$$\text{err}^{\text{harm}}/Nhc = G(0) - (\text{ZPVE}^{\text{harm}}/Nhc) = -\frac{1}{4}\omega_e x_e \quad (5)$$

On the other hand, use of fundamental frequencies (such as suitably scaled theoretical harmonic frequencies) to calculate ZPVE (ZPVE$^{\text{fund}}$) results in an error in ZPVE (err$^{\text{fund}}$) of

$$\text{err}^{\text{fund}}/Nhc = G(0) - (\text{ZPVE}^{\text{fund}}/Nhc) = \frac{3}{4}\omega_e x_e \qquad (6)$$

As is clear from eqs 5 and 6, and as shown in recent papers by Grev, Janssen, and Schaefer (GJS)[31] and by Del Bene, Aue, and Shavitt,[32] the calculation of ZPVEs from theoretical harmonic frequencies requires frequency scale factors that are somewhere in between those that relate theoretical harmonic frequencies to observed fundamentals and those that relate theoretical harmonic frequencies to experimental harmonic frequencies.

In our recent study,[6] we found, from a least-squares study of the same set of 24 molecules as used by GJS,[31] HF/6-31G(d) and MP2-fu/6-31G(d) scale factors for ZPVE of 0.9135 and 0.9646, respectively. In accord with the suggestions by GJS,
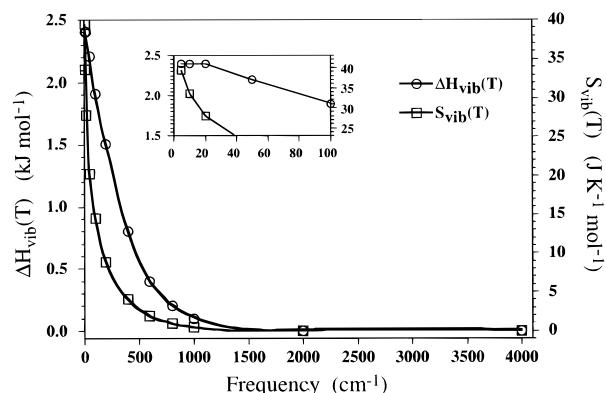
Figure 1. Plot of $\Delta H_{vib}(T)$ (kJ mol^{-1}, left-hand axis) and $S_{vib}(T)$ (J K^{-1} mol^{-1}, right-hand axis), at 298.15 K, as a function of frequency (cm^{-1}). (Insert) Expansion of 0−100 cm^{-1} region.

these factors are indeed larger than those relating theoretical harmonic vibrational frequencies to experimental fundamentals (0.8953 and 0.9427, respectively).

Knowledge of vibrational frequencies also plays a vital role in determining the thermal contributions to enthalpy and entropy [$\Delta H_{vib}(T)$ and $S_{vib}(T)$, respectively] which can be expressed[33] as

$$\Delta H_{vib}(T) = Nhc \sum_i \frac{\tilde{\nu}_i}{e^{\mu_i} - 1} \quad (7)$$

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

where N is Avogadro's number and $\mu_i = hc\tilde{\nu}_i/kT$, in which $\tilde{\nu}_i$ is the ith fundamental frequency in cm^{-1}.

Inspection of eqs 7 and 8 indicates that small frequencies contribute more to the thermal contributions to enthalpy and entropy than do larger frequencies. This can be readily confirmed by reference to Figure 1 which plots $\Delta H_{vib}(T)$ (left-hand axis) and $S_{vib}(T)$ (right-hand axis) as a function of frequency ($\tilde{\nu}_i$). We note that as the vibrational frequency tends to zero (see insert in Figure 1), $\Delta H_{vib}(T)$ reaches a limiting value which, within the confines of the harmonic oscillator model, is equal to RT (=2.479 kJ mol^{-1} at 298.15 K). However, since many very low frequencies are rotational in nature, it is often more appropriate to calculate the thermal component of enthalpy associated with very low frequencies using a free rotor approximation. In such circumstances, there is a contribution of $^1/_2RT$ for each such frequency. The "cross-over" frequency at which $\Delta H_{vib}(T)$ equals $^1/_2RT$ at 298.15 K is about 260 cm^{-1}. We note also that as the vibrational frequency tends to zero, the value for $S_{vib}(T)$ tends to infinity.

The use of scaling factors potentially *allows vibrational frequencies and thermochemical information of useful accuracy to be obtained from procedures of only modest computational cost.* Widespread application to molecules of moderate size is then possible.

In the present study, we examine the performance of 19 such procedures, with particular emphasis on density functional methods, since these have received relatively little previous attention in the literature. Specifically, we have computed harmonic vibrational frequencies for a large standard suite of test molecules at many of the levels of theory currently in popular use. The methods employed include the semiempirical procedures AM1 and PM3, the conventional ab initio procedures HF/3-21G, HF/6-31G(d), HF/6-31+G(d), HF/6-31G(d,p), HF/6-311G(d,p), HF/6-311G(df,p), MP2-fu/6-31G(d), MP2-fc/6-31G(d), MP2-fc/6-31G(d,p), MP2-fc/6-311G(d,p), and QCISD-fc/6-31G(d), and the DFT procedures B-LYP/6-31G(d), B-LYP/6-311G(df,p), B-P86/6-31G(d), B3-LYP/6-31G(d), B3-P86/6-31G(d), and B3-PW91/6-31G(d).

From these theoretical frequencies, we have determined a set of recommended scaling factors that relate theoretical harmonic frequencies to experimental fundamentals and have determined the rms errors for the various theoretical procedures. We have also determined a set of recommended scaling factors for the calculation of ZPVEs. Finally, we also present here, for the first time, a set of frequency scaling factors for calculating low-frequency vibrations and the thermal contributions to enthalpies and entropies.

The present work provides the most comprehensive compendium of theoretically determined harmonic vibrational frequencies and related scale factors available to date.

2. Theoretical Procedures

We define three sets of molecules for our present work. The first, designated F1, is the full set of 122 molecules and a total of 1066 vibrational frequencies (after counting degenerate modes) used in our previous paper.[6] This set is made up of the union of the set of polyatomic molecules listed by Shimanouchi[34] that contain no more than 4 heavy atoms of the first or second row, with no more than 10 atoms in total, and the set of 24 molecules listed by GJS.[31] The second set, named F2, is a subset of F1 and consists of those molecules that contain only H, C, N, O, and F atoms, no more than 4 heavy atoms, and no more than 10 atoms in total. The F2 set of molecules (37 molecules with a total of 477 vibrational frequencies) was used in earlier work by Pople et al.[3]

The third set, designated Z1, is comprised of 25 of the diatomic molecules from the G2 atomization list[14b] (all except Si$_2$) together with 14 additional molecules derived from the GJS set of molecules referred to above. This set is similar to that used by Bauschlicher and Partridge.[9] We have, however, elected not to include singlet or triplet CH$_2$ in our present study since, to the best of our knowledge, no experimental harmonic vibrational frequencies are available for these species. We have used the Z1 set to study zero-point vibrational energies.

The experimental frequencies for the F1 and F2 sets are obtained directly from the compilation of Shimanouchi.[34] The experimental ZPVE values for molecules in the Z1 set have been calculated according to standard formulas (cf. eq 3).[30,35] The requisite experimental harmonic frequencies (ω_e) and anharmonic constants ($\omega_e x_e$) for the diatomic molecules were obtained from the compilation of Huber and Herzberg.[36] Experimental harmonic frequencies and associated anharmonic corrections for HCN, CO$_2$, and C$_2$H$_2$ were obtained from Allen et al.,[37] those for H$_2$O, H$_2$S, H$_2$CO, HCO, and C$_2$H$_4$ were obtained from Clabo et al.,[38] those for CH$_4$ from Lee et al.,[39] and those for CH$_3$Cl from Duncan and Law.[40]

Most of the calculations performed in this study were carried out with the GAUSSIAN 92/DFT package of ab initio programs.[41a] Calculations for one of the DFT methods (B3-PW91) were performed with GAUSSIAN 94.[41b] Standard basis sets were used throughout and, unless otherwise stated (see below), the SG1 grid[42,43] was used as the quadrature grid for DFT calculations within GAUSSIAN 92. Møller−Plesset perturbation theory truncated at second order (MP2) was employed both with the core electrons of the heavy atoms held frozen (indicated by MP2-fc) and with the core electrons explicitly included (indicated by MP2-fu). Only the frozen-core approximation was employed for the QCISD calculations.

The geometry of each molecule was completely optimized at the appropriate level of theory by analytic gradient techniques.

Harmonic Vibration Frequencies

J. Phys. Chem., Vol. 100, No. 41, 1996 **16505**

Harmonic vibrational frequencies were determined by the analytic evaluation of the second derivative of the energy with respect to nuclear displacement in all of the theoretical methods other than QCISD. Frequencies derived at the QCISD level of theory were computed by finite central differences of the analytic gradients.

To examine the effect of grid size on the calculated frequencies, additional calculations were carried out on molecules in the F2 set at the B-LYP/6-31G(d) level of theory, using two finer grids. These two additional quadrature grids are designated (a) grid1,[44] a grid defined as having 75 radial shells and 302 angular points per shell, which when pruned[45] gives about 7000 points per atom, and (b) grid2,[46] a grid defined as having 50 radial shells and 194 angular points per shell giving a total of about 9700 points per atom. For comparison, the SG-1 grid, which is a pruned version of grid2, has about 3000 points per atom.

Only summary tables giving scale factors and *overall* root mean square errors (rms$_{ov}$) are presented in this paper. A complete listing of *molecular* root mean square errors (rms$_{mol}$) is available as supporting information (Tables S1−S11). For the sake of completeness, relevant results obtained from our previous work[6] are included within the tables of the present paper.

3. Results and Discussion

3.1. Vibrational Frequencies. *3.1.1. Fundamentals.* As in our previous study,[6] we determine optimum scaling factors λ through a least-squares procedure by minimizing the residuals

$$\Delta = \sum_i^{all} (\lambda \omega_i^{theor} - \tilde{\nu}_i^{expt})^2 \qquad (9)$$

leading to

$$\lambda = \sum_i^{all} \omega_i^{theor} \tilde{\nu}_i^{expt} / \sum_i^{all} (\omega_i^{theor})^2 \qquad (10)$$

where ω_i^{theor} and $\tilde{\nu}_i^{expt}$ are the *i*th theoretical harmonic and *i*th experimental fundamental frequencies (in cm^{-1}), respectively.

After the optimum scaling factor λ is obtained, we calculate a minimized residual, Δ_{min}, for each mode.

$$\Delta_{min} = (\lambda \omega_i^{theor} - \tilde{\nu}_i^{expt})^2 \qquad (11)$$

We then define the molecular root mean square error (rms$_{mol}$) as

$$rms_{mol} = (\sum_1^{n_{mol}} \Delta_{min}/n_{mol})^{1/2} \qquad (12)$$

where the sum is over all of the modes of a particular molecule (n_{mol}). The overall root mean square error (rms$_{ov}$) is defined as

$$rms_{ov} = (\sum_1^{n_{all}} \Delta_{min}/n_{all})^{1/2} \qquad (13)$$

where the sum is over all of the modes for all of the molecules considered (n_{all}).

Table 1 presents the harmonic vibrational frequency scale factors and rms$_{ov}$ values obtained for the F1 set of molecules for the semiempirical, conventional ab initio, and DFT methods. Tables 2 and 3 show the distributions of residual percentage errors for the entire F1 suite of molecules, after the appropriate

TABLE 1: Frequency Scaling Factors Suitable for Fundamental Vibrations and rms$_{ov}$ (cm^{-1}) Derived from a Least-Squares Fit of Frequencies^a

method	scale factor^b	rms$_{ov}$^{c}
AM1	0.9532	126
PM3	0.9761	159
HF/3-21G	0.9085	87
HF/6-31G(d)	0.8953	50
HF/6-31+G(d)	0.8970	49
HF/6-31G(d,p)	0.8992	53
HF/6-311G(d,p)	0.9051	54
HF/6-311G(df,p)	0.9054	56
MP2-fu/6-31G(d)	0.9427	61
MP2-fc/6-31G(d)	0.9434	63
MP2-fc/6-31G(d,p)	0.9370	61
MP2-fc/6-311G(d,p)	0.9496	60
QCISD-fc/6-31G(d)	0.9537	37
B-LYP/6-31G(d)	0.9945	45
B-LYP/6-311G(df,p)	0.9986	42
B-P86/6-31G(d)	0.9914	41
B3-LYP/6-31G(d)	0.9614	34
B3-P86/6-31G(d)	0.9558	38
B3-PW91/6-31G(d)	0.9573	34

^{a} Using F1 set of 1066 frequencies. ^{b} As defined by eq 10. ^{c} Overall root-mean-square error, as defined by eq 13.

scale factors have been applied. In the discussion that follows, we define 10% as an arbitrary target accuracy and we use the data of Tables 2 and 3 to note the proportion of frequencies calculated by the various methods that lie more than 10% from experimental values. Finally, Table 4 shows the effect of integral quadrature granularity for the B-LYP/6-31G(d) DFT procedure on the frequency scale factor and particularly on the rms$_{ov}$ values obtained for the F2 set of molecules.

(a) Semiempirical Theory. AM1 and PM3. The rms$_{ov}$ values for the AM1 and PM3 methods [126 cm^{-1} and 159 cm^{-1}, respectively, after scaling by 0.9532 (AM1) and 0.9761 (PM3), Table 1] are the largest of any of the methods employed in this study. Inspection of Table 2 reveals that large percentages (33% and 37%, respectively) of the total number of frequencies computed by AM1 or PM3 have an error outside our target accuracy. We will not discuss these methods further.

(b) Hartree−Fock Theory. 3-21G. After scaling by 0.9085 (Table 1), the percentage of calculated frequencies that lie outside our target accuracy is 21% (Table 2). A large rms$_{ov}$ value (87 cm^{-1}, Table 1) is found. Largest values for rms$_{mol}$ (Table S1 of the supporting information) are found for NSF (276 cm^{-1}), NO$_2$ (285 cm^{-1}), N$_2$O (281 cm^{-1}), OH (291 cm^{-1}), HF (272 cm^{-1}), and F$_2$ (283 cm^{-1}).

6-31G(d), 6-31+G(d), and 6-31G(d,p). The optimum scale factor (0.8953) and rms$_{ov}$ value (50 cm^{-1}) for the HF/6-31G(d) method have been previously published.[6] Similar rms$_{ov}$ values (49 and 53 cm^{-1}) are found at the 6-31+G(d) and 6-31G(d,p) levels after scaling by 0.8970 and 0.8992, respectively. The percentage of calculated frequencies that lie outside our target accuracy is reduced to 10% in all three cases. Largest values for rms$_{mol}$ at the three levels are found for F$_2$O (162−168 cm^{-1}), O$_3$ (212−225 cm^{-1}), O$_2$ (217−233 cm^{-1}), F$_2$ (211−225 cm^{-1}), and singlet CH$_2$ (163−191 cm^{-1}).

6-311G(d,p) and 6-311G(df,p). After scale factors of 0.9051 and 0.9054 (Table 1) are applied to the 6-311G(d,p) and 6-311G-(df,p) harmonic vibrational frequencies, respectively, the percentage of calculated frequencies that are outside our target accuracy remains around 10% (Table 2). The rms$_{ov}$ values have increased slightly to 54−56 cm^{-1} and the molecules F$_2$O, O$_3$, O$_2$, F$_2$, and singlet CH$_2$ again show the highest values for rms$_{mol}$.

(c) Møller−Plesset Theory. 6-31G(d) and 6-31G(d,p). We have previously investigated the MP2-fu/6-31G(d) method,

TABLE 2: Percentage of Theoretical Frequencies Derived from Semiempirical and Conventional ab Initio Procedures That Lie (after Scaling) within Specified Error Ranges when Compared with Experimental Fundamentals

% error	AM1	PM3	3-21G	6-31G(d)	6-31+G (d)	6-31G (d,p)	6-311G (d,p)	6-311G (df,p)	fu/ 6-31G(d)	fc/ 6-31G(d)	fc/ 6-31G(d,p)	fc/ 6-311G(d,p)	fc/ 6-31G(d)
			HF						MP2				QCISD
0−2	19.1	18.9	30.8	51.7	53.3	50.4	51.1	49.2	56.0	54.7	49.0	50.9	60.5
2−4	16.9	13.8	22.0	21.6	20.3	22.2	21.4	21.2	17.4	17.2	21.0	23.7	17.9
4−6	13.0	11.0	14.2	9.9	9.7	10.7	10.3	10.4	9.9	10.4	9.7	9.9	8.5
6−8	8.6	10.9	6.8	6.1	6.2	5.6	5.5	6.3	5.3	5.5	6.6	4.7	3.7
8−10	8.9	8.3	5.3	2.8	3.4	3.2	3.5	3.5	3.1	2.8	3.6	2.9	3.6
10−12	4.8	7.5	3.8	2.0	1.7	1.8	1.3	2.3	2.3	3.0	3.6	3.0	1.2
12−14	5.8	4.8	3.1	1.3	1.2	1.3	1.4	1.6	1.4	1.2	1.8	1.8	1.0
14−16	2.3	3.8	2.3	0.8	0.6	0.6	0.8	0.6	0.6	0.8	0.9	0.4	0.7
16−18	2.3	2.4	1.5	0.7	0.3	0.8	0.9	0.9	0.5	0.2	0.6	0.1	0.2
18−20	3.1	1.6	1.4	0.8	1.0	0.8	0.8	0.9	0.5	0.8	0.8	0.2	0.6
20−22	1.9	2.2	1.5	0.4	0.7	0.6	0.9	1.0	0.3	0.4	0.0	0.6	0.1
22−24	1.6	1.4	0.7	0.4	0.4	0.2	0.5	0.4	0.5	0.6	0.6	0.1	0.4
24−26	2.1	1.8	1.0	0.6	0.4	0.7	0.5	0.2	0.2	0.3	0.3	0.3	0.2
26−28	1.1	1.6	1.0	0.4	0.0	0.1	0.4	0.6	0.2	0.1	0.1	0.1	0.0
28−30	1.2	1.6	0.6	0.1	0.1	0.5	0.1	0.3	0.2	0.0	0.0	0.0	0.0
>30	7.2	8.4	4.1	0.6	0.9	0.6	0.7	0.6	1.7	2.1	1.5	1.4	1.5

TABLE 3: Percentage of Theoretical Frequencies Derived from Density Functional Theory Procedures That Lie (after Scaling) within Specified Error Ranges when Compared with Experimental Fundamentals

% error	SG-1[a]	SG-1[a,b]	grid1[b,c]	grid2[b,d]	6-311G(df,p) SG-1[a]	B-P86 6-31G(d) SG-1[a]	B3-LYP 6-31G(d) SG-1[a]	B3-P86 6-31G(d) SG-1[a]	B3-PW91 6-31G(d) SG-1[a]
	B-LYP								
	6-31G(d)								
0−2	48.3	61.8	64.2	61.2	50.1	62.7	57.5	67.3	69.6
2−4	20.0	20.1	18.0	19.9	18.8	19.9	18.1	19.3	16.8
4−6	10.5	6.3	6.1	5.7	11.7	5.9	10.2	3.8	4.0
6−8	6.8	3.1	2.5	4.4	6.1	2.9	5.3	3.6	4.2
8−10	4.2	1.5	2.1	1.7	4.7	2.1	3.2	1.5	1.7
10−12	2.9	2.1	2.1	1.9	2.6	2.3	2.3	1.5	0.6
12−14	2.2	1.3	0.6	1.3	2.1	1.0	1.1	1.0	1.0
14−16	1.6	1.0	1.5	0.6	1.3	0.8	0.8	0.2	0.2
16−18	1.2	0.8	0.6	1.3	0.7	0.4	0.5	0.0	0.0
18−20	0.4	0.2	0.6	0.4	0.6	0.2	0.1	0.2	0.2
20−22	0.2	0.0	0.0	0.0	0.1	0.0	0.0	0.4	0.4
22−24	0.1	0.2	0.2	0.0	0.4	0.2	0.1	0.2	0.2
24−26	0.5	0.4	0.2	0.2	0.1	0.2	0.1	0.4	0.2
26−28	0.1	0.0	0.0	0.2	0.2	0.6	0.1	0.0	0.0
28−30	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
>30	0.9	1.0	1.0	1.3	0.7	0.6	0.6	0.6	0.8

[a] Pruned version of a 50 194 grid. [b] Using F2 frequency set; see text. [c] Pruned version of a 75 302 grid. [d] Full version of a 50 194 grid.

TABLE 4: Scaling Factors and rms_{ov} Values (cm^{-1}) Derived from a Least-Squares Fit of Theoretical [B-LYP/6-31G(d)] Harmonic Frequencies to Observed Fundamentals for Various Grids[a]

grid specification	scale factor[b]	rms_{ov}[c]
SG-1[d]	0.9915	38
grid1[e]	0.9911	38
grid2[f]	0.9907	39

[a] Using F2 set of 477 frequencies. [b] As defined by eq 10. [c] Overall root-mean-square error, as defined by eq 13. [d] Pruned version of a 50 194 grid. [e] Pruned version of a 75 302 grid. [f] Full version of a 50 194 grid.

deriving a frequency scaling factor of 0.9427 with an rms$_{ov}$ value of 61 cm^{-1}.[6] In the present work, we have studied the effect of using a frozen-core approach. We find that the scaling factor at MP2-fc/6-31G(d) (0.9434) differs only marginally from the MP2-fu value, and the rms$_{ov}$ value has only slightly increased (to 63 cm^{-1}). At the MP2-fc/6-31G(d,p) level, the scale factor and rms$_{ov}$ values are 0.9370 and 61 cm^{-1}, respectively. About 10% of the scaled frequencies lie outside our target accuracy for all three methods. Largest values for rms$_{mol}$ are found for O_3 (651−660 cm^{-1}), NO_2 (296-313 cm^{-1}), N_2 (276−292 cm^{-1}), and O_2 (224−236 cm^{-1}). Omitting the asymmetric stretches in ozone and nitrogen dioxide from the analysis results in slightly larger scale factors but substantially reduced rms$_{ov}$ values [MP2-fu/6-31G(d), 0.9439, 47 cm^{-1}; MP2-fc/6-31G(d),

0.9446, 50 cm^{-1}; MP2-fc/6-31G(d,p), 0.9381, 48 cm^{-1}], the latter now being comparable to the HF/6-31G(d) rms$_{ov}$ values.

6-311G(d,p). The extension of the basis set to one of triple-zeta plus polarization quality [6-311G(d,p)] does not significantly change the derived scaling factor (0.9496) or rms$_{ov}$ (60 cm^{-1}) compared with the MP2-fc/6-31G(d) results. Ozone and nitrogen dioxide still possess very large values for rms$_{mol}$ (615 and 409 cm^{-1}, respectively) while N_2 and O_2 also have rms$_{mol}$ values that are quite large. Recalculation of the scaling factors and rms$_{ov}$ for the MP2-fc/6-311G(d,p) method with the frequencies for the asymmetric stretches in ozone and nitrogen dioxide omitted again results in a similar scale factor (0.9509) but a substantially reduced rms$_{ov}$ value (46 cm^{-1}).

(d) Quadratic Configuration Interaction. The scale factor for harmonic frequencies determined at the QCISD/6-31G(d) level is 0.9537 (Table 1). About 6% of the scaled frequencies lie outside our target accuracy at this level (Table 2). The rms$_{ov}$ value is reduced to 37 cm^{-1} (Table 1) with largest rms$_{mol}$ values occurring for acetylene (117 cm^{-1}), HF (129 cm^{-1}), and singlet CH_2 (202 cm^{-1}).

(e) Density Functional Theory Methods. We have determined harmonic vibrational frequencies for several variants of the DFT methodology using the 6-31G(d) basis. The procedures used in the present study are B-LYP, B-P86, B3-LYP, B3-P86, and B3-PW91. The B-LYP method has also been examined in

Harmonic Vibration Frequencies

J. Phys. Chem., Vol. 100, No. 41, 1996 **16507**

calculations with the 6-311G(df,p) basis set as well as with calculations using progressively tighter quadrature grids for the integrals.

B-LYP. After the B-LYP/6-31G(d) and B-LYP/6-311G(df,p) basis sets were scaled by 0.9945 and 0.9986, respectively (Table 1), about 10% of the frequencies lie outside our target accuracy (Table 3). The rms_{ov} values for the 6-31G(d) and 6-311G(df,p) basis sets are 45 and 42 cm^{-1}, respectively (Table 1). Our result for the B-LYP/6-31G(d) scale factor is similar to that found by Rauhut and Pulay[8] (0.995) for a smaller suite of molecules, but our RMS error is larger than their value (26.2 cm^{-1}). Largest rms_{mol} values are found with the 6-31G(d) basis set for H_2 (189 cm^{-1}), HF (165 cm^{-1}), and singlet CH_2 (224 cm^{-1}) and with the 6-311G(df,p) basis for H_2 (178 cm^{-1}) and singlet CH_2 (195 cm^{-1}).

We have investigated the effect of quadrature grid size on the harmonic vibrational frequencies calculated with the B-LYP/ 6-31G(d) method. Two grids, grid1 and grid2, in addition to the "standard" SG-1 grid have been employed. A summary of the results is presented for the molecules contained in the F2 set in Table 4. We note, first, that the scale factor and rms_{ov} value for the SG1 grid for the F2 set of molecules (Table 4) are somewhat smaller than those derived for the F1 set of molecules (Table 1). However, of special interest is our finding (Table 4) that increasing the size and extent of the grid does not significantly modify the scaling factor, nor does it significantly improve rms_{ov}. It appears from these results that the SG-1 grid does a particularly good job of mimicking a large grid size in a cost-effective manner. We use the SG1 grid in all our further calculations of harmonic vibrational frequencies with DFT procedures.

B-P86. After scaling by 0.9914 (Table 1), a value for rms_{ov} of 41 cm^{-1} is obtained for B-P86/6-31G(d). The percentage of frequencies that differ from experiment by more than our target accuracy is 6%. Largest rms_{mol} values are observed for H_2 (142 cm^{-1}) and singlet CH_2 (229 cm^{-1}).

B3-LYP. The calculated scaling factor for B3-LYP/6-31G- (d) (0.9614, Table 1) is lower (further from unity) than for B-LYP/6-31G(d). However, the rms_{ov} value (34 cm^{-1}) is smaller and the percentage of frequencies that lie outside our target accuracy is decreased to 6%. We note that the scaling factor for B3-LYP/6-31G(d) harmonic frequencies derived by Rauhut and Pulay[8] for their smaller suite of molecules (0.963) is similar to that obtained here, but again their rms error (18.5 cm^{-1}) is smaller than our value. Our largest rms_{mol} values occur for O_3 (110 cm^{-1}), H_2 (121 cm^{-1}), HF (132 cm^{-1}), F_2 (125 cm^{-1}), and singlet CH_2 (204 cm^{-1}). We note that these worst cases for B3-LYP/6-31G(d) are a combination of the molecules with which HF/6-31G(d) has most difficulty (O_3 and F_2) and those for which B-LYP/6-31G(d) has most difficulty (H_2, HF, and singlet CH_2) but the errors are significantly reduced with B3-LYP. This observation is not unexpected because of the hybrid nature of the B3 functional which includes both a Hartree−Fock contribution and a B contribution.

B3-P86. After scaling by 0.9558 (Table 1), a value for rms_{ov} of 38 cm^{-1} is obtained. The percentage of frequencies that differ from experimental values by more than our target accuracy is just 4%. Largest rms_{mol} values are found for O_3 (139 cm^{-1}), F_2 (146 cm^{-1}), and singlet CH_2 (204 cm^{-1}).

B3-PW91. After scaling by 0.9573 (Table 1), a value for rms_{ov} of 34 cm^{-1} is obtained. The percentage of frequencies that differ from experiment by more than our target accuracy is again just 4%. The results are similar to those for B3-P86, with largest rms_{mol} values again found for the molecules O_3 (137 cm^{-1}), F_2 (140 cm^{-1}), and singlet CH_2 (204 cm^{-1}).

(f) Evaluation. We conclude that the HF/3-21G level of

theory is not a particularly good level of ab initio theory from which to obtain quantitatively useful vibrational frequencies. On the other hand, HF/6-31G(d) would appear to represent a very good compromise between computational effort and the reliability of the scaled calculated harmonic frequencies. The use of larger basis sets does not appear to lead to a significant overall improvement in the computed HF frequencies.

Frequencies computed at the MP2-fu or MP2-fc levels are generally of comparable reliability to HF/6-31G(d) values but occasionally show large errors. Better results are obtained at QCISD/6-31G(d), but these are computationally more expensive.

We find that all of the DFT methods used in the present study are relatively inexpensive, can be routinely used to give accurate estimates of experimental fundamentals, and show no dramatic failures. The B exchange functional yields scaling factors very close to unity and could thus often be used directly without resorting to frequency scaling, an advantageous state of affairs particularly for the study of unusual systems. The B-LYP results are improved slightly by the use of a more complete basis set. A similar observation has been made for the B3-LYP method.[47] The B-LYP results do not appear to be significantly improved by the use of tighter quadrature grids for the integrals. The hybrid B3 exchange functional is found to yield scaling factors somewhat smaller (further from unity) than those determined by the B functional. However, in combination with any of the correlation functionals used in the present study, the B3 exchange functional also gives lower residual rms errors. Indeed, the lowest rms errors of any of the methods examined in the present study are found with B3-LYP and B3-PW91.

3.1.2. Low-Frequency Vibrations. The least-squares treatment of eqs 9 and 10 leads to scale factors that tend to minimize the absolute errors in frequencies that lie at the upper end of the frequency range. This is appropriate for many applications. However, there are also thermochemical quantities for which the evaluation is dominated by low frequencies, the contribution from high frequencies being minimal. It is thus important to examine whether more appropriate scale factors might be derived for low-frequency vibrations than those derived in section 3.1.1 that are weighted to the high end of the frequency scale.

To minimize the errors in frequencies at the low end of the frequency range, we have calculated an inverse frequency scaling factor. That is, given theoretical harmonic frequencies (ω_i^{theor}) and experimental fundamentals ($\tilde{\nu}_i^{expt}$), we determine a scale factor which minimizes the residual

$$\Delta = \sum_i^{all}\left(\frac{1}{\lambda\omega_i^{theor}} - \frac{1}{\tilde{\nu}_i^{expt}}\right)^2 \qquad (14)$$

giving

$$\lambda = \sum_i^{all}\left(\frac{1}{\omega_i^{theor}}\right)^2 / \sum_i^{all}\frac{1}{\omega_i^{theor}\tilde{\nu}_i^{expt}} \qquad (15)$$

The rms_{mol} and rms_{ov} values are obtained from equations analogous to eqs 12 and 13.

Initial analysis of our data showed that rms_{ov} was heavily dominated by the error associated with four torsional modes relating to facile methyl rotation in CH_3COOH, CH_3COCH_3, and, in particular, CH_3CCCH_3. Removing these frequencies from the data set (resulting in 1062 frequencies and a set that we shall refer to as F1') yielded the scale factors and rms_{ov} values shown in Table 5. There are clearly other vibrational modes in the F1' set that are better described as torsions rather than

TABLE 5: Frequency Scaling Factors Suitable for Low-Frequency Vibrations and Corresponding rms$_{ov}$ Values Derived from a Least-Squares Fit of Inverse Frequencies[a]

method	scale factor[b]	rms$_{ov}$[c]
HF/3-21G	1.0075	39
HF/6-31G(d)	0.9061	15
HF/6-31+G(d)	0.9131	15
HF/6-31G(d,p)	0.9089	15
HF/6-311G(d,p)	0.9110	15
HF/6-311G(df,p)	0.9085	15
MP2-fu/6-31G(d)	1.0214	24
MP2-fc/6-31G(d)	1.0485	29
MP2-fc/6-31G(d,p)	1.0229	23
MP2-fc/6-311G(d,p)	1.0127	23
QCISD-fc/6-31G(d)	1.0147	20
B-LYP/6-31G(d)	1.0620	19
B-LYP/6-311G(df,p)	1.0667	18
B-P86/6-31G(d)	1.0512	18
B3-LYP/6-31G(d)	1.0013	15
B3-P86/6-31G(d)	0.9923	14
B3-PW91/6-31G(d)	0.9930	14

^{a} Using F1′ set of 1062 frequencies; see text. ^{b} As defined by eq 15. ^{c} Overall rms error in inverse frequencies in units of 10^{-5} cm.

harmonic vibrations, but our treatment is aimed at assessing results obtained from a uniform use of the harmonic approximation.

(a) Hartree−Fock Theory. The rms$_{ov}$ value found for the 3-21G basis (0.00039 cm) principally arises from large rms$_{mol}$ values for S_2F_2 (0.00135 cm) and H_2O_2 (0.00345 cm) due to very poor estimates of the low-frequency torsional modes. The rms$_{ov}$ values for the 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-311G-(d,p), and 6-311G(df,p) basis sets are all about 0.00015 cm. The largest rms$_{mol}$ values for all of these levels of theory are found for $CSCl_2$ (0.00048 cm) and CH_3NNCH_3 (0.00046−0.00054 cm) and, in the case of HF/6-311G(d,p), for ClNO (0.00049 cm).

(b) Møller−Plesset Theory. The rms$_{ov}$ values for all of the MP2 procedures are found to be larger than those found for the corresponding HF methods. MP2-fc/6-31G(d) yields a slightly larger rms$_{ov}$ value than MP2-fu/6-31G(d) (0.00029 vs 0.00024 cm). The larger rms$_{ov}$ values for MP2/6-31G(d) and MP2/6-31G(d,p) compared with corresponding HF results are mainly attributable to poor predictions of the low frequencies and the consequent high rms$_{mol}$ values for ClCCCl (0.00145−0.00156 cm) and ClCCH (0.00091−0.00163 cm). Elaboration of the basis to 6-311G(d,p) results in a slight lowering of rms$_{ov}$ (to 0.00023 cm) with largest rms$_{mol}$ values for ClCCCl (0.00121 cm) and HCCCCH (0.00098 cm). Interestingly, the MP2/6-31G(d,p) rms$_{ov}$ value for HCCCCH (0.00017 cm) is significantly lower than the MP2/6-311G(d,p) value.

(c) Quadratic Configuration Interaction. The optimum scale factor for low-lying frequencies (1.0147) results in a value of rms$_{ov}$ for the QCISD/6-31G(d) method of 0.00020 cm, which lies between the HF and MP2 values. The largest rms$_{mol}$ values are now found for ClCCH (0.00068 cm) and ClCCCl (0.00118 cm).

(d) Density Functional Theory. B Exchange Functional. The rms$_{ov}$ values obtained after scaling are found to be 0.00019 cm [B-LYP/6-31G(d)] and 0.00018 cm [B-LYP/6-311G(df,p) and B-P86/6-31G(d)] (Table 5). The largest B-LYP/6-31G(d) rms$_{mol}$ values are found for $SOCl_2$ (0.00058 cm) and ClCCCl (0.00093 cm). Extending the basis set to 6-311G(df,p) at the B-LYP level of theory results in a similar rms$_{mol}$ value for $SOCl_2$, a much reduced error for ClCCCl (0.00035 cm) but moderate rms$_{mol}$ values for ClF_3 and $CSCl_2$ (0.00066 and 0.00054 cm, respectively). The B-P86 procedure gives largest rms$_{mol}$ values for $CSCl_2$ and ClCCCl (0.00054 and 0.00103 cm, respectively).

B3 Exchange Functional. Employing the B3 exchange functional lowers the rms$_{ov}$ value to 0.00015 cm [B3-LYP/6-31G(d)] and 0.00014 cm [for both B3-P86/6-31G(d) and B3-PW91/6-31G(d)]. The largest rms$_{mol}$ value with B3-LYP is just 0.00050 cm for $CSCl_2$. The B3-P86 method results in a substantial drop in the rms$_{mol}$ value for ClCCCl (0.00029 cm) and a similar error for $CSCl_2$ (0.00051 cm) when compared with B-P86. However, a moderate rms$_{mol}$ value for CH_3NNCH_3 (0.00042 cm) is also found. Similar rms$_{mol}$ values for $CSCl_2$ and CH_3NNCH_3 are found for the B3-PW91 method.

(e) Evaluation. We find that the scaling factors appropriate for the accurate prediction of low-frequency vibrations (Table 5) are consistently higher than those determined from the standard least-squares fit of theoretical harmonic frequencies to experimental fundamentals (Table 1). The difference is, however, quite small with HF/6-31G(d) (0.9061 vs 0.8953), which is an attractive feature. The HF/6-31G(d) procedure appears to provide a very cost-effective means of reliably predicting low-frequency vibrations. MP2 theory is found to be less successful in predicting low-lying frequencies than either HF or DFT methods, and QCISD is (only) slightly better. The best DFT results appear to be those obtained with methods that employ the B3 exchange functional, with rms$_{ov}$ values comparable to those of HF theory.

3.2. Thermodynamic Quantities. We now turn our attention to thermodynamic quantities that are derived from vibrational frequencies. In particular, we are interested in the zero-point vibrational energy (ZPVE), the vibrational component of the thermal contribution to enthalpy [$\Delta H_{vib}(T)$], and the vibrational component of the thermal contribution to entropy [$S_{vib}(T)$]. The derivation of frequency scaling factors for the computation of these quantities from theoretical harmonic vibrational frequencies is described below.

3.2.1. Zero-Point Energies. ZPVE scaling factors for the HF/6-31G(d) and MP2-fu/6-31G(d) methods and the methodology for their determination were reported in our previous study.[6] We have extended the treatment to a total of 19 levels of theory and have increased the number of molecules from 24 to 39 in the present work. We minimize the residual

$$\Delta = \sum_i^{all} (\lambda ZPVE_i^{theor} - ZPVE_i^{expt})^2 \qquad (16)$$

for each of the 39 molecules contained in the Z1 set. That is, we evaluate ZPVE^{theor} using theoretical harmonic frequencies for each molecule via eq 1 and compare with ZPVE^{expt} values obtained using experimental harmonic frequencies *and* their associated anharmonic corrections via eq 3.[36−40] Due to the linear relationship of frequency and ZPVE (cf. eq 1), λ can of course be used either to scale the calculated value of ZPVE^{theor} directly or as a scaling factor that can be applied to frequencies for the purpose of calculation of ZPVE^{theor}.

Table 6 displays the ZPVE scale factors and the resultant values for rms$_{ov}$. It might be expected that the performance of the various methods should parallel that for standard vibrational frequencies, and this is in fact observed. We therefore comment only briefly on the individual results. Because the Z1 set is relatively small (39 molecules, 89 modes), the rms errors can be strongly affected by individual poor cases and are therefore less significant than those from the previous sections based on the larger F1 set (1066 frequencies).

(a) Hartree−Fock Theory. 3-21G. We note that the HF/3-21G calculation for ClO failed to converge, and thus the analysis has been carried out for 88 (rather than 89) harmonic modes. The 3-21G basis set gives a large rms$_{ov}$ value (1.87 kJ mol^{-1}, Table 6) after application of the calculated ZPVE scaling factor of 0.9207.

Harmonic Vibration Frequencies

J. Phys. Chem., Vol. 100, No. 41, 1996 **16509**

TABLE 6: Frequency Scaling Factors and rms$_{ov}$ Values Derived from a Least-Squares Fit of ZPVEs^a

method	scale factor	rms$_{ov}$^{b}
HF/3-21G	0.9207^c	1.87^c
HF/6-31G(d)	0.9135	0.71
HF/6-31+G(d)	0.9153	0.70
HF/6-31G(d,p)	0.9181	0.73
HF/6-311G(d,p)	0.9248	0.79
HF/6-311G(df,p)	0.9247	0.80
MP2-fu/6-31G(d)	0.9661^d	0.83^d
MP2-fc/6-31G(d)	0.9670^d	0.88^d
MP2-fc/6-31G(d,p)	0.9608^d	0.78^d
MP2-fc/6-311G(d,p)	0.9748^d	0.48^d
QCISD-fc/6-31G(d)	0.9776	0.59
B-LYP/6-31G(d)	1.0126	0.62
B-LYP/6-311G(df,p)	1.0167	0.45
B-P86/6-31G(d)	1.0108	0.50
B3-LYP/6-31G(d)	0.9806	0.42
B3-P86/6-31G(d)	0.9759	0.37
B3-PW91/6-31G(d)	0.9772	0.37

^{a} Using Z1 set of 39 molecules, unless otherwise noted. ^{b} Overall rms error in ZPVEs in kJ mol^{-1}. ^{c} Values obtained with ClO removed from the analysis; see text. ^{d} Values obtained with NO and CN removed from the analysis; see text.

6-31G(d), 6-31+G(d), and 6-31G(d,p). There is a substantial improvement with these basis sets compared with the 3-21G results. We have previously reported a scale factor of 0.9135 as appropriate for the determination of ZPVEs at the HF/6-31G(d) level of theory.[6,48] Using the enlarged Z1 set of molecules of our present study also results in a scale factor of 0.9135. The new rms$_{ov}$ value is 0.71 kJ mol^{-1}. We note that no significant improvement is obtained by the addition of diffuse functions to the heavy atoms [6-31+G(d): scale factor 0.9153, rms$_{ov}$ 0.70 kJ mol^{-1}] or by adding polarization functions on hydrogen [6-31G(d,p): scale factor 0.9181, rms$_{ov}$ 0.73 kJ mol^{-1}].

6-311G(d,p) and 6-311G(df,p). Employing a basis set of triple−zeta quality [6-311G(d,p)] or its elaboration by the addition of *f*-like polarization functions on the heavy atoms [6-311G(df,p)] yields similar scale factors (0.9248 and 0.9247, respectively) for the determination of ZPVEs, with rms$_{ov}$ values of 0.79 and 0.80 kJ mol^{-1}, respectively.

(b) Møller−Plesset Theory. 6-31G(d). We have previously published[6,48] a ZPVE scaling factor of 0.9646 for the MP2-fu/6-31G(d) method. In the present study, the ZPVE scale factor for the MP2-fu/6-31G(d) method for the enlarged Z1 set is 0.9612. The rms$_{ov}$ is 2.07 kJ mol^{-1}, the result of very large values for rms$_{mol}$ in NO (11.1 kJ mol^{-1}) and CN (4.15 kJ mol^{-1}). A similar value for rms$_{ov}$ (2.10 kJ mol^{-1}) is found when the frozen-core approximation (MP2-fc) is used, after application of a ZPVE scale factor of 0.9620. This is again the result of very large values for rms$_{mol}$ in NO (11.2 kJ mol^{-1}) and CN (4.13 kJ mol^{-1}). Similar results are also obtained for MP2-fc/6-31G(d,p), with a scale factor and rms$_{ov}$ value of 0.9557 and 2.04 kJ mol^{-1}, respectively. It is well-known[49] that UMP theory performs poorly in calculating the frequencies of NO and CN because of large spin contamination. If NO and CN are removed from the data set (leaving 37 molecules and 87 frequencies), the ZPVE scaling factors for MP2-fu/6-31G(d), MP2-fc/6-31G(d), and MP2/6-31G(d,p) are found to be 0.9661, 0.9670, and 0.9608, respectively, while rms$_{ov}$ reduces to 0.78−0.88 kJ mol^{-1}.

6-311G(d,p). Our ZPVE scale factor for the MP2-fc/6-311G-(d,p) method is 0.9707 with a slight improvement in rms$_{ov}$ (1.71 kJ mol^{-1}) compared with that determined for the MP2/6-31G-(d) methods. The NO (rms$_{mol}$: 9.32 kJ mol^{-1}) and CN

(rms$_{mol}$: 4.24 kJ mol^{-1}) molecules continue to be the principal causes for the large rms$_{ov}$ value for this level of theory. Again, if NO and CN are removed from the data set, the ZPVE scaling factor for MP2-fc/6-311G(d,p) is found to be 0.9748 (rms$_{ov}$: 0.48 kJ mol^{-1}).

In the light of the specific problems encountered by UMP2 with NO and CN, we recommend the use of the scale factors noted above that have been derived with these two species removed from the analysis.

(c) Quadratic Configuration Interaction. The ZPVE scale factor for the QCISD/6-31G(d) method is 0.9776, which results in a value for rms$_{ov}$ of 0.59 kJ mol^{-1}. No major failings for this method are observed.

(d) Density Functional Theory. B Exchange Functional. B-LYP/6-31G(d) gives a scale factor of 1.0126 (rms$_{ov}$: 0.62 kJ mol^{-1}). The value for rms$_{ov}$ is reduced somewhat (to 0.45 kJ mol^{-1}) by elaboration of the basis to 6-311G(df,p) after scaling by 1.0167. The rms$_{ov}$ value (0.50 kJ mol^{-1}) determined for the B-P86/6-31G(d) method (after scaling by 1.0108) is found to be somewhat better than that derived for B-LYP/6-31G(d).

B3 Exchange Functional. The B3-based methods yield scaling factors less than unity but they give uniformly smaller rms$_{ov}$ values than the B-based methods when used in conjunction with the 6-31G(d) basis. Our scale factor of 0.9806 (with an rms$_{ov}$ of 0.42 kJ mol^{-1}) for B3-LYP/6-31G(d) is in good agreement with the scale factor determined by Bauschlicher and Partridge.[9] We find that all of the correlation functionals used in the present study with the B3 exchange functional yield similar values of rms$_{ov}$ for ZPVE.

(e) Evaluation. We conclude that HF/6-31G(d) provides a cost-effective means for the determination of ZPVEs from computed harmonic vibrational frequencies. Our calculated scale factor for the determination of ZPVEs from harmonic frequencies at this level of theory (0.9135) is different from the factor that has traditionally been used (0.8929). It is important to note, however, that because high-level methods such as G2 theory[14b] and its variants have been formulated using 0.8929 as the HF/6-31G(d) scale factor, i.e. the higher level correction (HLC) parameters have been derived on this basis, it would be inappropriate to use a different value unless the HLC parameters were re-evaluated. Likewise, if ZPVEs in a G2 calculation are calculated at a different level of theory [e.g. MP2/6-31G(d)] in particular cases in which HF/6-31G(d) frequencies are problematic, the appropriate scale factors would be those from Table 1 rather than those from Table 6, unless the HLC parameters were reoptimized.

We find that MP2 and QCISD do not perform significantly better than HF/6-31G(d) in predicting ZPVEs for this set of molecules.

Whereas the conventional ab initio methods show large errors for some molecules, the DFT procedures that we have investigated appear to be very well behaved, with no major failures of the theory. The B3-based/6-31G(d) methods perform particularly well and are the methods of choice here.

3.2.2. Enthalpies. Because the thermal contribution to enthalpy is particularly sensitive to low-frequency vibrations (cf. eq 7), it would be more appropriate to use low-frequency scaling factors (Table 5) than our standard values (Table 1). Further improvement might be anticipated if the frequency scaling factors are optimized specifically for the computation of $\Delta H_{vib}(T)$, but the general performance of the various theoretical methods should still parallel that found for the prediction of low-frequency vibrations.

We thus proceed by computing new frequency scale factors λ that, when applied to theoretical harmonic frequencies (ω_i^{theor}),

TABLE 7: Frequency Scaling Factors and rms$_{ov}$ Values Derived from a Least-Squares Fit of Theoretical and Experimental $\Delta H_{vib}(T)$ Values at Various Temperatures[a]

method	298.15 K		450 K	600 K
	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	scale factor[b]
HF/3-21G	0.9444	0.090	0.9227	0.9129
HF/6-31G(d)	0.8905	0.044	0.8847	0.8829
HF/6-31+G(d)	0.8945	0.044	0.8887	0.8870
HF/6-31G(d,p)	0.8912	0.044	0.8863	0.8855
HF/6-311G(d,p)	0.8951	0.044	0.8913	0.8909
HF/6-311G(df,p)	0.8908	0.046	0.8882	0.8886
MP2-fu/6-31G(d)	1.0084	0.062	0.9831	0.9704
MP2-fc/6-31G(d)	1.0211	0.074	0.9893	0.9743
MP2-fc/6-31G(d,p)	1.0084	0.057	0.9838	0.9715
MP2-fc/6-311G(d,p)	1.0061	0.059	0.9871	0.9783
QCISD-fc/6-31G(d)	1.0080	0.054	0.9860	0.9746
B-LYP/6-31G(d)	1.0633	0.049	1.0447	1.0318
B-LYP/6-311G(df,p)	1.0593	0.044	1.0459	1.0366
B-P86/6-31G(d)	1.0478	0.047	1.0327	1.0228
B3-LYP/6-31G(d)	0.9989	0.036	0.9886	0.9816
B3-P86/6-31G(d)	0.9864	0.036	0.9781	0.9730
B3-PW91/6-31G(d)	0.9885	0.036	0.9800	0.9747

[a] Using F1′ set of 1062 frequencies; see text. [b] As defined by eq 17. [c] Overall rms error in $\Delta H_{vib}(T)$ in units of kJ mol^{-1}.

will minimize the residuals

$$\Delta = \sum_i^{all} [\Delta H_{vib}^{theor}(T)_i - \Delta H_{vib}^{expt}(T)_i]^2 \qquad (17)$$

where $\Delta H_{vib}^{theor}(T)_i = \lambda \omega_i^{theor}/(e^{\mu_i^{theor}} - 1)$ (omitting the energy conversion enthalpy computed from the ith theoretical harmonic frequency (ω_i^{theor}) and in which $\mu_i^{theor} = h\lambda\omega_i^{theor}/kT$. In an exactly analogous manner, $\Delta H_{vib}^{expt}(T)_i$ is the enthalpy computed from the ith experimental fundamental frequency.

The derivation of λ based on eq 17 is more complex than the derivations of λ in previous sections and has been carried out with the aid of a small computer program.[50] As in section 3.1.2, we use the F1′ set of 1062 frequencies for our analysis. Our calculated scaling factors suitable for the determination of $\Delta H_{vib}(T)$ and corresponding rms$_{ov}$ values at 298.15 K are displayed in Table 7.

(a) Hartree−Fock Theory. The 3-21G basis yields, after scaling the computed individual modes by 0.9444, a value for rms$_{ov}$ for $\Delta H_{vib}(T)$ of 0.09 kJ mol^{-1}.

The 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-311G(d,p), and 6-311G(df,p) basis sets yield rms$_{ov}$ values, after scaling the theoretical frequencies by 0.8905, 0.8945, 0.8912, 0.8951, and 0.8908, respectively, that all lie between 0.04 and 0.05 kJ mol^{-1}. Largest rms$_{mol}$ values are found for ONF (0.10−0.12 kJ mol^{-1}), HCCF (0.12−0.15 kJ mol^{-1}), HCCCCH (0.07−0.14 kJ mol^{-1}), and ClNO (0.08−0.15 kJ mol^{-1}).

(b) Møller−Plesset Theory. The various MP2 procedures all yield rms$_{ov}$ values for $\Delta H_{vib}(T)$ that are larger than those found for HF theory when used with the same basis sets. The MP2-fu/6-31G(d) method results in a scaling factor of 1.0084 (rms$_{ov}$: 0.06 kJ mol^{-1}). Freezing the core electrons for the heavy atoms [MP2-fc/6-31G(d)] results in a somewhat larger frequency scaling factor (1.0211) together with a slightly larger rms$_{ov}$ value (0.07 kJ mol^{-1}). Extension of the method to MP2-fc/6-31G(d,p) or MP2-fc/6-311G(d,p) results in a slightly reduced rms$_{ov}$ value (0.06 kJ mol^{-1}) after the theoretical frequencies are scaled by 1.0084 or 1.0061, respectively. The largest rms$_{mol}$ values are found for ClCCCl (0.28−0.32 kJ mol^{-1}), ClCCH (0.18−0.34 kJ mol^{-1}), and HCCH [0.22 and 0.24 kJ mol^{-1}, respectively, for the MP2-fu/6-31G(d) and MP2-fc/6-31G(d) methods]. Interestingly, HCCCCH yields large

rms$_{mol}$ values (0.29 and 0.31 kJ mol^{-1}, respectively) for MP2-fc/6-31G(d) and MP2/6-311G(d,p) but a much smaller rms$_{mol}$ value (0.06 kJ mol^{-1}) for MP2/6-31G(d,p).

(c) Quadratic Configuration Interaction. A value for rms$_{ov}$ for $\Delta H_{vib}(T)$ of 0.05 kJ mol^{-1}, after individual frequencies are scaled by 1.0080, is obtained for the QCISD/6-31G(d) method. The largest rms$_{mol}$ values occur for ClCCCl (0.27 kJ mol^{-1}), ClCCH (0.18 kJ mol^{-1}), and HCCH (0.20 kJ mol^{-1}).

(d) Density Functional Theory. B Exchange Functional. All of the DFT methods that use the B exchange functional yield frequency scaling factors for the computation of $\Delta H_{vib}(T)$ that are greater than unity [B-LYP/6-31G(d), 1.0633; B-LYP/6-311G(df,p), 1.0593; and B-P86/6-31G(d), 1.0478]. The B-LYP/6-31G(d) and B-P86/6-31G(d) methods both show rms$_{ov}$ values of 0.05 kJ mol^{-1}, while extension of the basis set to 6-311G-(df,p) for the B-LYP method lowers the rms$_{ov}$ value slightly (to 0.04 kJ mol^{-1}). The largest rms$_{mol}$ values with B-LYP/6-31G(d) occur for ClF$_3$ (0.16 kJ mol^{-1}), ClCCCl (0.23 kJ mol^{-1}), and HCCH (0.16 kJ mol^{-1}). The largest rms$_{mol}$ value with B-P86/6-31G(d) is found for ClCCCl (0.25 kJ mol^{-1}).

B3 Exchange Functional. The B3 exchange functional when used with the 6-31G(d) basis set results in frequency scaling factors for the computation of $\Delta H_{vib}(T)$ that are less than unity (0.9989, 0.9864, and 0.9885 for the LYP, P86, and PW91 correlation functionals, respectively) and gives low rms$_{ov}$ values in each case (0.04 kJ mol^{-1}). The exact form of the correlation functional does not appear to influence the reliability of these DFT methods. The largest rms$_{mol}$ values occur for CSCl$_2$ (about 0.12 kJ mol^{-1}).

(e) Evaluation. It should be noted that the frequency scaling factors for the determination of $\Delta H_{vib}(T)$ are temperature dependant. The variation with temperature of these scaling factors is shown in Figure 2. While there are significant changes in the computed $\Delta H_{vib}(T)$ scale factors for lower temperatures, the variation diminishes as the temperature increases. Values of the scale factors at temperatures of 450 and 600 K are also included in Table 7 to allow interpolation to desired temperatures within the 298−600 K range.

The rms error in $\Delta H_{vib}(T)$ is significantly reduced in going from 3-21G to 6-31G(d) and larger basis sets. There appears to be little change to the rms errors in the computed $\Delta H_{vib}(T)$ values beyond 6-31G(d), so HF/6-31G(d) is again very cost effective.

MP2/6-31G(d) does not perform as well as HF/6-31G(d). The performance of QCISD for the evaluation of $\Delta H_{vib}(T)$ is intermediate between that of HF and MP2.

Employing frequencies determined with the B exchange functional results in $\Delta H_{vib}(T)$ values that are of comparable reliability to those determined with HF theory. The lowest rms errors of any of the methods investigated are achieved with the B3 functional.

To assess how the various scaling factors that we have derived in this paper perform relative to one another in predicting ΔH_{vib}-(T) values, we have calculated the rms$_{ov}$ values for $\Delta H_{vib}(T)$ for the F1′ set of molecules when $\Delta H_{vib}(T)$ is calculated using frequencies scaled by (a) unity, (b) the appropriate standard frequency scaling factors (Table 1), (c) the appropriate frequency scaling factors suitable for low frequencies (Table 5), and (d) the frequency scaling factors specifically derived for the evaluation of $\Delta H_{vib}(T)$ (Table 7). These results are presented in Table 8.

We find that at the HF level, the standard frequency scale factor, the low-frequency scale factor and that derived specifically for the evaluation of $\Delta H_{vib}(T)$ all perform comparably for the computation of $\Delta H_{vib}(T)$. However, for MP2, QCISD, and all of the DFT methods studied in this paper, there is a
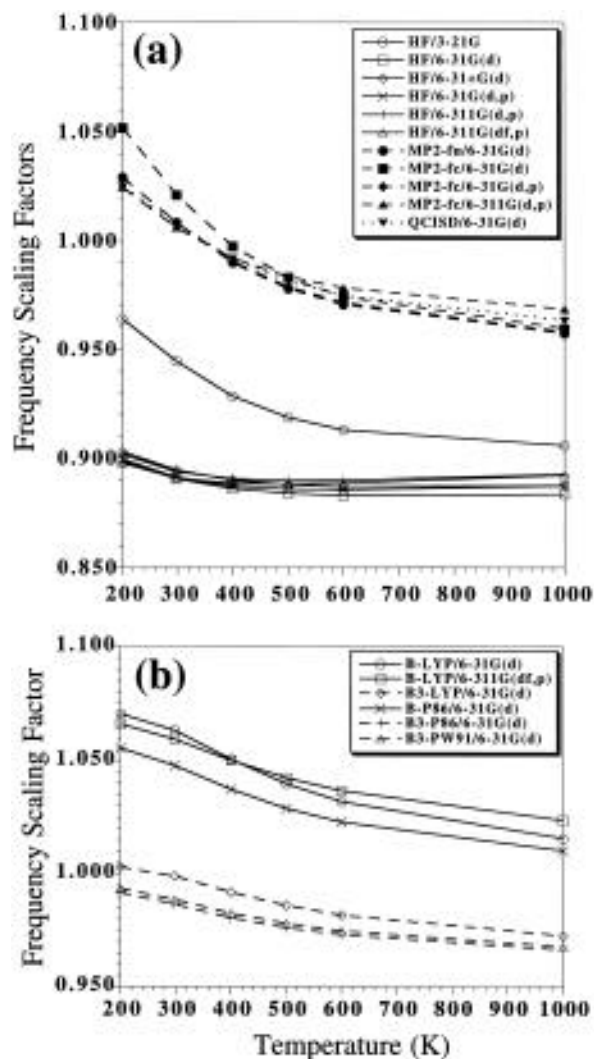
Harmonic Vibration Frequencies

J. Phys. Chem., Vol. 100, No. 41, 1996 **16511**

Figure 2. Plot showing the temperature dependence of the calculated frequency scaling factor applicable for the computation of $\Delta H_{vib}(T)$: (a) conventional ab initio methods; (b) density functional methods.

significant improvement in moving from the standard scale factors to the other two scale factors. We note that for all of the methods studied in the present paper, use of the low-frequency scaling factor is only marginally worse than use of the scale factor specifically optimized for the evaluation of $\Delta H_{vib}(T)$.

3.2.3. Entropies. As is evident from eq 8, low-lying frequencies contribute more to $S_{vib}(T)$ than do high-lying frequencies (cf. Figure 1). In a similar fashion to that employed in section 3.2.2, we have determined frequency scaling factors appropriate for the calculation of $S_{vib}(T)$ by minimizing the residuals

$$\Delta = \sum_{i}^{all}[S_{vib}^{theor}(T)_i - S_{vib}^{expt}(T)_i]^2 \qquad (18)$$

where $S_{vib}^{theor}(T)_i = [\mu_i^{theor}/(e^{\mu_i^{theor}} - 1)] - \ln(1 - e^{-\mu_i^{theor}})$ is the entropy (with energy conversion constants dropped for simplicity) computed from the ith theoretical harmonic frequency. In an exactly analogous manner, $S_{vib}^{expt}(T)_i$ is the entropy computed from the ith experimental fundamental frequency.

Table 9 presents the theoretical frequency scaling factors appropriate for the computation of $S_{vib}(T)$ together with the associated rms$_{ov}$ values obtained at 298.15 K, for the F1′ set of molecules.

(a) Hartree–Fock Theory. The $S_{vib}(T)$ frequency scaling factors are slightly larger than those determined for $\Delta H_{vib}(T)$.

TABLE 8: Values of rms$_{ov}$ (kJ mol^{-1}) for $\Delta H_{vib}(T)$ (at 298.15 K) Calculated with Theoretical Frequencies Scaled by Various Scaling Procedures[a]

	scaling procedure			
method	1.0[b]	ω[c]	$1/\omega$[d]	$\Delta H_{vib}(T)$[e]
HF/3-21G	0.095	0.092	0.096	0.090
HF/6-31G(d)	0.073	0.044[f]	0.045	0.044
HF/6-31+G(d)	0.072	0.044	0.046	0.044
HF/6-31G(d,p)	0.073	0.044	0.045	0.044
HF/6-311G(d,p)	0.071	0.044	0.045	0.044
HF/6-311G(df,p)	0.074	0.046	0.047	0.046
MP2-fu/6-31G(d)	0.063	0.071	0.063	0.062
MP2-fc/6-31G(d)	0.075	0.084	0.075	0.074
MP2-fc/6-31G(d,p)	0.057	0.069	0.058	0.057
MP2-fc/6-311G(d,p)	0.059	0.067	0.060	0.059
QCISD-fc/6-31G(d)	0.054	0.061	0.054	0.054
B-LYP/6-31G(d)	0.059	0.061	0.050	0.049
B-LYP/6-311G(df,p)	0.053	0.054	0.044	0.044
B-P86/6-31G(d)	0.053	0.056	0.047	0.047
B3-LYP/6-31G(d)	0.036	0.042	0.036	0.036
B3-P86/6-31G(d)	0.037	0.040	0.037	0.036
B3-PW91/6-31G(d)	0.036	0.040	0.036	0.036

[a] Using F1′ set of 1062 frequencies; see text. [b] Frequency scaling factors of unity. [c] Frequency scaling factors based on standard least-squares fits, from Table 1. [d] Frequency scaling factors based on least-squares fits of inverse frequencies, designed to be suitable for low-frequency vibrations, from Table 5. [e] Frequency scaling factors based on least-squares fits of $\Delta H_{vib}(T)$ values, from Table 7. [f] The rms$_{ov}$ value for the "standard" HF/6-31G(d) scale factor (0.8929) is also 0.044 kJ mol^{-1}.

TABLE 9: Frequency Scaling Factors and rms$_{ov}$ Values Derived from a Least-Squares Fit of Theoretical and Experimental $S_{vib}(T)$ Values at Various Temperatures[a]

	298.15 K		450 K	600 K
method	scale factor[b]	rms$_{ov}$[c]	scale factor[b]	scale factor[b]
HF/3-21G	0.9666	0.63	0.9465	0.9356
HF/6-31G(d)	0.8978	0.28	0.8917	0.8890
HF/6-31+G(d)	0.9027	0.28	0.8962	0.8933
HF/6-31G(d,p)	0.8990	0.28	0.8931	0.8907
HF/6-311G(d,p)	0.9021	0.28	0.8970	0.8952
HF/6-311G(df,p)	0.8981	0.29	0.8934	0.8920
MP2-fu/6-31G(d)	1.0228	0.44	1.0050	0.9937
MP2-fc/6-31G(d)	1.0444	0.53	1.0196	1.0050
MP2-fc/6-31G(d,p)	1.0232	0.41	1.0055	0.9944
MP2-fc/6-311G(d,p)	1.0175	0.42	1.0037	0.9955
QCISD-fc/6-31G(d)	1.0187	0.37	1.0040	0.9944
B-LYP/6-31G(d)	1.0670	0.34	1.0571	1.0487
B-LYP/6-311G(df,p)	1.0641	0.31	1.0559	1.0496
B-P86/6-31G(d)	1.0527	0.33	1.0437	1.0368
B3-LYP/6-31G(d)	1.0015	0.26	0.9957	0.9910
B3-P86/6-31G(d)	0.9902	0.25	0.9847	0.9808
B3-PW91/6-31G(d)	0.9920	0.24	0.9865	0.9826

[a] Using F1′ set of 1062 frequencies; see text. [b] As defined by eq 18. [c] Overall rms error in $S_{vib}(T)$ in units of J K^{-1} mol^{-1}.

As in previous cases, the largest value for rms$_{ov}$ (0.63 J K^{-1} mol^{-1}) is found at the HF/3-21G level. Increasing the size of the basis set to 6-31G(d) leads to a large improvement in rms$_{ov}$ (to 0.28 J K^{-1} mol^{-1}). The largest rms$_{mol}$ value is due to CSCl$_2$ (0.84 J K^{-1} mol^{-1}). Further extension of the basis does not decrease rms$_{ov}$. The largest rms$_{mol}$ values found for the larger basis sets are again found for CSCl$_2$ (0.84−0.87 J K^{-1} mol^{-1}). A large rms$_{mol}$ value for the triple-zeta basis sets is also found for HCCF (0.87 J K^{-1} mol^{-1}).

(b) Møller–Plesset Theory. As was observed for scaling factors applicable to the determination of $\Delta H_{vib}(T)$, the values for rms$_{ov}$ that result from the use of MP2 procedures are found

to be larger than those found at HF theory when the same basis set is employed. This arises from poor MP2 predictions of the $S_{vib}(T)$ values for ClCCCl (rms$_{mol}$: 2.2–2.6 J K^{-1} mol^{-1}) and ClCCH (1.3–2.8 J K^{-1} mol^{-1}). Additionally, for the MP2-fc/6-31G(d) and MP2-fc/6-311G(d,p) methods, the $S_{vib}(T)$ values for HCCCCH (rms$_{mol}$: 1.8 and 2.1 J K^{-1} mol^{-1}) are also found to be poorly predicted. As noted above, MP2-fc/6-31G(d,p) gives better results for the low-frequency modes of this molecule and hence yields a signficantly lower rms$_{mol}$ (0.4 J K^{-1} mol^{-1}) for $S_{vib}(T)$. We find that MP2-fc/6-31G(d) performs slightly worse than MP2-fu/6-31G(d), as noted above also for low-frequency vibrations and $\Delta H_{vib}(T)$.

(c) Quadratic Configuration Interaction. A value for rms$_{ov}$ for $\Delta H_{vib}(T)$ of 0.37 J K^{-1} mol^{-1} is obtained for the QCISD/6-31G(d) method after individual frequencies are scaled by 1.0187. Largest rms$_{mol}$ values are found for ClCCCl (2.1 J K^{-1} mol^{-1}) and ClCCH (1.3 J K^{-1} mol^{-1}).

(d) Density Functional Theory. B Exchange Functional. All of the DFT methods that use the B exchange functional yield $S_{vib}(T)$ scale factors that are greater than unity [B-LYP/6-31G-(d), 1.0670; B-LYP/6-311G(df,p), 1.0641; and B-P86/6-31G-(d), 1.0527]. The B-LYP and B-P86 methods when used in conjunction with the 6-31G(d) basis give values for rms$_{ov}$ of 0.33–0.34 J K^{-1} mol^{-1}. Extension of the basis set to 6-311G-(df,p) for B-LYP lowers rms$_{ov}$ slightly (to 0.31 J K^{-1} mol^{-1}). Largest B-LYP rms$_{mol}$ values are found for ClF$_3$ [1.1 and 1.4 J K^{-1} mol^{-1} for the 6-31G(d) and 6-311G(df,p) basis sets, respectively]. The B-LYP/6-31G(d) procedure also yields a large rms$_{mol}$ value for ClCCCl (1.7 J K^{-1} mol^{-1}), which is substantially reduced (to 0.7 J K^{-1} mol^{-1}) when determined with the larger 6-311G(df,p) basis. Largest rms$_{mol}$ values for B-P86/6-31G(d) occur for CSCl$_2$ and ClCCCl (1.0 and 1.9 J K^{-1} mol^{-1}, respectively).

B3 Exchange Functional. The B3 exchange functional with the 6-31G(d) basis set gives frequency scale factors for $S_{vib}(T)$ that are close to unity (1.0015, 0.9902, and 0.9920 for the LYP, P86, and PW91 correlation functionals, respectively) and gives low values for rms$_{ov}$ (0.24–0.26 J K^{-1} mol^{-1}). The exact form of the correlation functional does not appear to influence the reliability of these DFT methods. The largest rms$_{mol}$ value of about 0.96 J K^{-1} mol^{-1} is found for CSCl$_2$.

(e) Evaluation. As with $\Delta H_{vib}(T)$, the frequency scaling factors for the determination of $S_{vib}(T)$ are temperature dependent (Table 9).

As in other cases, HF/6-31G(d) provides a very cost-effective means of reliably predicting $S_{vib}(T)$ values. The rms$_{ov}$ values for $S_{vib}(T)$ determined with MP2 methods are slightly worse than those found at the HF level of theory with the same basis set, with QCISD in between HF and MP2.

Employing frequencies determined with any of the DFT methods used in this study results in $S_{vib}(T)$ values that are of comparable quality to those determined with HF theory. The B3 exchange functional gives best results.

4. Conclusions

The purpose of this work was to determine optimum frequency scale factors suitable for the prediction of vibrational fundamentals, low-frequency vibrations, zero-point vibrational energies, and thermal contributions to enthalpy and entropy, from calculated harmonic vibrational frequencies. We have calculated the harmonic vibrational frequencies for 122 molecules (1066 frequencies) at 19 different levels of theory that include semiempirical, Hartree–Fock, Møller–Plesset, quadratic configuration interaction, and density functional theory procedures in conjunction with a variety of basis sets. A summary of our recommended scaling factors appears in Table 10. We make the following observations and recommendations.

TABLE 10: Summary of Recommended Frequency Scaling Factors

level of theory	$\omega^{a,b}$	$1/\omega^{c,d}$	ZPVE^{e,f}	$\Delta H_{vib}(T)^{c,g}$	$S_{vib}(T)^{c,h}$
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^i	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^j	1.0084	1.0228
MP2-fc/6-31G(d)	0.9434	1.0485	0.9670^j	1.0211	1.0444
MP2-fc/6-31G(d,p)	0.9370	1.0229	0.9608^j	1.0084	1.0232
MP2-fc/6-311G(d,p)	0.9496	1.0127	0.9748^j	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 the F1 set, 122 molecules, 1066 frequencies. ^{b} Suitable for relating theoretical harmonic frequencies to observed fundamentals. These are also the values recommended for use in conjunction with G2 theory and its variants, both for frequencies and for ZPVEs; see text. ^{c} From the F1′ set, 122 molecules, 1062 frequencies. ^{d} Suitable for the prediction of low-frequency vibrations. ^{e} From the Z1 set. ^{f} Suitable for the prediction of zero-point vibrational energies. See, however, footnote b. ^{g} Suitable for the prediction of $\Delta H_{vib}(T)$. ^{h} Suitable for the prediction of $S_{vib}(T)$. ^{i} The previous "standard" value of 0.8929 should continue to be used, however, in G2 theory; see text. ^{j} Values obtained with NO and CN removed from the analysis; see text.

4.1. Fundamentals. The most cost-effective procedures found in this study for predicting vibrational frequencies are HF/6-31G(d) and the B3-based/6-31G(d) density functional theory procedures. The latter give the lowest rms$_{ov}$ values of any of the procedures examined. The B-based DFT procedures, while not performing quite as well as the corresponding B3-based procedures, have the attraction of standard frequency scale factors close to unity, meaning that they can often be used without scaling. MP2/6-31G(d) does not appear to offer a significant improvement in performance over HF/6-31G(d) and occasionally shows large errors. Harmonic frequencies computed at the MP2 level of theory with all electrons correlated are only slightly better than those computed with the frozen-core approximation. While the QCISD method yields frequencies that are more reliably predicted than those computed at the MP2 level of theory, the improvement comes at a significant additional computational cost and, at least for the range of molecules included in our standard set, the results are generally not better than those for the much less expensive B3-based DFT procedures.

4.2. Low-Frequency Vibrations. In general, the optimum scale factor for low-frequency vibrations is not the same as the standard value for the particular method. For HF/6-31G(d), however, an attractive feature is that the two scale factors are reasonably close to one another and so the use of a single scale factor would be unlikely to introduce significant error. In contrast, significant differences are found between the low-frequency and standard scale factors at the MP2, QCISD, and DFT levels. HF and DFT methods are found to yield low frequencies that are of comparable reliability, but MP2 performs slightly worse.

4.3. Zero-Point Vibrational Energies. ZPVE scaling factors are found to be uniformly larger than the standard frequency scaling factors, as anticipated. The B3-based DFT procedures perform best in this case.

Harmonic Vibration Frequencies

J. Phys. Chem., Vol. 100, No. 41, 1996 **16513**

4.4. Enthalpy and Entropy. The performance of the various methods in the prediction of $\Delta H_{vib}(T)$ and $S_{vib}(T)$ parallels that for low-frequency vibrations, and the frequency scale factors have similar values. HF and DFT methods are found to perform better than MP2, the B3-based DFT procedures again being the best.

An overall conclusion is that B3-based DFT procedures, such as those used in the present paper, provide a very cost-effective means of determining harmonic vibrational frequencies and derived thermochemical quantities. They show fewer poorer cases than do HF- and MP2-based procedures. B3-PW91/6-31G(d) gives the best results, but the widely used B3-LYP/6-31G(d) procedure is almost as successful.

Supporting Information Available: Listing of rms$_{mol}$ values associated with the prediction of (a) fundamentals (Tables S1−S3), (b) low frequencies (Tables S4 and S5), (c) ZPVE (Tables S6 and S7), (d) $\Delta H_{vib}(T)$ (Tables S8 and S9), and (e) $S_{vib}(T)$ (Tables S10 and S11) (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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