# Approximating Coupled Cluster Level Vibrational Frequencies with Composite Methods

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An extensive study of the harmonic frequencies of a large set of small polyatomic closed-shell molecules computed at both single level ab initio and composite approximations is presented here. Using various combinations of basis sets, composite methods are capable of predicting single level ab initio CCSD(T) harmonic frequencies to within 5 cm$^{-1}$ on average, which suggests a computationally affordable means of obtaining highly accurate vibrational frequencies compared to the CCSD(T) level. A general approach for calculating the composite level equilibrium geometries and harmonic frequencies for polyatomic systems that uses the Collin's method of interpolating potential energy surfaces is also described here. This approach is further tested on tetrafluoromethane, and an estimation of the potential CPU time savings that may be obtained is also presented. It is envisaged that the findings here will enable theoretical studies of fundamental frequencies and energetics of significantly larger molecular systems.

## 1. Introduction

Since the introduction of G1 theory by Pople and co-workers in 1989[1] a sizable literature has appeared that utilizes composite methods or, more generally, methods that use various lower levels of ab initio or DFT theory to approximate significantly higher levels of theory. The advantage in doing so lies in the very significant saving in computational expense resulting from the lower level computations. G1 theory and its descendants, G2[2], G3[3], G3S,[4] G3X[5] were originally developed to achieve "chemical accuracy" (energies to within 4 kJ mol$^{-1}$ when compared with experiment) in the computation of thermochemical properties (enthalpies, ionization energies, electron affinities, etc.) of gases. Indeed, this level of accuracy has been achieved for many molecules.

The G*n* theories of Pople and co-workers are by no means the only methods that aim to, and achieve, chemical accuracy by approximating expensive higher level methods using several lower level results and empirical parameters. Some of the more popular include the complete basis set (CBS) methods from Petersson and co-workers,[6] the Weizmann-*n* theories and their variants of Martin and co-workers[7] and the multicoefficient correlation methods (MCCMs)[8] of Truhlar's group.

Significantly fewer studies have appeared in the literature that utilize composite methods for predicting potential energy surfaces (PES). Collins and co-workers have successfully utilized a G3X(MP2) type method in the construction of PES for reactive systems and the calculation of various kinetic parameters.[9] Such methods have also been used in a nine-dimensional bound-state problem for the determination of zero-point energies and ground-state rotational constants.[10] Császár and co-workers utilized a CBS approach to generate a base PES for water and then added in a core-correlation surface, a relativistic correction surface, a quantum electrodynamics correction surface and an adiabatic correction surface.[11]

Other groups have considered up to quartic expansions of the potential about an equilibrium configuration. In these studies it is the fundamental frequencies of vibration that are of interest, as well as other spectroscopic constants. Bose and Martin[12] published a detailed study on the azabenzene series, which included considering the possibility of combining DFT anharmonic force fields with coupled cluster geometries and harmonic frequencies. Pouchan and co-workers have also combined harmonic ab initio force constants with DFT anharmonicity constants in a number of studies.[13]

Although high accuracy can be obtained using the above approach for computing fundamentals, high-level ab initio calculations are still required of the harmonic frequencies. Furthermore, such approaches to obtaining a PES, although perfectly suited for the determination of spectroscopic observables of tightly bound systems, are not applicable over the entire PES but presumably can only be applied to turning points. An alternative approach is to define a potential energy that can be computed for any single configuration that is composed of contributions from various levels of theory in a manner similar to G*n* theory. In this way, not only can composite force constants and anharmonic force constants be computed, but composite energies, gradients and second and higher derivatives can also be evaluated for *any* configuration.

Though the high accuracy of composite methods has been demonstrated by numerous studies for total energies, at least at and around minima on the PES, almost no work has been done on examining the general accuracy of the approach for first and higher order derivatives. One way of measuring the accuracy of the curvature of the PES is by comparing composite harmonic frequencies to those obtained using a high single level of theory.

The computation of vibrational frequencies has seen much interest in recent years, with frequencies determined on average to within 8 cm$^{-1}$ of experimental values using CCSD(T) and large basis sets.[14] However, the CPU time associated with this method scales as the seventh power of the number of basis functions, which makes the calculation for even medium-sized molecules prohibitive. Of course, one must include the effects of correlating the core−electrons to achieve such high levels of accuracy. Dunning and Peterson have examined the use of composite methods for making reliable estimates of the elec-

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tronic energy, spectroscopic properties ($D_e$, $r_e$, $\omega_e$, $\omega_e x_e$), ionization energy, and electron affinities compared with the single level CCSD(T)/aug-cc-pV5Z for a test set of diatomic molecules.[15] Specifically, the authors calculated an energy at the CCSD(T) level using a smaller basis aug-cc-pVXZ, X = D, T, and Q, and then added to this energy a correction, $\Delta_{\text{basis}}$, to account for the inadequate basis set. Their study revealed that for the test set of molecules, the composite approach is capable of predicting single level CCSD(T) harmonic frequencies to within 2 cm$^{-1}$ on average when X = T. This approach has also been successfully applied for the calculation of harmonic and fundamental frequencies for first-row closed shell diatomic molecules.[16] Thus, if the success of composite methods for computing energies could be carried over into the calculation of vibrational frequencies, then significantly larger molecular systems can be studied with high accuracy.

However, for this to be possible, it is first necessary to establish the general applicability of composite methods for the calculation of other vibrational modes viz. molecular bends and torsions. To the best of the authors' knowledge, all previous studies utilizing a G*n*-type approach have been restricted to simple diatomic systems, where only uncomplicated stretching modes are assessed. In this work, the harmonic frequencies at both single level ab initio and G*n*-type composite approximations of CCSD(T) theory, are reported for 19 tri- and 18 tetratomic nonlinear molecules where the bends and torsions are examined as well. Additionally, a general scheme for calculating the composite level equilibrium geometries and harmonic frequencies for polyatomic systems that utilizes the Collins' method of interpolating potential energy surfaces is also described. The accuracy of the composite-level harmonic frequencies are evaluated through comparison with the corresponding single level CCSD(T) calculations.

It is envisaged that the results of this study should provide a clearer indication of the general applicability of composite methods for the calculation of vibrational frequencies of more complicated molecules. Furthermore, this would also contribute toward an alternative procedure for calculating highly accurate ab initio frequencies of larger molecules with significant reductions in computational cost.

## 2. Computational Details

The single level ab initio calculations were carried out at CCSD(T)/aug-cc-pVXZ, where X = D, T and Q. The calculations were performed using the MOLPRO 2002.1[17] and Gaussian 98[18] suite of programs. The composite energies were based on the ad hoc expression

$$E_{\text{L/S}} = E[\text{CCSD(T)/S}] + \Delta_{\text{basis}} \quad (1)$$

where $\Delta_{\text{basis}} = E[\text{MP}n/\text{L}] - E[\text{MP}n/\text{S}]$, MP*n* refers to *n*th-order Moller Plesset perturbation theory, and S and L denote small and large basis sets, respectively. $E_{\text{L/S}}$ is an approximation to the energy at the CCSD(T)/L level of theory. Note that if the MP*n* treatment in the basis set correction term $\Delta_{\text{basis}}$ was substituted with the CCSD(T) treatment, then this would yield exactly the CCSD(T)/L energies. This expression is similar to the electronic energy given in G3X(MP*n*) theory in refs 9 and 10 and is the same as that used in refs 15 and 16. It can thus be seen from eq 1 that one significant source of error in this approximation is the difference in treatment of electron correlation between the MP*n* and CCSD(T) levels.

In the subsequent sections, short-hand notations to describe the above calculations are D, T and Q for CCSD(T)/aug-cc-pVDZ, CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ, respectively. Similarly, composite methods are denoted by L/S, where L and S are shorthand notations of the above basis sets. It should be noted from eq 1 that the energy is defined for *any* molecular configuration, not just locally at and around minima, and provides a means to generate a composite potential energy surface (PES), as discussed earlier. Because each term in eq 1 is differentiable with respect to Cartesian displacements of the atoms so too is the composite energy. Thus we are able to obtain a composite equilibrium structure and harmonic frequencies. All molecular structures in this work have been optimized using both composite and single level ab initio methods specifying tight convergence. A threshold for the convergence of the energy in the SCF procedure of $10^{-10}$ Hatree has also been chosen in all calculations.

To calculate the L/S harmonic frequencies of a molecule, a PES is first required to locate its L/S optimized geometry. The PES was constructed using Collins' method of interpolation and has been described in detail elsewhere.[19] Once the PES minimum is located, the second derivative matrix is calculated numerically at this geometry and the harmonic frequencies obtained. The algorithm for obtaining the L/S harmonic frequencies of an $N$-atom nonlinear polyatomic molecule is described below:

1. Obtain an approximate set of normal coordinates ($Z_1$, $Z_2$, ..., $Z_{3N-6}$) at a lower level ab initio method such as MP2/6-31G(d), where analytic calculation of the Hessian matrix is possible. The optimized geometry, $\mathbf{Z_o}$, at this level of theory serves as an initial guess to the composite method equilibrium structure.

2. The L/S gradient and Hessian matrices are evaluated numerically by central difference formulas at $\mathbf{Z_o}$. This generates the initial L/S PES, which corresponds to a second-order Taylor polynomial about $\mathbf{Z_o}$.

3. The minimum point, $\mathbf{Z_1}$, of this PES is located using the Newton−Raphson method. The process repeats from step two, generating the next data point. After more than one data point is generated, the PES is expressed as an interpolation over the total number of data points, $N_{\text{data}}$, based on eq 2, where $w_n(\mathbf{Z})$ and $T_n(\mathbf{Z})$ refer to the normalized distance-based weight function and second-order Taylor approximation of the *n*th data point at $\mathbf{Z}$.

$$V(\mathbf{Z}) = \sum_{n=1}^{N_{\text{data}}} w_n(\mathbf{Z})\, T_n(\mathbf{Z}) \quad (2)$$

where

$$w_n(\mathbf{Z}) = \frac{v_n(\mathbf{Z})}{\sum_{i=1}^{N_{\text{data}}} v_i(\mathbf{Z})} \qquad v_n(\mathbf{Z}) = ||\mathbf{Z} - \mathbf{Z}(n)||^{-2p}$$

$$2p > 3N - 3 \quad (3)$$

4. The optimization is deemed converged if all the calculated gradient elements ($\nabla V_i$, $i = 1, ..., 3N - 6$) of the newest data point are less than or equal to an ad hoc value, $\epsilon_{\text{tol}}$; otherwise the algorithm repeats from step 2. The final data point is the L/S optimized geometry, $\mathbf{Z_{eq}}$ expressed in terms of the MP2/6-31G(d) normal coordinates.

5. $\mathbf{Z_{eq}}$ is expressed in terms of the $3N - 6$ standard $\mathbf{Z}$-matrix internal coordinates, where the Hessian with respect to these coordinates is calculated numerically. The L/S harmonic

**TABLE 1: Test Set of Molecules Used**

| | |
|---|---|
| triatomic | $H_3^+$ $H_2F^+$ $CH_2$ CHF $H_2O$ HNO HON $NH_2^+$ $NH_2^-$ $HO_2^+$ $HO_2^-$ $OCF^-$ $HF_2^+$ HOF $HNF^-$ $HCO^-$ $CF_2$ $C_2O$ $F_2O$ |
| tetratomic | $CFH_2^-$ $NFH_2$ $H_2CO$ $H_2O_2$ $OFH_2^+$ *cis*-$N_2H_2$ *trans*-$N_2H_2$ *trans*-HCOH *cis*-HCOH *cis*-$HCNH^-$ *trans*-$HCNH^-$, $CH_3^-$ $NH_3$ $OH_3^+$ $H_2NO^+$ $H_2NO^-$ $H_2NN$ $H_2CN^-$ |

**TABLE 2: Comparison of D and T/D Frequencies with T Harmonic Frequencies for Triatomic Systems**

| method | MAD | RMS | $\lvert\Delta\omega\rvert_{\text{median}}$ | $\lvert\Delta\omega\rvert_{\text{max}}$ |
|---|---|---|---|---|
| D | 37.0 | 45.7 | 28.4 | 108.1 |
| T/D | 4.46 | 6.88 | 3.12 | 27.1 |

frequencies are obtained in the usual manner from the Hessian and atomic masses.

All numerical derivatives were evaluated using a step size of $5 \times 10^{-4}$ au and $\epsilon_{\text{tol}}$ was specified as $5 \times 10^{-5}$ au, which corresponds to the tight convergence criteria in the Gaussian software package. In all the molecules examined, the geometry optimization converged within three cycles.

## 3. Results and Discussion

Table 1 shows the full list of molecules that were examined in this study. Unless otherwise stated, all composite frequencies were evaluated using MP2 theory in eq 1. We shall first examine the results for the triatomic molecules, followed by the tetratomic and larger systems.

**3.1. Triatomics.** The single level D, T and composite T/D harmonic frequencies for 19 triatomic molecules have been calculated, providing a sample of 57 bending and stretching frequencies for comparison (see Table S1 in the Supporting Information). The data for the T/D and D harmonic frequencies are compared to the T frequencies and are summarized in Table 2. As mentioned earlier, the CCSD(T) theory has an intrinsic error of about 8 cm$^{-1}$ in terms of the calculation of experimental vibrational frequencies, and including core-correlation (not included in this work). Thus, it is desirable that the composite harmonic frequencies lie within the same range of their single level CCSD(T) counterparts. It is clear by examining the data in Table 2 that a substantial improvement in the accuracy of the harmonic frequencies is achieved using composite methods compared with the D frequencies. For example, the T/D mean absolute deviation (MAD) and root-mean-square (RMS) values are 4.46 cm$^{-1}$ and 6.88 cm$^{-1}$, which are about 8 times smaller compared to the D frequencies with MAD and RMS values of 37.0 and 45.7 cm$^{-1}$ respectively.

The distribution of the absolute deviation (AD) values for the 57 T/D and D frequencies is illustrated in Figure 1. From the distribution curves, it was observed that the absolute deviations in the D frequencies are fairly evenly distributed, with errors as large as 108 cm$^{-1}$. On the other hand, about 70% of the T/D frequencies are within 5 cm$^{-1}$ of the T frequencies, and at least 95% within 15 cm$^{-1}$. However, it was noted that two (originating from $HCO^-$ and HON) of the 57 T/D frequencies had absolute deviations in excess of 20 cm$^{-1}$, where the maximum was 27.1 cm$^{-1}$. Likewise, the absolute deviations in the corresponding D frequencies were found to be in excess of 40 cm$^{-1}$. Further inspection revealed that these frequencies arose from the highest frequency stretching modes of these two molecules. Curiously, the remaining T/D vibrational frequencies of the two molecules are relatively accurate and fall within 12 cm$^{-1}$ of the corresponding T frequencies.

Generally speaking, the errors in the composite expression in eq 1 are likely to propagate and impact most on the high frequency vibrational modes. The fact that the two outlying frequencies correspond to the highest stretching frequencies of two molecules attest to this. There are two main sources of error in the composite frequencies: First, the gradient vectors and Hessians were evaluated numerically via central difference and must therefore incur some errors in the harmonic frequencies. More significantly, the use of MP*n* in the basis set correction term $\Delta_{\text{basis}}$ must be taken into consideration. Presumably, the anomalously large deviations in the composite frequencies for the two systems are due to the inadequate treatment of electron correlation by the MP2 procedure. As pointed out earlier, this error can be improved by systematically increasing the level of electron correlation in the basis set correction term.

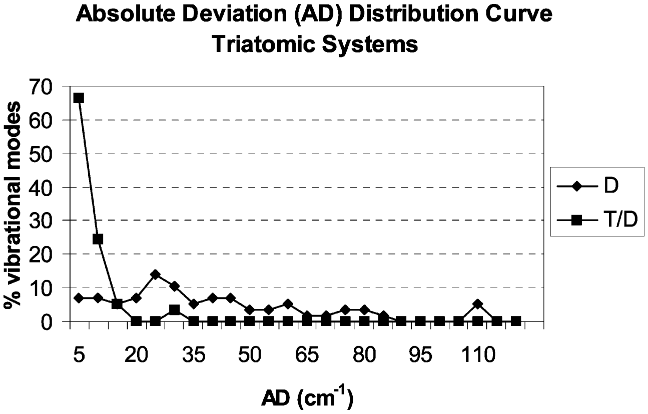

**Figure 1.** Plot of the percentage of vibrational modes against the absolute deviation from the T frequencies for the triatomic systems.

**TABLE 3: Comparison of Q/T, Q/D, T and D Frequencies with Q Harmonic Frequencies for Triatomic Systems**

| method | MAD | RMS | $\lvert\Delta\omega\rvert_{\text{median}}$ | $\lvert\Delta\omega\rvert_{\text{max}}$ |
|---|---|---|---|---|
| T | 9.1 | 11.0 | 10.2 | 20.7 |
| D | 44.7 | 54.0 | 34.9 | 118.0 |
| Q/T | 1.3 | 1.61 | 1.2 | 2.9 |
| Q/D | 4.1 | 5.0 | 3.9 | 9.8 |
| T/D | 12.2 | 14.3 | 12.9 | 24.7 |

As such, the harmonic frequencies for the two molecules were reevaluated by substitution of MP3 (see Table S4 in the Supporting Information) for MP2 in eq 1. This led to a marked improvement in the two outlying frequencies where the deviations were reduced to less than 7 cm$^{-1}$. There was also further improvement in the other frequencies of these molecules where the AD with the T frequencies was reduced to less than 3 cm$^{-1}$. Similarly, upon substitution with the corresponding MP3 T/D frequencies for the two molecules, the MAD and RMS values were further reduced from 4.46 and 6.88 cm$^{-1}$ to 3.31 and 4.95 cm$^{-1}$, respectively. These observations suggest that the high-frequency vibrations tend to be more sensitive to the inexactness of the composite expression.

Additionally, the single level Q and composite levels Q/T and Q/D were also computed for a subset of the six lightest triatomic molecules shown in Table S2 of the Supporting Information, and summarized in Table 3. Also provided in Tables S2 and 3 are the results for T/D, T and D harmonic frequencies versus the Q frequencies. The Q/T frequencies were of comparable accuracy to the Q frequencies, with a MAD of only 1.3 cm$^{-1}$, compared to a MAD of 9.1 cm$^{-1}$ in the T frequencies. It was also noted that the performance of the Q/D frequencies was slightly worse compared to the Q/T frequencies, with an MAD of 4.1 cm$^{-1}$, although this is within the acceptable error range. Not surprisingly, the T/D frequencies do not predict the Q frequencies as accurately as the former two but compares

**TABLE 4: Comparison of D and T/D Frequencies with T Harmonic Frequencies for Tetratomic Systems**

| method | MAD | RMS | $\lvert\Delta\omega\rvert_{\mathrm{median}}$ | $\lvert\Delta\omega\rvert_{\mathrm{max}}$ |
|---|---|---|---|---|
| D | 20.3 | 23.7 | 18.9 | 63.9 |
| T/D | 4.2 | 5.4 | 3.5 | 20.0 |

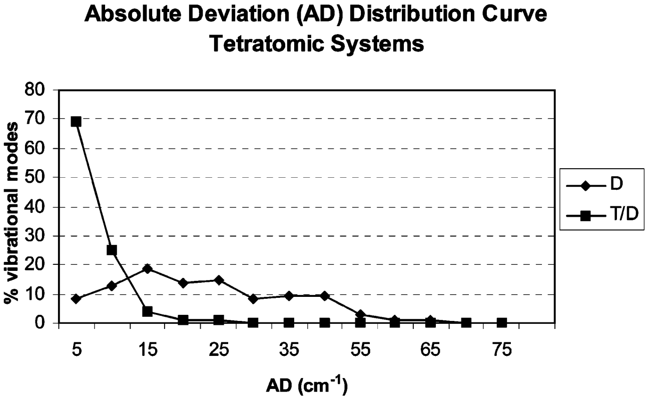

**Figure 2.** Plot of the percentage of vibrational modes against the absolute deviation from the T frequencies for the test set of tetratomic systems.

well with the T frequencies as illustrated by the good agreement between their MAD and $|\Delta\omega|_{\mathrm{median}}$ values.

The above observations imply that the optimal combination of basis sets (L and S) for predicting single level L harmonic frequencies is when they differ by no more than one in the valence designation. It is possible that the widening difference in the valence designation of the two basis sets (L and S) would deteriorate the quality of the basis set correction term $\Delta_{\mathrm{basis}}$, thereby leading to poor agreement with the CCSD(T)/L frequencies.

**3.2. Tetratomics Systems.** The single level T, D and composite T/D harmonic frequencies are also calculated for a set of 18 tetratomic molecules, providing a sample of 108 stretching, bending and torsional modes for comparison. These molecules have geometries ranging from tetrahedral, trigonal pyramidal to planar structures. Table 4 summarizes our results, whereas Table S3 in the Supporting Information provides all the frequencies.

The performance of the composite frequencies in the tetratomic systems is consistent with the triatomic systems. Here, the MAD value of the T/D frequencies from the T calculations is merely 4.2 cm$^{-1}$, which is about a 5-fold reduction compared to that of the D frequencies at 20 cm$^{-1}$. The distribution of the AD of the 108 T/D and vibrational frequencies is plotted in Figure 2.

The distribution curves in Figure 2 illustrates a trend similar to that in Figure 1 where about 95% of the T/D frequencies lie within 10 cm$^{-1}$ of the T frequencies, although it was observed that a small number had absolute deviations greater than 12 cm$^{-1}$ with $|\Delta\omega|_{\mathrm{max}}$ of 20 cm$^{-1}$. Further examination revealed that these frequencies arose from high frequency stretching modes of several tetratomic molecules. On the contrary, the remaining vibrations of these molecules generally showed good agreement with deviations of 10 cm$^{-1}$ or less. To assess the errors due to the composite approximation, the composite frequencies were reevaluated using the MP3 rather than MP2 in eq 1 for the two of molecules, $H_2CN^-$ and $H_2NN$, with the largest deviations (19.3 and 20.0 cm$^{-1}$).

**TABLE 5: CPU Times Associated with the MP2 and CCSD(T) Calculation at the Equilibrium Geometry of $CF_4$**

| basis set | no. of basis functions | MP2 | MP3 | CCSD(T) |
|---|---|---|---|---|
| aug-cc-pVDZ | 115 | | | 1702.90 |
| aug-cc-pVTZ | 230 | 112.68 | 593.96 | 24687.76 |

Consequently, both deviations were substantially reduced to 0.36 and 10.7 cm$^{-1}$, respectively (see Table S4 in the Supporting Information). Likewise, the deviations for the remaining frequencies were further reduced to less than 4 cm$^{-1}$. Substitution of these frequencies for the two molecules with the MP3 composite frequencies led to improved MAD and RMS values of 3.75 and 4.58 cm$^{-1}$, respectively.

Thus far, the results have been supportive of the capacity of the composite procedure to make reliable predictions of the harmonic frequencies corresponding to bending and torsional modes. However, it has also been noted that the high frequency vibrational modes, specifically stretches, tend to be more sensitive to the errors incurred in the composite approximation. These errors are primarily due to the inaccuracy of the basis set correction term in eq 1. Our preliminary assessment shows that the correction term may be systematically refined by using higher-order perturbation methods such as the MP3 procedure. This observation was also reported in the study by Dunning and Peterson on diatomic molecules, where the MP3 composite procedure out-performed its MP2 counterpart.[15]

Despite the higher accuracy and consistency in the MP3 approximation, there is also the added computational cost as the CPU time associated with this method scales as the sixth power of the number of basis functions. On the other hand, the MP2 composite procedure is generally very accurate with errors less than 5 cm$^{-1}$ on average. Hence, for a given CPU time budget, the MP2 approximation should be useful for many molecular studies.

**3.3. CPU Time Savings.** The major advantage with the composite approach is the ability to predict single level CCSD(T) harmonic frequencies accurately, while only requiring a significantly shorter CPU time. Based on the MP2 procedure, the composite approach is approximately a factor of *n* times faster:

$$n = \frac{t\{\mathrm{CCSD(T)/L}\}}{t\{\mathrm{MP2/L}\} + t\{\mathrm{CCSD(T)/S}\}} \tag{4}$$

where $t\{\mathrm{CCSD(T)/L}\}$ refers to the CPU time incurred for the CCSD(T) and large basis set calculation, and so forth.

To estimate the CPU time-savings that may be obtained, the composite procedure was applied to tetrafluoromethane, which is composed of five heavy atoms. Based on a single point calculation at the T/D equilibrium geometry, the CPU times required by the T and T/D procedures are tabulated in Table 5.

Accordingly, it is estimated that the CCSD(T)/aug-cc-pVDZ calculations are approximately 14.5 times faster than CCSD(T)/aug-cc-pVTZ. Quite remarkably, the CPU times associated with the composite approximations are exceedingly close, where *n* has been estimated to be 13.5 and 10.7 for the MP2 and MP3 procedures, respectively.

Additionally, the T/D frequencies for $CF_4$ have also been computed and compared with the corresponding T harmonic frequencies from earlier work of Wang et al.[20] The frequencies are tabulated in Table 6.

As shown in Table 6, all the T/D frequencies are in excellent agreement with the T frequencies, with errors of 3.0 cm$^{-1}$ or less. This result is most noteworthy considering the mere additional cost of performing a MP2 energy calculation. It also appears that for a medium-sized system molecule such as tetrafluoromethane, the difference in the CPU times required

**TABLE 6: Computed CCSD(T) Harmonic Frequencies (cm$^{-1}$)**

| vibrational mode | T | T/D | T-T/D |
|---|---|---|---|
| 1 | 435.2 | 434.1 | 1.1 |
| 2 | 630.4 | 628.4 | 2.0 |
| 3 | 915.2 | 912.4 | 2.8 |
| 4 | 1301.3 | 1298.5 | 2.8 |

for MP3 and MP2 is somewhat small when compared with the single level CCSD(T) calculations. Accordingly, the MP3 approximation may be more advantageous in terms of reliability for small to medium-sized molecules.

## 4. Concluding Remarks

In this paper, the harmonic frequencies for a test set of closed shell triatomic and tetratomic molecules have been calculated at both single level and composite approximations of the CCSD(T) method. The results of this study demonstrate the ability of the composite approximation to make very accurate predictions of the harmonic frequencies that are within 5 cm$^{-1}$ of the corresponding single level CCSD(T) calculation. All previous studies have focused exclusively on simple diatomic molecules, where only stretching modes were examined. Through the work presented here it is established that the composite procedure is equally capable of making accurate predictions of other vibrational frequencies corresponding to bending and torsional modes for more complicated polyatomic systems.

The poorer estimation of the stretching frequencies for polyatomic molecules has been attributed to the fact that stretching modes are invariably the high-frequency vibrations and are therefore more sensitive to the errors in the energy expression in eq 1. Nevertheless, it has been demonstrated in problematic systems that the large deviations in the T/D harmonic frequencies are readily remedied through the use of MP3 procedure. The tradeoff, however, is the increased computational cost associated with this method, which scales as the sixth power of the number of basis functions.

To summarize, it is conceivable that the combination of efficient Hessian update schemes combined with the theoretical procedure presented here should enable the study of significantly larger molecular systems.

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**Supporting Information Available:** Table S1 contains the CCSD(T)/aug-cc-pVXZ (X = D and T) and the composite, T/D, harmonic frequencies (cm$^{-1}$) for the triatomic molecules. Table S2 contains the CCSD(T)/aug-cc-pVXZ (X = D, T and Q) and the composite Q/T, Q/D and T/D harmonic frequencies (cm$^{-1}$) for the six lightest triatomics. Table S3 contains the CCSD(T)/aug-cc-pVXZ (X = D and T) and composite, T/D, harmonic frequencies (cm$^{-1}$) for the tetratomic molecules. Table S4 contains the two tetratomics $H_2CN^-$ and $H_2NN$, and two triatomics, $HCO^-$ and HON, CCSD(T)/aug-cc-pVTZ and composite T/D harmonic frequencies (cm$^{-1}$) using MP3 and MP2 in the $\Delta_{\mathrm{basis}}$ correction. This material is available free of charge via the Internet at http://pubs.acs.org.

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