# An Assessment of the Performance of High-Level Theoretical Procedures in the Computation of the Heats of Formation of Small Open-Shell Molecules

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The heats of formation at 0 K ($\Delta_f H_0$) of 29 small (containing up to 3 heavy atoms) open-shell molecules, with accurately known experimental values, have been calculated using a number of high-level theoretical procedures. The theoretical methods examined include variants of Gaussian-n (G2, G2-RAD(RMP2), G2-RAD(B3-LYP), G2-RAD(QCISD), G3, G3-RAD, G3X, G3X-RAD, G3(MP2), G3(MP2)-RAD, G3X(MP2) and G3X(MP2)-RAD), CBS (CBS-APNO, CBS-Q, CBS-RAD and CBS-QB3), and Martin extrapolation (Martin-2, Martin-3, W1, W1′, W1h, W2h and W2) procedures. The open-shell systems include doublet radicals ($\bullet$BeH, $\bullet$CH, $\bullet CH_3$, $\bullet NH_2$, $\bullet$OH, $\bullet SiH_3$, $\bullet PH_2$, $\bullet$SH, $\bullet N_2^+$, $\bullet$NO, $\bullet$ONO, $\bullet O_2^-$, $\bullet$CN, $\bullet CO^+$, $\bullet CS^+$, $\bullet$CCH, $\bullet$CHO, $\bullet$OOH, $\bullet CHCH_2$, $\bullet CH_2CH_3$, $\bullet CH_2OH$, $\bullet OCH_3$, $\bullet SCH_3$ and $\bullet COCH_3$) and triplet biradicals ($:CH_2$, $:$NH, $:SiH_2$, $:O_2$, and $:S_2$). The results for these systems are used to assess the performance of the various theoretical methods. The smallest mean absolute deviations (MADs) from experiment are found with the G3-RAD, G3X-RAD, G3X, W1h, W2, W1, and W2h procedures with MADs lying in the range 2.0−2.5 kJ mol$^{-1}$. The smallest values for the largest deviation (LD) from experiment are found with the G3X, G3X-RAD, W2, and W2h procedures and are ±6.4 kJ mol$^{-1}$. A selection of the most accurate theoretical procedures (G3-RAD, G3X-RAD, G3X, W1h, W2, W1, and W2h) is used to predict the heats of formation for several radicals ($\bullet$OF, $\bullet CH_2CHCH_2$, $\bullet CH_2CN$, $\bullet CH_2COOH$, and $\bullet CH_2C_6H_5$) for which there are greater uncertainties associated with the experimental values.

## 1. Introduction

The calculation of thermochemical properties (such as heats of formation) of molecules is becoming an increasingly important application of ab initio molecular orbital theory.[1] Several different families of theoretical approaches to molecular thermochemistry have been developed. These include variants of G2 theory[2] and G3 theory[3] of Curtiss, Raghavachari, Pople and co-workers, the CBS methods of Petersson and co-workers,[4] the W1, W2 and related methods of Martin and co-workers,[5] and the extrapolation procedures of Dunning, Feller, Dixon, Peterson, and co-workers.[6] The G2, G3, and CBS procedures have been found to give heats of formation ($\Delta_f H$) with mean absolute deviations (MADs) from experiment of 3.6 to 6.5 kJ mol$^{-1}$ while the MADs for the Martin methods are in the range 2.1−2.9 kJ mol$^{-1}$. While a number of general theoretical studies of heats of formation have appeared in the literature,[1] fewer studies have focused on open-shell species. [7−9]

In this paper we assess the performance of a number of high-level theoretical procedures for the calculation of the heats of formation of free radicals. Results for 29 small radicals with well-known experimental $\Delta_f H_0$ values (experimental uncertainties ≤ 5 kJ mol$^{-1}$) are used to assess these techniques. The theoretical results are then used to suggest improved values of the radical $\Delta_f H_0$ in several cases where the uncertainties in the experimental heats of formation are larger. The theoretical methods investigated represent variants of Gaussian-n (G2,[2a] G2-RAD(RMP2),[9b] G2-RAD(B3-LYP),[9b] G2-RAD(QCISD),[9b] G3,[3a] G3-RAD, G3X,[3f] G3X-RAD, G3(MP2)[3b] G3(MP2)-RAD,[9d,10] G3X(MP2)[3f] and G3X(MP2)-RAD), CBS (CBS-APNO,[4a] CBS-Q,[4b] CBS-RAD,[9a] and CBS-QB3[4d,e]), and Martin extrapolation (Martin-2,[9a] Martin-3,[9a] W1,[5e,i] W1′,[5g] W1h,[1g] W2h[1g,5h] and W2[5e,i]) procedures. The G3-RAD, G3X-RAD, and G3X(MP2)-RAD methods are introduced for the first time in the present study.[10]

## 2. Theoretical Procedures

Ab initio molecular orbital calculations[11] were performed using the Gaussian 98,[12] ACES II,[13] and MOLPRO 2000.6[14] computer programs. Unless indicated otherwise, unrestricted open-shell reference wave functions (e.g., UHF and UMP2) and the frozen-core (fc) approximation were used. In the cases where restricted open-shell calculations were used, they are designated with an “R” prefix. Correlation of all electrons in a molecule is denoted (fu). Zero-point vibrational energy (ZPVE) scaling factors were either standard for the particular method or optimized,[15] as noted.

Molecular energies were used to derive heats of formation at 0 K ($\Delta_f H_0$) using the atomization method outlined by Nicolaides et al.[16] Unless otherwise noted, atomic $\Delta_f H_0$ values were taken from the compendium of experimental values of Lias et al.[17] We note that there has been some debate in the literature[6c,18] over the heat of formation of silicon atom. In this study we adopt the theoretical value ($\Delta_f H_0(Si_{(g)}) = 448.3$ kJ mol$^{-1}$) proposed by Martin and Taylor,[18e] based on high-level benchmark calculations on $SiF_4$. The theoretical value proposed by Ochterski et al.[19] for beryllium atom ($\Delta_f H_0(Be_{(g)} = 317.1$ kJ mol$^{-1}$) has also been used.[20]

The principal features of the Gaussian-n (Gn), CBS-n, Martin-n, and Wn procedures investigated in this study are presented in Table 1and summarized below.

Standard G2 theory[2a] includes an MP2(fu)/6-31G(d) optimized geometry and a scaled (by 0.8929) HF/6-31G(d) ZPVE.

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**TABLE 1: Principal Features of Selected Compound Methods**

| method | geometry | ZPVE | energy |
|---|---|---|---|
| G2 | UMP2(fu)/6-31G(d) | UHF/6-31G(d)[a] | estimated UQCISD(T)/6-311+G(3df,2p) |
| G2-RAD(RMP2) | RMP2/6-31G(d) | UB3-LYP/6-31G(d)[b] | estimated URCCSD(T)/6-311+G(3df,2p) |
| G2-RAD(B3-LYP) | UB3-LYP/6-31G(d) | UB3-LYP/6-31G(d)[b] | estimated URCCSD(T)/6-311+G(3df,2p) |
| G2-RAD(QCISD) | UQCISD/6-31G(d) | UB3-LYP/6-31G(d)[b] | estimated URCCSD(T)/6-311+G(3df,2p) |
| G3 | UMP2(fu)/6-31G(d) | UHF/6-31G(d)[a] | estimated UQCISD(T)(fu)/G3large |
| G3-RAD | UB3-LYP/6-31G(d) | UB3-LYP/6-31G(d)[b] | estimated URCCSD(T)(fu)/G3large |
| G3X | UB3-LYP/6-31G(2df,p) | UB3-LYP/6-31G(2df,p)[c] | estimated UQCISD(T)(fu)/G3Xlarge |
| G3X-RAD | UB3-LYP/6-31G(2df,p) | UB3-LYP/6-31G(2df,p)[c] | estimated URCCSD(T)(fu)/G3Xlarge |
| G3(MP2) | UMP2(fu)/6-31G(d) | UHF/6-31G(d)[a] | estimated UQCISD(T)/G3MP2large |
| G3(MP2)-RAD | UB3-LYP/6-31G(d) | UB3-LYP/6-31G(d)[b] | estimated URCCSD(T)/G3MP2large |
| G3X(MP2) | UB3-LYP/6-31G(2df,p) | UB3-LYP/6-31G(2df,p)[c] | estimated UQCISD(T)/G3Xlarge |
| G3X(MP2)-RAD | UB3-LYP/6-31G(2df,p) | UB3-LYP/6-31G(2df,p)[c] | estimated URCCSD(T)/G3Xlarge |
| CBS-APNO | UQCISD/6-311G(d,p) | UHF/6-311G(d,p)[d] | extrapolated UQCISD(T) |
| CBS-Q | UMP2/6-31G† | UHF/6-31G†[e] | extrapolated UQCISD(T) |
| CBS-RAD | UB3-LYP/6-31G(d) | UB3-LYP/6-31G(d)[b] | extrapolated UCCSD(T) |
| CBS-QB3 | UB3-LYP/6-311G(2d,d,p) | UB3-LYP/6-311G(2d,d,p)[f] | extrapolated UCCSD(T) |
| Martin-2, Martin-3 | URCCSD(T)/cc-pVTZ | UQCISD/6-31G(d)[g] | extrapolated URCCSD(T) |
| W1, W1′, W1h | UB3-LYP/cc-pVTZ+1 | UB3-LYP/cc-pVTZ+1[h] | extrapolated URCCSD(T) |
| W2, W2h | URCCSD(T)/cc-pVQZ+1 | UB3-LYP/cc-pVTZ+1[h] | extrapolated URCCSD(T) |

[a] Scaled by 0.8929. [b] Scaled by 0.9806. [c] Scaled by 0.9854. [d] Scaled by 0.9251. [e] Scaled by 0.9184. [f] Scaled by 0.9900. [g] Scaled by 0.9776. [h] Scaled by 0.9850.

A QCISD(T)/6-311G(d,p) base energy is corrected to QCISD(T)/6-311+G(3df,2p) using several additivity approximations at the MP2 and MP4 levels. A "higher-level correction" (HLC) is added to correct for residual basis set and other deficiencies.

The Gn-RAD procedures are designed to give improved performance for radicals over their standard Gn counterparts. The principal general differences of Gn-RAD include (a) the replacement of all UMP energies by restricted open-shell Møller−Plesset (RMP) energies and (b) determining the final level of electron correlation using the URCCSD(T) method of MOLPRO rather than the QCISD(T) level. Additional differences relevant to specific Gn-RAD procedures are noted below.

The G2-RAD(RMP2), G2-RAD(B3-LYP), and G2-RAD(QCISD) procedures,[9b] in addition to the general Gn-RAD modifications listed above, also differ from standard G2 in that they (a) make use of RMP2/6-31G(d), B3-LYP/6-31G(d), or QCISD/6-31G(d) optimized geometries, respectively, and (b) they use a B3-LYP/6-31G(d) ZPVE scaled by 0.9806.[15] In addition, (c) they employ a modified higher level correction of 5.32 millihartrees per electron pair[2c] because the frequency scaling factor is chosen to reproduce ZPVEs rather than fundamental frequencies.

The G3 method[3a] is generally similar to G2 theory but makes use of smaller basis sets for the MP4 and QCISD(T) calculations of the additivity scheme. Core-correlation is also included, by performing the MP2/G3large single-point calculation with correlation of all electrons (fu). Additionally, a spin−orbit correction is included for atoms, while separate HLCs are used for molecules and atoms. These HLCs were derived to give a best fit to 299 of the 302 energies in the G2/97 test set.[2f]

The G3-RAD procedure, introduced in the present study, includes the standard Gn-RAD modifications. It differs additionally from standard G3 theory in that it (a) uses a B3-LYP/6-31G(d) optimized geometry and ZPVE (scaled by 0.9806),[15] (b) evaluates the RMP4/6-31G(2df,p), RMP2/6-31G(2df,p), and RMP2(fu)/G3large energies using Cartesian (6d, 10f) basis functions,[21] and (c) includes a redetermined HLC (yielding $A = 6.884$, $B = 2.747$, $C = 6.561$, and $D = 1.341$ mhartrees),[21b] optimized to give a best fit to 296 of the 302 energies[22] in the G2/97 test set, to account for the use of the B3-LYP/6-31G(d) ZPVE, Cartesian basis sets, and the standard RAD modifications.

G3X[3f] is a modified G3 procedure, which makes use of a B3-LYP/6-31G(2df,p) geometry and ZPVE (scaled by 0.9854). An additional calculation is performed at the Hartree−Fock level, with the G3Xlarge basis set, formed by adding a single g polarization function to all second-row atoms in the G3large basis set, to help account for deficiencies observed for species containing these atoms.

G3X-RAD, also introduced in the present study, follows G3X in using a B3-LYP/6-31G(2df,p) geometry and ZPVE (scaled by 0.9854). In addition, like G3-RAD, all energies are evaluated using Cartesian (6d, 10f, 15g) basis sets.[21] The Hartree−Fock calculation with the G3Xlarge basis set is performed with the restricted open-shell formalism, and the HLC has been redetermined to minimize the mean absolute deviation from experiment for 296 energies[22] of the G2/97 test set (yielding $A = 6.894$, $B = 2.719$, $C = 6.655$, and $D = 1.351$ mhartrees).[21b]

G3(MP2)[3b] uses an MP2(fu)/6-31G(d) optimized geometry and a scaled (by 0.8929) HF/6-31G(d) ZPVE. A base energy evaluated at the QCISD(T)/6-31G(d) level is corrected to QCISD(T)/G3MP2large using an additivity approximation at the MP2 level. The G3(MP2)-RAD procedure used in the present study is an improved version of the previously reported G3(MP2)-RAD.[9d,10] It continues to make use of a B3-LYP/6-31G(d) optimized geometry and ZPVE (scaled by 0.9806). However, our improved version of G3(MP2)-RAD includes a new HLC ($A = 9.413$, $B = 3.969$, $C = 9.438$, and $D = 1.888$ mhartrees)[21b] optimized on 301 energies[23] of the G2/97 test set to account for the Gn-RAD modifications.

G3X(MP2) and G3X(MP2)-RAD correspond to modified G3X and G3X-RAD procedures, respectively. Like G3X, both of these methods make use of a B3-LYP/6-31G(2df,p) geometry and ZPVE (scaled by 0.9854). An additional calculation is performed at the Hartree−Fock level (UHF for G3X(MP2) and RHF for G3X(MP2)-RAD) with the G3Xlarge basis set. Like the new G3(MP2)-RAD, the G3X(MP2)-RAD HLC ($A = 9.556$, $B = 3.992$, $C = 9.684$, and $D = 1.970$ mhartrees)[21b] has been calculated to give the best fit to 301 energies[23] of the G2/97 test set.

Several members of the CBS family of procedures[4] were also examined (CBS-APNO, CBS-Q, CBS-RAD, and CBS-QB3). These methods aim to estimate the energy of a species at the QCISD(T) or CCSD(T) level with an infinite basis set. The two main features in each are an extrapolation of the total energy to the infinite-basis-set limit using pair-natural-orbital energies at the MP2 correlation level and an additive correction to the QCISD(T) or CCSD(T) electron correlation level.

CBS-APNO[4a] employs QCISD/6-311G(d,p) optimized geometries while CBS-Q[4b] makes use of MP2/6-31G$^\dagger$ geometries. Additionally, CBS-APNO uses larger basis sets for the extrapolation and for the additive correlation correction, as well as including a core-correlation correction, which is absent in CBS-Q (except for sodium). CBS-Q includes a spin-correction factor to account for spin-contamination in open-shell species. HF/6-311G(d,p) and HF/6-31G$^\dagger$ ZPVEs are used in CBS-APNO and CBS-Q, respectively.

The CBS-RAD(B3-LYP,B3-LYP) procedure,[9a] referred to here as CBS-RAD, was introduced particularly for free radicals and differs from standard CBS-Q in that it (a) uses a B3-LYP/6-31G(d) optimized geometry, (b) contains a scaled (by 0.9806)[15] B3-LYP/6-31G(d) ZPVE, and (c) calculates the final level of electron correlation using CCSD(T) rather than QCISD(T).

The CBS-QB3[4d,e] method includes features similar to those in CBS-RAD.[9a] It differs from CBS-Q by (a) employing a B3-LYP/6-311G(2d,d,p) optimized geometry, (b) using a B3-LYP/6-311G(2d,d,p) ZPVE (scaled by 0.99), (c) determining the ultimate electron correlation with CCSD(T), and (d) including a spin−orbit correction for atoms.

The final group of methods investigated are variations of Martin's extrapolation-based procedures[1b,g,5,9a] which use Dunning basis sets with systematically increasing highest angular momentum quantum number to approximate infinite-basis-set calculations.

The Martin-2 and Martin-3 methods[9a] use URCCSD(T)/cc-pVTZ optimized geometries and scaled (by 0.9776)[15] QCISD/6-31G(d) ZPVEs. URCCSD(T)/cc-pV$n$Z energies are used in three-point ($n$ = T, Q, and 5) and two-point ($n$ = T and Q) extrapolations for Martin-2 and Martin-3, respectively, to approximate the infinite-basis-set limit. A core-correlation correction is obtained from the difference in URCCSD(T)(fu)/cc-pCV$n$Z and URCCSD(T)(fc)/cc-pCV$n$Z energies ($n$ = Q for Martin-2 and $n$ = T for Martin-3). However, since the cc-pCV$n$Z basis sets are available for B−Ne only, the core-correlation correction for radicals containing second-row atoms was calculated using the MTSmall basis set.[5e] Additional corrections for triple bonds and spin−orbit coupling in atoms are also included.[9a]

Martin's Wn methods (W1, W1′, W1h, W2, and W2h)[1g,5] also attempt to approximate infinite-basis-set URCCSD(T) calculations. The W1 and W2 procedures use UB3-LYP/cc-pVTZ+1 and URCCSD(T)/cc-pVQZ+1 optimized geometries, respectively, where +1 indicates the addition to all second-row atoms of a single high-exponent d-type inner polarization function. URCCSD and URCCSD(T) calculations are then performed with basis sets of systematically increasing size (aug′-cc-pVDZ+2d and aug′-cc-pV$n$Z+2d1f, where $n$ = T, Q or 5, and +2d and +2d1f indicate the addition of high exponent d and f functions to all second-row atoms). Separate extrapolations are performed to determine the SCF, URCCSD valence-correlation, and triple-excitation components of the total atomization energy at the basis-set limit. The W1h and W2h procedures[1g,5h] use aug-cc-pV$n$Z basis sets on the elements of groups V, VI, VII, and VIII but regular cc-pV$n$Z basis sets on atoms from groups I, II, III, and IV. We make use of the recently proposed[5i] two-point SCF extrapolation for W1, W1h, W2, and W2h, while retaining the original three-point extrapolation for W1′.[24] The W1′ procedure also differs from W1 in that the URCCSD(T)/aug′-cc-pVTZ+2d1f energy is replaced with URCCSD(T)/aug′-cc-pVTZ+2d. All of the Wn procedures include contributions from core correlation, scaled ZPVE, scalar relativistic effects, and first-order spin−orbit coupling on molecules and atoms. The new formulation of W1, W1h, W2, and W2h[1g,5i] also calls for the deep-lying (1s)-like orbitals to be frozen on second-row atoms in the core-correlation and scalar relativistic calculations.

## 3. Results and Discussion

**A. Radical Geometries.** The accurate determination of radical heats of formation can depend greatly on the quality of the optimized geometry. It is therefore necessary to assess the performance of various procedures for obtaining reliable radical geometries. Table 2 presents bond lengths for 26 of the 29 radicals in our set, optimized at several of the levels of theory on which the high-level theoretical procedures discussed in the next section are based, and for which accurate experimental geometries are available.[25] Also included are mean absolute deviations (MADs), mean deviations (MDs), and largest deviations (LDs) from experiment. A positive sign for an MD or LD indicates an overestimation by theory.

As can be seen from the mean absolute deviations from experiment, all levels of theory give good overall performance for bond lengths. URCCSD(T)/cc-pVQZ+1 performs the best, with an MAD of 0.003 Å and an LD of only +0.011 Å.[26] URCCSD(T)/cc-pVTZ performs slightly less well with an MAD of 0.006 Å and LD of +0.026 Å. The positive mean deviation from experiment (MD = +0.006 Å) indicates that URCCSD(T)/cc-pVTZ tends to slightly overestimate most bond lengths. This has also been previously noted by Martin.[27] Byrd et al.[28] found similar behavior for RCCSD(T)/cc-pVTZ (MAD = 0.006 Å, MD = +0.004 Å). However, UCCSD(T)/cc-pVTZ is less satisfactory (MAD = 0.012 Å, MD = +0.010 Å). Interestingly, they find RCCSD(T) only marginally improves on RCCSD while UCCSD(T) is in fact statistically inferior to UCCSD for radical geometries.[28]

The computationally inexpensive UB3-LYP/6-31G(d), UB3-LYP/6-31G(2df,p), and UB3-LYP/cc-pVTZ+1 methods also perform well, with MADs of 0.008 Å, 0.005 Å, and 0.005 Å, respectively. The LDs (+0.038 Å, +0.023 Å, and −0.015 Å) for UB3-LYP with the 6-31G(d), 6-31G(2df,p), and cc-pVTZ+1 basis sets are larger in magnitude than that of URCCSD(T)/cc-pVQZ+1 but smaller in the last two cases than URCCSD(T)/cc-pVTZ. Byrd et al.[28] found a slight improvement in bond lengths at UB3-LYP in going from the 6-31G(d,p) basis set to cc-pVTZ. For the radicals of Table 2, there is also slight improvement in performance in going from UB3-LYP/6-31G(d) to UB3-LYP/cc-pVTZ+1. Bond lengths are generally slightly overestimated by UB3-LYP/6-31G(d) (MD = +0.007 Å), while the mean deviations with the 6-31G(2df,p) and cc-pVTZ+1 basis sets are close to zero (MDs = +0.002 Å and −0.001 Å, respectively). Our UB3-LYP/cc-pVTZ+1 level shows a slight improvement over the UB3-LYP/cc-pVTZ results of Byrd et al.[28] (MAD = 0.008 Å) as does UB3-LYP/6-31G(2df,p) over UB3-LYP/6-31G(d,p) (MAD = 0.008 Å, MD = +0.006 Å).

The UQCISD/6-31G(d) level performs less well than the much more economical UB3-LYP, with an MAD of 0.012 Å and an LD of +0.027 Å, while systematically overestimating radical bond lengths (MD = +0.012 Å). The UCCSD/6-31G(d,p) results of Byrd et al.[28] suggest that it performs slightly better than UQCISD/6-31G(d) with an MAD of 0.009 Å and an MD of +0.007 Å.

UMP2(fu) and RMP2 (MADs of 0.014 and 0.016 Å, respectively) give very similar results for species with minimal

**TABLE 2: Calculated and Experimental Bond Lengths (Å)**

| radical | bond | UMP2/ 6-31G(d) | $\langle S^2\rangle$[a] | RMP2/ 6-31G(d) | UB3-LYP/ 6-31G(d) | UB3-LYP/ 6-31G(2df,p) | UB3-LYP/ VTZ+1 | UQCISD/ 6-31G(d) | URCCSD(T)/ VTZ | URCCSD(T)/ VQZ+1 | expt[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| •BeH | Be−H | 1.347 | 0.752 | 1.347 | 1.349 | 1.344 | 1.342 | 1.357 | 1.350 | 1.346 | 1.343 |
| •CH | C−H | 1.120 | 0.756 | 1.120 | 1.133 | 1.131 | 1.124 | 1.131 | 1.122 | 1.120 | 1.120 |
| •CH$_3$ | C−H | 1.078 | 0.762 | 1.079 | 1.082 | 1.081 | 1.078 | 1.084 | 1.079 | 1.078 | 1.079[c] |
| •NH$_2$ | N−H | 1.028 | 0.758 | 1.028 | 1.034 | 1.031 | 1.028 | 1.034 | 1.027 | 1.025 | 1.025[c] |
| •OH | O−H | 0.979 | 0.755 | 0.979 | 0.983 | 0.976 | 0.975 | 0.984 | 0.971 | 0.970 | 0.971 |
| •SiH$_3$ | Si−H | 1.483 | 0.754 | 1.484 | 1.489 | 1.485 | 1.482 | 1.491 | 1.484 | 1.480 | 1.486[d] |
| •PH$_2$ | P−H | 1.420 | 0.763 | 1.419 | 1.431 | 1.427 | 1.426 | 1.430 | 1.423 | 1.420 | 1.429[c] |
| •SH | S−H | 1.344 | 0.758 | 1.344 | 1.355 | 1.350 | 1.350 | 1.353 | 1.346 | 1.344 | 1.345 |
| •N$_2^+$ | N≡N | 1.147 | 0.766 | 1.155 | 1.117 | 1.112 | 1.105 | 1.133 | 1.123 | 1.119 | 1.116 |
| •NO | N=O | 1.143 | 0.768 | 1.177 | 1.159 | 1.151 | 1.146 | 1.175 | 1.157 | 1.153 | 1.151 |
| •ONO | O=N | 1.216 | 0.766 | 1.223 | 1.203 | 1.196 | 1.192 | 1.209 | 1.199 | 1.196 | 1.195[c] |
| •O$_2^-$ | O=O | 1.380 | 0.767 | 1.393 | 1.353 | 1.346 | 1.352 | 1.358 | 1.358 | 1.352 | 1.341 |
| •CN | C≡N | 1.135 | 1.127 | 1.207 | 1.174 | 1.169 | 1.163 | 1.181 | 1.179 | 1.175 | 1.175 |
| •CO$^+$ | C=O | 1.103 | 0.940 | 1.143 | 1.122 | 1.115 | 1.110 | 1.133 | 1.123 | 1.118 | 1.115[c] |
| •CS$^+$ | C=S | 1.459 | 1.383 | 1.513 | 1.499 | 1.493 | 1.486 | 1.502 | 1.508 | 1.498 | 1.495 |
| •CCH | C≡C | 1.180 | 1.187 | 1.222 | 1.209 | 1.204 | 1.200 | 1.218 | 1.215 | 1.211 | 1.207 |
|  | C−H | 1.064 |  | 1.067 | 1.068 | 1.063 | 1.063 | 1.069 | 1.065 | 1.065 | 1.061 |
| •CHO | C=O | 1.191 | 0.762 | 1.195 | 1.183 | 1.176 | 1.173 | 1.192 | 1.183 | 1.178 | 1.175[c] |
|  | C−H | 1.123 |  | 1.120 | 1.129 | 1.129 | 1.124 | 1.125 | 1.121 | 1.120 | 1.119[c] |
| •OOH | O−O | 1.325 | 0.760 | 1.326 | 1.332 | 1.324 | 1.329 | 1.353 | 1.336 | 1.330 | 1.330[c] |
| •CHCH$_2$ | C=C | 1.287 | 0.935 | 1.317 | 1.310 | 1.306 | 1.301 | 1.320 | 1.317 | 1.314 | 1.316[c] |
| •CH$_2$CH$_3$ | C−C | 1.489 | 0.763 | 1.490 | 1.490 | 1.489 | 1.484 | 1.495 | 1.492 | 1.489 | 1.492[e] |
| •OCH$_3$ | O−C | 1.386 | 0.758 | 1.388 | 1.369 | 1.363 | 1.362 | 1.389 | 1.376 | 1.372 | 1.363[c] |
| •SCH$_3$ | S−C | 1.799 | 0.758 | 1.800 | 1.813 | 1.805 | 1.799 | 1.809 | 1.807 | 1.799 | 1.791[c] |
| :CH$_2$ | C−H | 1.077 | 2.015 | 1.078 | 1.082 | 1.081 | 1.077 | 1.083 | 1.079 | 1.077 | 1.075[f] |
| :NH | N−H | 1.039 | 2.014 | 1.039 | 1.048 | 1.045 | 1.041 | 1.049 | 1.039 | 1.037 | 1.038 |
| :O$_2$ | O=O | 1.246 | 2.037 | 1.270 | 1.215 | 1.206 | 1.206 | 1.221 | 1.212 | 1.208 | 1.208[g] |
| :S$_2$ | S=S | 1.920 | 2.029 | 1.929 | 1.927 | 1.912 | 1.903 | 1.916 | 1.915 | 1.899 | 1.889 |
| MAD |  | 0.014 |  | 0.016 | 0.008 | 0.005 | 0.005 | 0.012 | 0.006 | 0.003 |  |
| MD |  | +0.002 |  | +0.014 | +0.007 | +0.002 | −0.001 | +0.012 | +0.006 | +0.001 |  |
| LD |  | −0.040 |  | +0.062 | +0.038 | +0.023 | −0.015 | +0.027 | +0.026 | +0.011 |  |

[a] Spin-squared expectation value at the UMP2(fu)/6-31G(d) level. [b] Data taken from the *JANAF Thermochemical Tables*,[25d] unless otherwise noted. [c] From *Landolt-Börnstein, New Series*, "*Structure Data of Free Polyatomic Molecules*".[25e] [d] From Yamada and Hirota.[25c] [e] From Davis et al.[25f] [f] From Jensen et al.[25b] [g] From *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*.[25a]

**TABLE 3: Calculated and Experimental Bond Angles (°)**

| radical | angle | UMP2/ 6-31G(d) | RMP2/ 6-31G(d) | UB3-LYP/ 6-31G(d) | UB3-LYP/ 6-31G(2df,p) | UB3-LYP/ VTZ+1 | UQCISD/ 6-31G(d) | URCCSD(T)/ VTZ | URCCSD(T)/ VQZ+1 | expt[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| •CH$_3$ | H−C−H | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 | 120.0 |
| •NH$_2$ | H−N−H | 103.3 | 103.0 | 102.1 | 101.9 | 102.7 | 102.9 | 102.2 | 102.7 | 102.9 |
| •PH$_2$ | H−P−H | 92.5 | 92.6 | 91.6 | 91.6 | 91.7 | 92.1 | 91.9 | 91.9 | 91.7 |
| •ONO | O−N−O | 133.7 | 132.4 | 133.8 | 134.3 | 134.4 | 134.2 | 134.2 | 134.2 | 133.9 |
| •CCH | C−C−H | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0[b] |
| •CHO | H−C−O | 123.4 | 123.4 | 123.6 | 124.0 | 124.3 | 124.3 | 124.4 | 124.4 | 124.4 |
| •OOH | O−O−H | 104.5 | 104.5 | 105.1 | 105.4 | 105.2 | 103.9 | 103.9 | 104.2 | 104.3 |
| •CHCH$_2$ | H−C−C | 136.9 | 136.1 | 137.5 | 138.7 | 138.6 | 136.0 | 136.9 | 137.0 | 137.3 |
| •OCH$_3$ | O−C−H | 113.6 | 112.4 | 113.6 | 113.2 | 113.5 | 112.5 | 113.9 | 112.8 | 113.9 |
| •SCH$_3$ | S−C−H | 111.6 | 111.6 | 111.7 | 111.6 | 111.7 | 111.5 | 111.4 | 111.4 | - |
| :CH$_2$ | H−C−H | 131.6 | 131.1 | 133.2 | 133.8 | 135.0 | 132.2 | 133.4 | 133.6 | 133.9[c] |
| :SiH$_2$ | H−Si−H | 118.3 | 118.3 | 118.2 | 118.4 | 118.5 | 118.3 | 118.4 | 118.3 | - |
| MAD |  | 0.6 | 0.9 | 0.4 | 0.5 | 0.5 | 0.6 | 0.2 | 0.2 |  |
| MD |  | −0.3 | −0.7 | −0.2 | +0.1 | +0.3 | −0.4 | −0.1 | −0.1 |  |
| LD |  | −2.2 | −2.7 | ±0.8 | +1.4 | +1.3 | −1.6 | −0.7 | −1.1 |  |

[a] From *Landolt-Börnstein, New Series*, "*Structure Data of Free Polyatomic Molecules*",[25e] unless otherwise noted. [b] Data taken from the *JANAF Thermochemical Tables*.[25d] [c] From Jensen et al.[25b]

spin-contamination, as expected. For those species displaying significant spin-contamination (•CN, •CO$^+$, •CS$^+$, •CCH, and •CHCH$_2$), UMP2 generally gives significantly shorter bond lengths than experiment, while RMP2 often gives significantly longer bond lengths than experiment, consistent with previous observations.[28,29] Large deviations from experiment ($>$ 0.030 Å) are also observed at UMP2 and RMP2 for •N$_2^+$, •O$_2^-$, :O$_2$, and :S$_2$. In these cases, the spin-contamination is small and both UMP2 and RMP2 significantly overestimate the experimental bond lengths. Byrd et al.[28] suggest that, while in many individual cases UMP2 and RMP2 may give satisfactory radical bond lengths, the occurrence of large outliers makes these methods too erratic for general use with radicals and they therefore must be used with caution. Our findings generally support this view.

As the data in Table 3 indicate, all the theoretical levels investigated generally perform well in predicting bond angles at the radical center. MADs range from 0.2° to 0.9° while LDs range from −2.7 to +1.4°.

Overall, the URCCSD(T)/cc-pVQZ+1 procedure gives the best geometries of the selected methods for the radicals in Tables 2 and 3. In accord with the results of Byrd et al.,[28] we find that UB3-LYP/6-31G(2df,p) and UB3-LYP/cc-pVTZ+1 also perform well and are therefore very cost effective. UB3-LYP/6-31G(d), UQCISD/6-31G(d), and URCCSD(T)/cc-pVTZ perform

**TABLE 4: Calculated and Experimental Heats of Formation (0 K, kJ mol$^{-1}$)**

| radical | | $\langle S^2\rangle$[a] | G2[b] | G2-RAD (RMP2) | G2-RAD (B3-LYP) | G2-RAD (QCISD) | G3[c] | G3-RAD | G3X[d] | G3X-RAD | G3(MP2)[e] | G3(MP2)-RAD | G3X(MP2)[f] | G3X(MP2)-RAD | expt[g] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| •BeH | $^2\Sigma^+$ | 0.752 | 342.7 | 343.4 | 343.4 | 343.4 | 338.5 | 339.3 | 339.5 | 339.6 | 348.1 | 349.6 | 348.9 | 350.0 | 337.3±5.0[h] |
| •CH | $^2\Pi_r$ | 0.756 | 590.4 | 589.5 | 589.7 | 589.6 | 587.0 | 587.8 | 586.5 | 588.2 | 585.3 | 584.4 | 584.5 | 585.0 | 592.9±0.8[i] |
| •$CH_3$ | $^2A_2''$ | 0.762 | 149.5 | 151.9 | 152.0 | 152.0 | 144.8 | 148.9 | 147.0 | 149.1 | 145.6 | 147.1 | 147.5 | 147.4 | 150.0±0.3[j] |
| •$NH_2$ | $^2B_1$ | 0.758 | 191.2 | 189.9 | 190.1 | 190.1 | 189.2 | 190.6 | 188.1 | 191.1 | 189.1 | 187.1 | 187.7 | 187.6 | 189.0±0.3[k] |
| •OH | $^2\Pi_I$ | 0.755 | 37.8 | 37.0 | 37.2 | 37.2 | 35.1 | 35.7 | 35.2 | 36.4 | 34.7 | 34.3 | 34.7 | 35.1 | 36.9±0.4[l] |
| •$SiH_3$ | $^2A_1$ | 0.754 | 203.0 | 203.2 | 203.3 | 203.4 | 203.9 | 207.5 | 202.5 | 207.5 | 200.3 | 201.2 | 198.1 | 200.3 | 201.9±3.4[m] |
| •$PH_2$ | $^2B_1$ | 0.763 | 141.4 | 138.9 | 139.0 | 139.0 | 140.4 | 139.4 | 138.5 | 139.5 | 137.2 | 133.8 | 134.3 | 133.2 | 142.3±2.5 |
| •SH | $^2\Pi_i$ | 0.758 | 144.1 | 143.4 | 143.5 | 143.5 | 141.0 | 141.7 | 141.0 | 142.1 | 138.1 | 138.3 | 137.6 | 138.4 | 142.5±3.0 |
| •$N_2^+$ | $^2\Sigma_g^+$ | 0.766 | 1506.8 | 1511.7 | 1505.6 | 1506.1 | 1510.4 | 1503.0 | 1505.7 | 1504.0 | 1509.3 | 1508.5 | 1505.2 | 1506.5 | 1503.1±0.1[n] |
| •NO | $^2\Pi$ | 0.768 | 87.5 | 90.4 | 88.1 | 90.0 | 91.2 | 89.6 | 89.9 | 90.4 | 91.7 | 90.0 | 89.6 | 90.4 | 89.8±0.2[o] |
| •ONO | $^2A_1$ | 0.766 | 32.8 | 37.5 | 32.8 | 33.5 | 36.9 | 34.8 | 33.6 | 36.0 | 41.0 | 39.9 | 37.6 | 40.4 | 35.9±0.8[o] |
| •$O_2^-$ | $^2\Pi_g$ | 0.767 | −34.9 | −41.4 | −43.8 | −43.7 | −34.0 | −46.4 | −36.3 | −45.0 | −27.3 | −40.6 | −30.4 | −39.8 | −42.5±0.8[o] |
| •CN | $^2\Sigma$ | 1.127 | 445.5 | 443.2 | 439.6 | 439.5 | 443.2 | 438.5 | 435.1 | 439.3 | 444.0 | 434.4 | 432.8 | 434.9 | 438.5±4.6 |
| •$CO^+$ | $^2\Sigma$ | 0.940 | 1230.5 | 1235.6 | 1232.6 | 1233.6 | 1237.4 | 1238.4 | 1236.9 | 1239.3 | 1235.7 | 1235.0 | 1234.6 | 1236.0 | 1238.4±0.2[p] |
| •$CS^+$ | $^2\Sigma$ | 1.383 | 1373.7 | 1369.8 | 1369.4 | 1369.4 | 1370.8 | 1369.8 | 1369.8 | 1370.9 | 1364.8 | 1358.5 | 1361.7 | 1357.7 | 1367.4±4.8[q] |
| •CCH | $^2\Sigma$ | 1.187 | 576.6 | 570.5 | 570.4 | 570.3 | 566.6 | 562.3 | 563.0 | 564.1 | 564.6 | 557.8 | 560.3 | 559.7 | 561.1±2.9 |
| •CHO | $^2A'$ | 0.762 | 38.5 | 39.8 | 38.9 | 39.4 | 40.3 | 41.0 | 39.0 | 41.7 | 39.2 | 39.7 | 37.9 | 40.2 | 41.3±0.8/ 44.6±0.4[r,s] |
| •OOH | $^2A_2''$ | 0.760 | 16.9 | 16.6 | 16.6 | 17.6 | 16.7 | 15.1 | 16.4 | 16.6 | 18.4 | 17.5 | 17.7 | 18.7 | 16.7±5.0[t] |
| •$CHCH_2$ | $^2A'$ | 0.935 | 308.2 | 307.5 | 307.7 | 307.6 | 299.3 | 300.8 | 298.6 | 301.4 | 298.4 | 297.3 | 297.4 | 297.9 | 303.8±3.3 |
| •$CH_2CH_3$ | $^2A'$ | 0.763 | 135.5 | 137.3 | 137.4 | 137.4 | 130.3 | 132.3 | 131.1 | 132.2 | 131.2 | 131.4 | 131.7 | 131.3 | 131.8±2.1 |
| •$CH_2OH$ | $^2A$ | 0.759 | −9.2 | −8.5 | −8.7 | −8.3 | −9.6 | −7.7 | −8.6 | −7.1 | −8.2 | −8.4 | −8.6 | −8.0 | −11.5±1.3[u] |
| •$OCH_3$ | $^2A'$ | 0.758 | 27.6 | 26.1 | 26.1 | 26.2 | 28.2 | 28.0 | 25.3 | 27.4 | 29.7 | 27.8 | 26.6 | 27.1 | 28.5±1.7[v] |
| •$SCH_3$ | $^2A'$ | 0.758 | 132.2 | 131.8 | 132.0 | 131.9 | 128.7 | 129.5 | 127.9 | 129.4 | 126.9 | 126.8 | 125.2 | 125.8 | 131.4±2.1 |
| •$COCH_3$ | $^2A'$ | 0.764 | −5.7 | −3.2 | −4.0 | −3.4 | −4.4 | −3.2 | −5.3 | −2.9 | −4.1 | −2.9 | −5.0 | −2.8 | −3.8±1.3 |
| :$CH_2$ | $^3B_1$ | 2.015 | 395.8 | 396.7 | 396.5 | 396.5 | 386.0 | 389.1 | 386.2 | 389.1 | 385.6 | 386.3 | 385.2 | 386.7 | 389.9±0.8[j] |
| :NH | $^3\Sigma^-$ | 2.014 | 360.7 | 359.7 | 359.8 | 359.8 | 352.6 | 354.5 | 351.8 | 355.0 | 351.1 | 350.3 | 349.7 | 350.9 | 356.5±1.7[w] ≤ 356.9±0.6[x] |
| :$SiH_2$ | $^3B_1$ | 2.005 | 362.5 | 362.7 | 362.9 | 362.9 | 359.3 | 363.4 | 358.2 | 363.5 | 352.7 | 354.8 | 350.6 | 354.5 | 358.2±4.9[y] |
| :$O_2$ | $^3\Sigma_g^-$ | 2.037 | 10.1 | 12.1 | 1.1 | 1.5 | 4.7 | −7.6 | 0.0 | −6.4 | 8.5 | −1.3 | 2.7 | −0.3 | 0.0[z] |
| :$S_2$ | $^3\Sigma_g^-$ | 2.029 | 141.8 | 137.4 | 137.3 | 136.7 | 132.0 | 128.8 | 129.8 | 126.7 | 126.2 | 118.9 | 122.3 | 116.0 | 128.3±0.3[o] |
| MAD | | | 4.3 | 3.5 | 3.0 | 3.0 | 2.8 | 2.0 | 2.4 | 2.0 | 4.3 | 4.0 | 4.3 | 4.0 | |
| MD | | | +2.7 | +2.6 | +1.4 | +1.6 | +0.4 | −0.4 | −1.0 | +0.1 | 0.0 | −2.0 | −2.0 | −1.9 | |
| LD | | | +15.5 | +12.1 | +9.3 | +9.2 | +8.5 | −7.6 | −6.4 | −6.4 | +15.2 | +12.3 | +12.1 | +12.7 | |

[a] Spin-squared expectation value at the UMP2(fu)/6-31G(d) level. [b] From Curtiss et al.[2a,e,32] [c] From Curtiss et al.[3a,32] [d] From Curtiss et al.[3f,32] [e] From Curtiss et al.[3b,32] [f] From Curtiss et al.[3f,32] [g] Berkowitz et al.,[30g] unless otherwise noted. [h] Calculated from the bond dissociation energy reported in *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*.[25a] [i] From Ervin et al.[30c] [j] Ruscic et al.[30o] [k] From Song et al.[30q] [l] From Ruscic et al.[30p,r] [m] Calculated from $\Delta_f H_0(SiH_4) = 39.7 \pm 1.3$ kJ mol$^{-1}$ from Gunn and Green[18a] and BDE($H_3Si-H$) = 378.2 ± 2.1 kJ mol$^{-1}$ from Berkowitz et al.[30g] [n] From Kong et al.[30e] [o] From the *JANAF Thermochemical Tables*.[25d] [p] Calculated from $\Delta_f H_0(CO) = -113.8 \pm 0.17$ kJ mol$^{-1}$ from the *JANAF Thermochemical Tables*[25d] and IE(CO) = 1352.16 ± 0.03 kJ mol$^{-1}$ from Erman et al.[30f] [q] Calculated from $\Delta_f H_0(CS) = 275.3 \pm 3.8$ kJ mol$^{-1}$ from Prinslow and Armentrout[30d] and IE(CS) = 1092.1 ± 0.6 kJ mol$^{-1}$ from Coppens and Drowart.[30i] [r] From Becerra et al.[30l] [s] $\Delta_f H_{298}$ back-corrected to 0 K using theoretical temperature correction from B3-LYP/6-31G(d) frequencies (scaled by 0.9989).[15] [t] From Litorja and Ruscic.[30n] [u] From Johnson and Hudgens.[30k] [v] From Osborn et al.[30h] [w] From Gibson et al.[30a] [x] From Tarroni et al.[30m] [y] Calculated using the singlet−triplet splitting S−T($SiH_2$) = 87.9 ± 2.9 kJ mol$^{-1}$ from Berkowitz et al.[30b] and $\Delta_f H_0(SiH_2) = 270.3 \pm 2.0$ kJ mol$^{-1}$ from Becerra et al.,[30j] corrected to 0 K and adjusted for $\Delta_f H_0(SiH_4) = 39.7 \pm 1.3$ kJ mol$^{-1}$. [z] The heat of formation of :$O_2$ is 0.0 kJ mol$^{-1}$ by definition.

slightly less well but acceptably in most cases. UMP2(fu)/6-31G(d) and RMP2/6-31G(d) generally give reasonable geometries but are not reliable for radicals that display significant spin contamination and in some additional cases involving multiple bonds (e.g., •$N_2^+$) as well. This may lead to occasional problems in the calculation of heats of formation for methods that use UMP2 geometries.

**B. Radical Heats of Formation: Assessment.** Calculated heats of formation at 0 K are compared with experimental values[25a,d,30,31] in Tables 4 and 5, for the Gn, and CBS, and Martin procedures, respectively.[32−34] Also listed are mean absolute deviations, mean deviations and largest deviations. As the data in Tables 4 and 5 show, all theoretical levels give good overall performance (MADs = 2.0−4.3 kJ mol$^{-1}$). W2 is the highest level of theory represented in these tables and indeed performs very well, with an MAD of 2.4 kJ mol$^{-1}$ and an LD of +6.4 kJ mol$^{-1}$. The G3-RAD and G3X-RAD procedures give the best statistical performance with MADs of 2.0 kJ mol$^{-1}$.

The standard G2 procedure gives one of the larger MADs (4.3 kJ mol$^{-1}$) and generally overestimates the selected radical heats of formation (MD = +2.7 kJ mol$^{-1}$). At the standard G2 level, several species (•CCH, :$O_2$, and :$S_2$) give deviations from experiment of more than 10 kJ mol$^{-1}$. The G2-RAD variants show improved performance over standard G2 with MADs of 3.0 to 3.5 kJ mol$^{-1}$. In the case of the •CCH radical, the difference between G2 and G2-RAD is largely due to a poor UMP2 geometry (in the former), resulting from significant spin-contamination (Table 2). A similar situation is observed for the •CN radical, for which the UMP2(fu)/6-31G(d) geometry is markedly inferior to UB3-LYP/6-31G(d) and UQCISD/6-31G(d). It was also noted in the previous section that UMP2 gives poor geometries for •$O_2^-$, :$O_2$, and :$S_2$, which in turn contributes to the large deviations in the $\Delta_f H_0$ values for these species at the G2 level. Curtiss et al.[2e] report that the MAD for the 148 G2 heats of formation in the G2/97 test set is 6.6 kJ mol$^{-1}$. For the subset of 29 radicals an MAD of 4.8 kJ mol$^{-1}$ is obtained, which is slightly higher (0.5 kJ mol$^{-1}$) than we observe for our slightly different test set.[35]

At G2-RAD(RMP2), only :$O_2$ gives a deviation of greater than 10 kJ mol$^{-1}$, which is clearly due to the poor RMP2 geometry for this species. Inferior RMP2 geometries also lead to moderately large deviations from experiment for G2-

**TABLE 5: Calculated and Experimental Heats of Formation (0 K, kJ mol$^{-1}$)**

| radical | | CBS-APNO[a] | CBS-Q[b] | CBS-RAD | CBS-QB3 | Martin-2 | Martin-3 | W1[c] | W1′ | W1h | W2h | W2[c] | expt[d] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| •BeH | $^2\Sigma^+$ | 336.4 | 339.7 | 340.1 | 339.9 | 334.7 | 331.9 | 332.8 | 331.5 | 332.8 | 333.4 | 333.4 | 337.3±5.0[e] |
| •CH | $^2\Pi_r$ | 593.1 | 593.3[f] | 593.3 | 593.0 | 592.4 | 592.1 | 592.1 | 592.2 | 592.3 | 592.2 | 592.3 | 592.9±0.8[g] |
| •$CH_3$ | $^2A_2''$ | 146.9 | 150.1 | 153.1 | 152.1 | 149.2 | 148.2 | 148.0 | 148.3 | 148.0 | 148.6 | 148.8 | 150.0±0.3[h] |
| •$NH_2$ | $^2B_1$ | 191.0 | 193.1 | 192.7 | 191.4 | 188.1 | 188.6 | 188.0 | 188.2 | 188.0 | 189.2 | 189.2 | 189.0±0.3[i] |
| •OH | $^2\Pi_I$ | 37.9 | 37.5 | 37.4 | 37.8 | 36.1 | 36.5 | 35.9 | 35.9 | 35.9 | 36.3 | 36.3 | 36.9±0.4[j] |
| •$SiH_3$ | $^2A_1$ | | 199.2[f] | 199.4 | 199.8 | 199.7 | 199.6 | 201.4 | 196.1 | 201.4 | 202.7 | 202.4 | 201.9±3.4[k] |
| •$PH_2$ | $^2B_1$ | | 136.7 | 136.5 | 134.5 | 136.2 | 137.2 | 137.5 | 136.2 | 137.5 | 137.8 | 137.8 | 142.3±2.5 |
| •SH | $^2\Pi_i$ | | 141.3 | 141.3 | 142.6 | 141.5 | 142.5 | 140.7 | 139.9 | 140.7 | 140.7 | 140.7 | 142.5±3.0 |
| •$N_2^+$ | $^2\Sigma_g^+$ | 1507.4 | 1509.4[f] | 1510.0 | 1509.6 | 1509.2 | 1509.3 | 1509.8 | 1510.1 | 1509.8 | 1509.5 | 1509.5 | 1503.1±0.1[l] |
| •NO | $^2\Pi$ | 92.2 | 88.3[f] | 86.2 | 87.8 | 93.8 | 95.2 | 92.4 | 92.1 | 92.4 | 93.0 | 93.0 | 89.8±0.2[m] |
| •ONO | $^2A_1$ | 29.6[f] | 26.4[f] | 30.2 | 29.9 | 41.2 | 43.0 | 40.2 | 40.1 | 40.2 | 42.2 | 42.2 | 35.9±0.8[m] |
| •$O_2^-$ | $^2\Pi_g$ | −41.6 | −46.2[f] | −45.7 | −45.1 | −39.0[n] | −39.2[n] | −40.8 | −40.8 | −40.8 | −40.4 | −40.4 | −42.5±0.8[m] |
| •CN | $^2\Sigma$ | 441.5 | 444.6 | 443.3 | 443.0 | 440.5 | 440.6 | 440.6 | 440.9 | 440.9 | 440.8 | 440.8 | 438.5±4.6 |
| •$CO^+$ | $^2\Sigma$ | 1239.8 | 1238.7[f] | 1240.9 | 1241.0 | 1241.1 | 1239.3 | 1238.9 | 1239.0 | 1238.9 | 1240.2 | 1240.1 | 1238.4±0.2[o] |
| •$CS^+$ | $^2\Sigma$ | | 1359.0[f] | 1361.8 | 1364.6 | 1381.0 | 1377.1 | 1374.7 | 1373.3 | 1375.4 | 1373.0 | 1372.8 | 1367.4±4.8[p] |
| •CCH | $^2\Sigma$ | 571.4 | 570.4 | 569.2 | 570.0 | 564.9 | 564.7 | 563.0 | 563.6 | 564.2 | 563.9 | 564.1 | 561.1±2.9 |
| •CHO | $^2A'$ | 39.6 | 39.5 | 40.8 | 41.4 | 42.2 | 41.9 | 40.6 | 40.9 | 40.8 | 41.5 | 41.6 | 41.3±0.8/<br>44.6±0.4[q,r] |
| •OOH | $^2A_2''$ | 13.8[f] | 16.0[f] | 14.8 | 13.2 | 16.0 | 17.2 | 15.5 | 15.8 | 15.5 | 16.6 | 16.6[f] | 16.7±3.3[s] |
| •$CHCH_2$ | $^2A'$ | 302.0 | 304.7 | 306.1 | 304.9 | 302.8 | 301.8 | 299.6 | 300.3 | 300.6 | 300.6 | 300.9[f] | 303.8±3.3 |
| •$CH_2CH_3$ | $^2A'$ | 127.1 | 136.4 | 138.2 | 135.9 | | 130.5 | 127.7 | 128.3 | 128.1 | 128.8 | 129.3[f] | 131.8±2.1 |
| •$CH_2OH$ | $^2A$ | −11.6[f] | −8.7 | −8.1 | −9.0 | −10.4 | −11.2 | −13.0 | −12.5 | −12.3 | −11.6 | −11.2[f] | −11.5±1.3[t] |
| •$OCH_3$ | $^2A'$ | 25.8[f] | 29.4 | 28.5 | 26.9 | 24.7 | 24.6 | 25.4 | 25.8 | 25.6 | 26.5 | 26.3[f] | 28.5±1.7[u] |
| •$SCH_3$ | $^2A'$ | | 128.3 | 128.8 | 129.7 | 134.6 | 140.7 | 126.8 | 127.1 | 127.1 | 126.7 | 126.8[f] | 131.4±2.1 |
| •$COCH_3$ | $^2A'$ | −8.6[f] | −4.2 | −1.7 | −2.4 | | | −6.3 | −5.6 | −5.8 | | | −3.8±1.3 |
| :$CH_2$ | $^3B_1$ | 391.7 | 395.9[f] | 396.5 | 395.9 | 391.3 | 390.6 | 390.0 | 390.2 | 390.0 | 390.3 | 390.5 | 389.9±0.8[h] |
| :NH | $^3\Sigma^-$ | 360.7 | 361.8[f] | 361.6 | 361.0 | 358.2 | 358.6 | 358.6 | 358.7 | 358.6 | 358.9 | 358.9 | 356.5±1.7[v]<br>≤356.9±0.6[w] |
| :$SiH_2$ | $^3B_1$ | | 358.1[f] | 358.0 | 359.0 | 358.1 | 357.7 | 359.4 | 355.6 | 359.0 | 360.3 | 360.1 | 358.2±4.9[x] |
| :$O_2$ | $^3\Sigma_g^-$ | −2.1 | −1.6[f] | −2.5 | −1.6 | 3.1 | 4.4 | 1.7 | 1.6 | 1.7 | 2.9 | 2.9 | 0.0[y] |
| :$S_2$ | $^3\Sigma_g^-$ | | 122.4[f] | 123.0 | 125.5 | 120.1 | 126.6 | 126.9 | 126.8 | 126.9 | 124.0 | 124.0 | 128.3±0.3[m] |
| MAD | | 2.8 | 3.3 | 3.4 | 2.9 | 2.6 | 2.9 | 2.5 | 2.7 | 2.4 | 2.5 | 2.4 | |
| MD | | 0.0 | +0.1 | +0.8 | +0.6 | +0.9 | +1.1 | −0.3 | −0.6 | +0.1 | +0.5 | +0.5 | |
| LD | | +10.3 | −9.5 | +8.1 | +8.9 | +12.5 | +9.3 | +6.7 | +7.0 | +6.9 | +6.4 | +6.4 | |

[a] From Montgomery et al.,[4a,33] unless otherwise noted. [b] From Ochterski et al.,[19] unless otherwise noted. [c] Parthiban and Martin.[5i,34] [d] From Berkowitz et al.,[30g] unless otherwise noted. [e] Calculated from the bond dissociation energy reported in *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*.[25a] [f] Present work. [g] From Ervin et al.[30c] [h] Ruscic et al.[30o] [i] From Song et al.[30q] [j] From Ruscic et al.[30p,r] [k] Calculated from $\Delta_f H_0(SiH_4) = 39.7 \pm 2.1$ kJ mol$^{-1}$ from Gunn and Green[18a] and BDE($H_3Si-H$) = 378.2 ± 1.3 kJ mol$^{-1}$ from Berkowitz et al.[30g] [l] From Kong et al.[30e] [m] From the *JANAF Thermochemical Tables*.[25d] [n] Calculated using aug-cc-pV*n*Z basis sets. [o] Calculated from $\Delta_f H_0(CO) = -113.8 \pm 0.17$ kJ mol$^{-1}$ from the *JANAF Thermochemical Tables*.[25d] and IE(CO) = 1352.16 ± 0.03 kJ mol$^{-1}$ from Erman et al.[30f] [p] Calculated from $\Delta_f H_0(CS) = 275.3 \pm 3.8$ kJ mol$^{-1}$ from Prinslow and Armentrout[30d] and IE(CS) = 1093.2 ± 1.0 kJ mol$^{-1}$ from Coppens and Drowart.[30i] [q] From Becerra et al.[30l] [r] $\Delta_f H_{298}$ back-corrected to 0 K using theoretical temperature correction from B3-LYP/6-31G(d) frequencies (scaled by 0.9989).[15] [s] Litorja and Ruscic.[30n] [t] From Johnson and Hudgens.[30k] [u] From Osborn et al.[30h] [v] From Gibson et al.[30a] [w] From Tarroni et al.[30m] [x] Calculated using the singlet−triplet splitting S−T($SiH_2$) = 87.9 ± 2.9 kJ mol$^{-1}$ from Berkowitz et al.[30b] $\Delta_f H_0(SiH_2) = 270.3 \pm 2.0$ kJ mol$^{-1}$ from Becerra et al.,[30j] corrected to 0 K and adjusted for $\Delta_f H_0(SiH_4) = 39.7 \pm 1.3$ kJ mol$^{-1}$. [y] The heat of formation of :$O_2$ is 0.0 kJ mol$^{-1}$ by definition.

RAD(RMP2) for •$N_2^+$ and •CN. Despite the significant overestimation of the O−O bond length in the •$O_2^-$ radical at RMP2, the G2-RAD(RMP2) procedure gives quite a good heat of formation for this species. The generally improved performance of G2-RAD(B3-LYP) and G2-RAD(QCISD) can be attributed to the better geometries associated with calculations at these levels. All three G2-RAD variants generally slightly overestimate the selected radical heats of formation (MDs = +1.4 to +2.6 kJ mol$^{-1}$).

Standard G3 theory performs better than standard G2 for the selected radical heats of formation (MAD = 2.8 kJ mol$^{-1}$) with no significant systematic deviations from experiment (MD = +0.4 kJ mol$^{-1}$). The G3-RAD procedure demonstrates further improvement with an MAD of 2.0 kJ mol$^{-1}$. The G3-RAD heats of formation also show no significant systematic deviations from experiment (MD = −0.4 kJ mol$^{-1}$). The largest deviations from experiment for G3 are observed for •$O_2^-$ (+8.5 kJ mol$^{-1}$) and •$N_2^+$ (+7.3 kJ mol$^{-1}$). These are reduced to −3.9 and −0.1 kJ mol$^{-1}$, respectively, with G3-RAD. The largest deviation from experiment for G3-RAD is observed for :$O_2$ (−7.6 kJ mol$^{-1}$). Curtiss et al.[3a] report for G3 theory that the mean absolute deviation from experiment for the 148 heats of formation in the G2/97 test set is 3.9 kJ mol$^{-1}$. For the G3(CCSD)//B3-LYP procedure,[3d] which is very similar to G3-RAD, the MADs for the total set of heats of formation of the G2/97 test set and the subset of 29 radicals are 3.8 and 3.5 kJ mol$^{-1}$, respectively.[35]

G3X shows an improved performance over G3 with an MAD of 2.4 kJ mol$^{-1}$ and an LD of −6.4 kJ mol$^{-1}$. Overall, G3X-RAD performs very similarly to G3-RAD with an MAD of 2.0 kJ mol$^{-1}$ and an LD −6.4 kJ mol$^{-1}$.

The G3 procedures based on reduced Møller−Plesset order (G3(MP2), G3(MP2)-RAD, G3X(MP2), and G3X(MP2)-RAD) give some of the highest mean absolute deviations from experiment for the selected methods (MADs = 4.3, 4.0, 4.3, and 4.0 kJ mol$^{-1}$, respectively). G3(MP2)-RAD, G3X(MP2), and G3X(MP2)-RAD generally give $\Delta_f H_0$s lower than experiment (MDs = −2.0, −2.0, and −1.9 kJ mol$^{-1}$, respectively), while G3(MP2) gives an MD of 0.0 kJ mol$^{-1}$. All four methods give quite large deviations from experiment for •BeH, •CH, •$PH_2$, •$CHCH_2$, and :NH while G3(MP2) and G3X(MP2) also significantly overestimate $\Delta_f H_0$ for •$O_2^-$, and G3(MP2)-RAD and G3X(MP2)-RAD significantly underestimate the heat of formation of •$CS^+$ and :$S_2$. For comparison, the G3(MP2) and G3X(MP2) procedures give MADs for the 29 radicals of the

G2/97 test set of 5.1 and 5.2 kJ mol$^{-1}$, respectively.[3b,f,35] For the G3(MP2,CCSD)//B3-LYP procedure, which is similar to G3(MP2)-RAD, Curtiss et al.[3d] report an MAD of 5.1 kJ mol$^{-1}$.

CBS-APNO, which is defined for first-row atoms only, performs quite well overall with an MAD of 2.8 kJ mol$^{-1}$ but displays one of the larger LDs of the selected methods (+10.3 kJ mol$^{-1}$ for $\bullet$CCH). The CBS-Q and CBS-RAD methods give similar performance with MADs of 3.3 and 3.4 kJ mol$^{-1}$, respectively, and MDs = +0.1 and +0.8 kJ mol$^{-1}$, respectively.[36] CBS-QB3 performs somewhat better (MAD = 2.9 kJ mol$^{-1}$) due largely to the inclusion of atomic spin−orbit corrections and tends also to slightly overestimate the experimental $\Delta_f H_0$s (MD = +0.6 kJ mol$^{-1}$).[37] Petersson et al.[38] have also shown that the inclusion of atomic spin−orbit corrections improves the performance of the CBS-Q and G2 methods. Curtiss et al.[1e,4c] have assessed CBS-Q and CBS-QB3 on the G2/97 test set and obtained MADs for the subset of 29 radicals of 4.2 and 3.9 kJ mol$^{-1}$, respectively.[35]

The Martin-2 and Martin-3 procedures perform quite well with MADs of 2.6 and 2.9 kJ mol$^{-1}$, respectively. The $\bullet O_2^-$ radical, the only anionic species in the set, gives large deviations from experiment at Martin-2 and Martin-3 (+8.2 and +21.4 kJ mol$^{-1}$, respectively), when the standard cc-pVnZ basis sets are used in the URCCSD(T) extrapolation, as might have been anticipated. The results in Table 5 indicate that significantly better $\Delta_f H_0$s are obtained for $\bullet O_2^-$ with the aug-cc-pV$n$Z basis sets. The largest differences between Martin-2 and Martin-3 occur for $\bullet SCH_3$ (6.1 kJ mol$^{-1}$) and $:S_2$ (6.5 kJ mol$^{-1}$).

Martin's high-level Wn procedures perform particularly well, with MADs of 2.4 to 2.7 kJ mol$^{-1}$, and LDs in the range +6.4 to +7.0 kJ mol$^{-1}$. The W1 and W2 procedures all give mean deviations from experiment close to zero (MDs = −0.6 to +0.5 kJ mol$^{-1}$). It is quite pleasing that the less computationally expensive W1h and W2h procedures give almost identical performance to their standard counterparts (the largest difference between W1 and W1h is 1.2 kJ mol$^{-1}$ while for W2 and W2h this is reduced to 0.5 kJ mol$^{-1}$).[39] This is not so surprising, however, since they differ only in that unaugmented basis sets are used on atoms of groups I to IV, for which Martin and Parthiban[1g] note the inclusion of diffuse functions is generally less important. The largest deviations between W1 and W1′ occur for $\bullet SiH_3$ (5.3 kJ mol$^{-1}$) and $:SiH_2$ (3.8 kJ mol$^{-1}$).

We note that all levels of theory underestimate the heat of formation of $\bullet PH_2$ by amounts ranging from ∼1 to 8 kJ mol$^{-1}$, suggesting that the experimental value may be too high. This has also been noted by Martin et al.,[5i] with the highest-level calculations (W2 and W2h) predicting $\Delta_f H_0(\bullet PH_2) = 137.8$ kJ mol$^{-1}$, approximately 5 kJ mol$^{-1}$ less than experiment.

All levels of theory give $\Delta_f H_0$s for the $\bullet$CHO radical in closer agreement with the experimental value of Berkowitz et al.[30g] than the more recent value of Becerra et al.[30l]

Martin and Parthiban[1g] noted in a previous study "that large deviations from what appeared to be reliable experimental data tend to be associated with strong nondynamical correlation, and a small SCF component of TAE (total atomization energy)". Examination of $T_1$ diagnostic values,[40,41] at URCCSD/aug′-cc-pVQZ+2d1f, suggests that the wave functions for a significant number of the radicals of Tables 4 and 5 exhibit significant nondynamical correlation, with 9 of the 29 radicals having $T_1$ values greater than 0.02. Despite this, quite good results are obtained for most of the radicals investigated. The largest $T_1$ values at URCCSD/aug′-cc-pVQZ+2d1f are found for $\bullet$CN (0.0520), $\bullet$OOH (0.0372), $\bullet CO^+$ (0.0278), $\bullet CS^+$ (0.0258), $\bullet$CHO (0.0252), $\bullet$ONO (0.0251), $:SiH_2$ (0.0213), $\bullet COCH_3$ (0.0214), and $\bullet$NO (0.0214). The corresponding deviations from experiment at W1 are 2.1, −1.2, 0.5, 7.3, −0.7, 4.3, 1.2, −2.5, and 2.6 kJ mol$^{-1}$. As noted above, the size of the SCF component of the TAE (in Wn calculations) has also been proposed as a guide to detecting problems. Small SCF contributions are observed for $\bullet O_2^-$ (9%), $:O_2$ (23%), $\bullet$ONO (27%), $\bullet$NO (37%), $\bullet$OOH (43%), $\bullet$CN (48%), $:S_2$ (49%), $\bullet CO^+$ (51%), and $\bullet N_2^+$ (53%). The corresponding deviations from experiment at W1 are 1.7, 1.7, 4.3, 2.6, −1.2, 2.1, −1.4, 0.5, and 6.7 kJ mol$^{-1}$. Five species exhibit both large $T_1$ values and small SCF contributions ($\bullet$NO, $\bullet$ONO, $\bullet$CN, $\bullet CO^+$, and $\bullet$OOH).

In summary, all of the methods shown in Tables 4 and 5 give good overall performance for the prediction of radical heats of formation (MADs = 2.0−4.3 kJ mol$^{-1}$). For species displaying significant spin contamination, methods based on a UMP2 reference geometry may give heats of formation for radicals that show larger-than-normal deviations from experiment. The RAD variants of the Gn and CBS procedures generally give improved performance in such circumstances. The G3-RAD, G3X-RAD, G3X, W1h, W2, W1, and W2h methods yield the smallest mean absolute deviations from experiment of 2.0 to 2.5 kJ mol$^{-1}$. The G2, G3(MP2), and G3X(MP2) methods give the largest MADs from experiment, 4.3 kJ mol$^{-1}$. The G3X, G3X-RAD, W2, and W2h procedures yield the smallest values for the largest deviation from experiment of ±6.4 kJ mol$^{-1}$, while G2 theory exhibits the highest LD, +15.5 kJ mol$^{-1}$.

**C. Radical Heats of Formation: Predictions.** Table 6 contains a small selection of radicals for which there are greater uncertainties associated with the experimental heats of formation.[42] On the basis of our assessment study, we use the G3-RAD, G3X-RAD, G3X, W1h, W1, W2h, and W2 methods to attempt to assign reliable heats of formation.

*$\bullet$OF Radical.* The most accurate levels of theory used in this study predict heats of formation for the $\bullet$OF radical which are ∼1−7 kJ mol$^{-1}$ higher than experiment[25d] but within the quoted uncertainty. Ventura et al.[43] found that CCSD(T) with a large uncontracted atomic natural orbital (ANO) basis set also gave heats of formation for $\bullet$OF radical higher than experiment when used with the atomization approach or in isodesmic reactions. Their prediction based on the reaction of formation from the homonuclear diatomic molecules gave a value close to our results (113.1 kJ mol$^{-1}$). Our calculations suggest that the heat of formation of $\bullet$OF radical is 113 ± 4 kJ mol$^{-1}$.

*$\bullet CH_2CHCH_2$ Radical.* Our selected methods generally give values for the heat of formation for allyl radical that lie within the range spanned by the experimental values of Seetula,[42g] Berkowitz et al.,[30g] and Ellison et al.[42e] A recent high level study by Feller and Dixon,[6d] involving extrapolations to the complete one-particle basis set limit, obtained a value of 178.6 ± 6.3 kJ mol$^{-1}$ for the heat of formation of allyl radical, in close agreement with our Wn results. In addition, we have previously[9c] calculated values for $\Delta_f H_0(\bullet CH_2CHCH_2)$ at a range of levels including G2, G2-RAD(QCISD), G3, G3//B3-LYP, CBS-RAD, CBS-QB3, CBS-APNO, and Martin-3. Of these, the G3, G3//B3-LYP, CBS-Q, CBS-APNO, and Martin-3 values are in close agreement with those of the present study. Based on the present results we suggest that the heat of formation of allyl radical is 179 ± 4 kJ mol$^{-1}$.

*$\bullet CH_2CN$ Radical.* The experimental values for the heat of formation of cyanomethyl radical cover a significant range (245.6 to 255.6 kJ mol$^{-1}$). Berkowitz et al.[30g] report that the C−H bond dissociation energy (BDE) of cyanomethane is 390.4 ± 8.8 kJ mol$^{-1}$ and make use of $\Delta_f H_0(CH_3CN) = 71.5 \pm 7.1$

**TABLE 6: Predicted and Experimental Heats of Formation (0 K, kJ mol$^{-1}$)**

| | | $\langle S^2\rangle^a$ | G3-RAD | G3X-RAD | G3X | W1h | W1 | W2h | W2 | expt |
|---|---|---|---|---|---|---|---|---|---|---|
| •OF | $^2\Pi$ | 0.766 | 109.4 | 111.3 | 111.7$^b$ | 114.7 | 114.7$^c$ | 115.2 | 115.2$^c$ | 108±10$^d$ |
| •$CH_2CHCH_2$ | $^2A_2$ | 0.959 | 179.8 | 180.5 | 180.2$^b$ | 178.4 | 176.9$^c$ | 178.6 | 179.0$^c$ | 177.9±4.3$^e$<br>184.5±2.1$^f$<br>182.0±8.8$^g$ |
| •$CH_2CN$ | $^2A'$ | 0.898 | 260.8 | 261.8 | 259.2$^b$ | 263.6 | 263.2$^c$ | 264.1 | 263.9$^c$ | 255.2±4.0$^h$<br>255.6±8.8$^i$<br>246±13$^j$<br>245.6±11.3$^g$ |
| •$CH_2COOH$ | $^2A''$ | 0.797 | −226.1 | −224.7 | −229.0 | −228.0 | −228.9 | | | −243.5±12.1$^k$<br>−252.2±12.6$^l$<br>−235$^m$ |
| •$CH_2C_6H_5$ | $^2B_1$ | 1.305 | 224.0 | 225.3 | 234.4$^b$ | 225.7 | | | | 226.4±2.5$^f$<br>221.8±6.3$^g$ |

[a] Spin-squared expectation value at the UMP2(fu)/6-31G(d) level. [b] From Curtiss et al.[3f,32] [c] From Parthiban and Martin.[5i,34] [d] From the *JANAF Thermochemical Tables*.[25d] [e] From Seetula.[42g] [f] From Ellison et al.[42e] [g] From Berkowitz et al.[30g] [h] From Lafleur et al.[42h] [i] From Shea et al.,[42f] back-corrected to 0 K using theoretical temperature correction from B3-LYP/6-31G(d) frequencies (scaled by 0.9989).[15] [j] From Holmes and Mayer,[42d] back-corrected to 0 K using theoretical temperature correction from B3-LYP/6-31G(d) frequencies (scaled by 0.9989).[15] [k] From Wenthold and Squires.[42c] [l] From Holmes et al.,[42b] back-corrected to 0 K using theoretical temperature correction from B3-LYP/6-31G(d) frequencies (scaled by 0.9989).[15] [m] From Orlov et al.[42a]

kJ mol$^{-1}$ to obtain $\Delta_f H_0$(•$CH_2CN$) = 245.6 ± 11.3 kJ mol$^{-1}$. In comparison, Shea et al.[42f] make use of the same BDE but combine this with a higher estimate of the heat of formation of cyanomethane (81.0 ± 0.4 kJ mol$^{-1}$) to obtain $\Delta_f H_0$(•$CH_2CN$) = 255.6 ± 8.8 kJ mol$^{-1}$. High-level theoretical calculations for the heat of formation of $CH_3CN$[9c,44] support the choice of the higher experimental value for this molecule. The value of $\Delta_f H_0$(•$CH_2CN$) reported by Lafleur et al.[42h] also relies on the higher estimate of the heat of formation of cyanomethane. Holmes and Mayer[42d] determined $\Delta_f H_0$(•$CH_2CN$) from electron impact appearance energies for $HOCH_2{+}$ from $HOCH_2CH_2CN$ and $CH_3OCO^+$ from $CH_3OC(O)CH_2CN$.

The calculated $\Delta_f H_0$ values for •$CH_2CN$ are somewhat higher than experiment and cover the range 259.2 to 264.1 kJ mol$^{-1}$. Consistent with this observation, we have noted[9d] a similar difference between theory and experiment for the C−H bond dissociation energy (BDE) of cyanomethane and the radical stabilization energy (RSE) of cyanomethyl radical. Our previously reported G2 and G2-RAD(QCISD) values for the heat of formation for cyanomethyl radical are higher than those reported here while the G3, CBS, and Martin values are in closer agreement.[9c,44] In their study of the pyrolysis of acetonitrile, Sendt et al.[45] proposed $\Delta_f H_0$(•$CH_2CN$) = 266 ± 9 kJ mol$^{-1}$, based on G2 calculations and supported by comparisons of kinetic modeling with experiment. Our predicted theoretical value for $\Delta_f H_0$(•$CH_2CN$) is 263 ± 4 kJ mol$^{-1}$.

•*$CH_2COOH$ Radical.* The calculated values for the heat of formation for the •$CH_2COOH$ radical range from −224.7 kJ mol$^{-1}$ at G3X-RAD to −229.0 kJ mol$^{-1}$ at G3X. All values are significantly higher than the experimental values of both Wenthold and Squires[42c] (−243.5 ± 12.1 kJ mol$^{-1}$) and Orlov et al.[42a] (−235 kJ mol$^{-1}$). Yu, Rauk, and Armstrong[46] obtained $\Delta_f H_0$(•$CH_2COOH$) = −234.2 kJ mol$^{-1}$ at the G2(MP2) level using the atomization approach. However, they obtained an average value of −229.9 ± 9.3 kJ mol$^{-1}$ from four isodesmic reactions at the G2(MP2) level. This latter value is in close agreement with three of the five high-level values we have calculated. As for •$CH_2CN$ radical, we have previously noted[9d] a large difference between theory and experiment for the C−H BDE of $CH_3COOH$ and the RSE of •$CH_2COOH$. Based on our present calculations, we suggest $\Delta_f H_0$(•$CH_2COOH$) = −227 ± 5 kJ mol$^{-1}$.

•*$CH_2C_6H_5$ Radical.* The G3-RAD, G3X-RAD, and W1h values for the heat of formation for benzyl radical are in close agreement with the experimental value of Ellison et al.[42e] and support this result over the earlier experimental value of Berkowitz et al.[30g] The G3X result is likely to be less reliable in this strongly spin-contaminated case. Smith and Hall[47] obtained a value of $\Delta_f H_0$(•$CH_2C_6H_5$) = 227.8 ± 7.8 kJ mol$^{-1}$ using a set of six isogyric reactions at the G2(MP2,SVP) level. Their value is in close agreement with our W1h, G3-RAD, and G3X-RAD results and the experimental value of Ellison et al.[42e] Our suggested value for the heat of formation of benzyl radical is 225 ± 4 kJ mol$^{-1}$.

## 4. Concluding Remarks

We have assessed the performance of a number of high-level theoretical procedures for the calculation of radical heats of formation against accurately known experimental values. In conjunction with this, we have assessed the performance of several commonly used levels of theory for the prediction of the structures of radicals. We find that URCCSD(T)/cc-pVQZ+1 performs the best for geometry optimizations, while the computationally much less expensive UB3-LYP/6-31G(d), UB3-LYP/6-31G(2df,p), and UB3-LYP/cc-pVTZ+1 methods also perform particularly well. UQCISD/6-31G(d) and URCCSD(T)/cc-pVTZ give acceptable overall performance. UMP2(fu)/6-31G(d) and RMP2/6-31G(d) generally give reasonable geometries but are not reliable for radicals that display significant spin contamination, and in some other multiply bonded systems.

All theoretical levels investigated give good overall performance (MADs = 2.0−4.3 kJ mol$^{-1}$) for the prediction of radical heats of formation. The G3-RAD, G3X-RAD, G3X, W1h, W2, W1, and W2h procedures are the most accurate of the theoretical procedures used in the present study with MADs of 2.0−2.5 kJ mol$^{-1}$.

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**Supporting Information Available:** Tables S1, S2, S3, S4, S5, and S6 contain Gaussian archive entries for the UMP2(fu)/6-31G(d), RMP2/6-31G(d), UB3-LYP/6-31G(d), UB3-LYP/6-31G(2df,p), UB3-LYP/cc-pVTZ+1, and UQCISD/6-31G(d) optimized geometries of the radicals considered in this study. Tables S7 and S8 contain the Cartesian coordinates for the URCCSD(T)/cc-pVTZ and URCCSD(T)/cc-pVQZ+1 optimized geometries. Tables S9, S10, S11, and S12 contain total energies that lead to the heats of formation of Tables 4 and 5. Table S13 contains total energies that lead to the heats of formation of Table 6. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

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(21) (a) In the G3 and G3X procedures, energies evaluated with the 6-31G(2df,p), G3large, and G3Xlarge basis sets use (6d,7f), (5d,7f), and (5d,7f) basis functions, respectively. In the G3-RAD and G3X-RAD procedures, we require RMP4/6-31G(2df,p) energies that need to be evaluated using ACES II, which allows only either spherical (5d,7f) or Cartesian (6d,10f) basis functions (but not mixtures of the two such as (6d,7f)). In addition, we find[21b] that evaluating the RMP2(fu)/G3large and RHF/G3Xlarge energies with the (6d,10f) combination leads to better performance for G3-RAD and G3X-RAD on the G2/97 test set, perhaps through adding flexibility to the underlying sp basis. We therefore consistently use the (6d,10f) combination for all the energy evaluations in G3-RAD and G3X-RAD. (b) Henry, D. J.; Sullivan, M. B.; Radom, L., results to be published.

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(32) Standard total energies for the radicals in this study may also be found in (a) G2: Curtiss et al.[2a,e] and http://chemistry.anl.gov/compmat/g2theory.htm. (b) G3: Curtiss et al.[3a] and http://chemistry.anl.gov/compmat/g3theory.htm. (c) G3X: Curtiss et al.[3f] and http://chemistry.anl.gov/compmat/g3xtheory.htm. (d) G3(MP2): Curtiss et al.[3b] and http://chemistry.anl.gov/compmat/g3theory.htm. (e) G3X(MP2): Curtiss et al.[3f] and http://chemistry.anl.gov/compmat/g3xtheory.htm.

(33) CBS-APNO total energies for radicals in the G2−1 test set may also be found in Montgomery et al.[4a]

(34) W1 (for G2−1 and a subset of G2−2 test sets) and W2 (for G2−1 test set) total energies from Parthiban and Martin[5i] are available from the website http://theochem.weizmann.ac.il/web/papers/w1w2.html.

(35) (a) Twenty-four of the radical heats of formation in our test set are common to the G2/97 test set (the union of G2−1 and G2−2). These include •BeH, •CH, •$CH_3$, •$NH_2$, •OH, •$SiH_3$, •$PH_2$, •SH, •NO, •ONO, •CN, •CCH, •CHO, •CHCH$_2$, •$CH_2CH_3$, •$CH_2OH$, •$OCH_3$, •$SCH_3$, •C(O)$CH_3$, **:**$CH_2$, **:**NH, **:**$SiH_2$, **:**$O_2$, and **:**$S_2$. The •SH radical is actually included in the subset of inorganic hydrides for the G2/97 test set. (b) Our MADs differ from those of Curtiss et al.[2a,e,3a,b,f] partly because of the slightly different test sets, partly because of our use of updated experimental values for the heats of formation of some of the radicals, and partly because of our use of amended heats of formation for the Be and Si atoms.

(36) We note that Ochterski et al.[19] report CBS-Q $\Delta_f H_0$s for several of the radicals in our study while Curtiss et al.[4c] report CBS-Q deviations from experiment for $\Delta_f H_{298}$ for the G2/97 test set.

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