

G3-RAD and G3X-RAD: Modified Gaussian-3 (G3) and Gaussian-3X (G3X) procedures for radical thermochemistry

David J. Henry, Michael B. Sullivan, and Leo Radom

Citation: *The Journal of Chemical Physics* **118**, 4849 (2003); doi: 10.1063/1.1544731

View online: <http://dx.doi.org/10.1063/1.1544731>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/118/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Thermochemistry of new molecular species: SBr and HSB](#)
J. Chem. Phys. **126**, 204314 (2007); 10.1063/1.2737776

[Thermochemistry of disputed soot formation intermediates C₄H₃ and C₄H₅](#)
J. Chem. Phys. **121**, 8800 (2004); 10.1063/1.1787496

[Adiabatic electron affinity and ionization potential for BrO radical](#)
J. Chem. Phys. **109**, 10818 (1998); 10.1063/1.477778

[Erratum: "An assessment of theoretical procedures for the calculation of reliable free radical thermochemistry: A recommended new procedure" \[*J. Chem. Phys.* 108, 604 \(1998\)\]](#)
J. Chem. Phys. **108**, 9598 (1998); 10.1063/1.476372

[An assessment of theoretical procedures for the calculation of reliable free radical thermochemistry: A recommended new procedure](#)
J. Chem. Phys. **108**, 604 (1998); 10.1063/1.476256



AIP | APL Photonics

APL Photonics is pleased to announce
Benjamin Eggleton as its Editor-in-Chief



G3-RAD and G3X-RAD: Modified Gaussian-3 (G3) and Gaussian-3X (G3X) procedures for radical thermochemistry

David J. Henry, Michael B. Sullivan, and Leo Radom

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

(Received 4 November 2002; accepted 17 December 2002)

The G3-RAD, G3X-RAD, G3(MP2)-RAD, and G3X(MP2)-RAD, procedures, designed particularly for the prediction of reliable thermochemistry for free radicals, are formulated and their performance assessed using the G2/97 test set. The principal features of the RAD procedures include (a) the use of B3-LYP geometries and vibrational frequencies (in place of UHF and UMP2), including the scaling of vibrational frequencies so as to reproduce ZPVEs, (b) the use of URCCSD(T) [in place of UQCISD(T)] as the highest-level correlation procedure, and (c) the use of RMP (in place of UMP) to approximate basis-set-extension effects. G3-RAD and G3X-RAD are found to perform well overall with mean absolute deviations (MADs) from experiment of 3.96 and 3.65 kJ mol⁻¹, respectively, compared with 4.26 and 4.02 kJ mol⁻¹ for standard G3 and G3X. G3-RAD and G3X-RAD successfully predict heats of formation with MADs of 3.68 and 3.11 kJ mol⁻¹, respectively (compared with 3.93 and 3.60 kJ mol⁻¹ for standard G3 and G3X), and perform particularly well for radicals with MADs of 2.59 and 2.50 kJ mol⁻¹, respectively (compared with 3.51 and 3.18 kJ mol⁻¹ for standard G3 and G3X). The G3(MP2)-RAD and G3X(MP2)-RAD procedures give acceptable overall performance with mean absolute deviations from experiment of 5.17 and 4.92 kJ mol⁻¹, respectively, compared with 5.44 and 5.23 kJ mol⁻¹ for standard G3(MP2) and G3X(MP2). G3(MP2)-RAD and G3X(MP2)-RAD give improved performance over their standard counterparts for heats of formation (MADs=4.73 and 4.44 kJ mol⁻¹, respectively, versus 4.94 and 4.64 kJ mol⁻¹). G3(MP2)-RAD shows similar performance to G3(MP2) for radical heats of formation (MAD=5.10 versus 5.15 kJ mol⁻¹) while G3X(MP2)-RAD performs significantly better than G3X(MP2) (MAD=4.67 versus 5.19 kJ mol⁻¹). © 2003 American Institute of Physics. [DOI: 10.1063/1.1544731]

I. INTRODUCTION

An increasingly important application of *ab initio* molecular orbital theory is the calculation of accurate thermochemical properties.^{1,2} The Gaussian-*n* (*Gn*) procedures of Curtiss, Raghavachari, Pople, and co-workers³⁻¹² represent a particular class of theoretical methods that have been developed to calculate reliable thermochemical data and they perform particularly well in this regard. For example, the G3 procedure⁴ has been found to give a mean absolute deviation from experiment of 4.26 kJ mol⁻¹ for 299 of the 302 energies of the G2/97 test set.⁵ The full G2/97 test set comprises 148 heats of formation, 88 ionization energies, 58 electron affinities, and 8 proton affinities.

A number of modified *Gn*-procedures have been proposed in recent years. These include the G2(B3-LYP/MP2/CC) method of Bauschlicher and Partridge,¹³ which is a modified version of G2(MP2) that makes use of B3-LYP/6-31G(d) geometries and zero-point vibrational energies and replaces QCISD(T) with CCSD(T). Morokuma and co-workers^{14,15} have developed variants of G2 theory [e.g., G2(PU) and G2M(RCC)] designed particularly to deal with spin-contaminated open-shell systems. We have also previously developed procedures for radical thermochemistry [e.g., G2-RAD(QCISD) (Ref. 16) and G2-RAD(B3-LYP) (Ref. 16)] that incorporate several of the features suggested by Bauschlicher and Morokuma, plus additional features

such as the use of restricted-open-shell methods in place of unrestricted methods. Recently we introduced the G3-RAD, G3X-RAD, G3(MP2)-RAD, and G3X(MP2)-RAD procedures as part of an assessment of 23 high-level theoretical methods in the computation of heats of formation of small open-shell systems.¹⁷ All four of these procedures were found to give improved performance compared with their standard G3 counterparts for a test set of 29 small open-shell systems, for which accurate experimental data are available. We present here the formulation and broad assessment of these new G3-RAD-type methods.

II. THEORETICAL PROCEDURES

An important consideration in any calculation of open-shell species is the choice of reference wave function. This leads to treatments that are referred to as spin-restricted (R), spin-unrestricted (U), and spin-projected (P).

Spin-restricted procedures, signified by an R prefix (e.g., RHF, RMP), constrain the α and β orbitals to be the same. As such, these wave functions are eigenfunctions of the spin-squared operator (S^2) and lead to pure spin states (doublets, triplets, etc.). The disadvantage of this approach is that it restricts the flexibility in the electronic description and may result in unrealistic spin-localization in radicals.

Spin-unrestricted procedures, designated by the prefix U (e.g., UHF, UMP), treat the α and β electrons independently.

TABLE I. Principal features of G3, G3//B3-LYP, G3(CCSD)//B3-LYP, G3-RAD, and G3-RAD(5*d*).

	G3	G3//B3-LYP	G3(CCSD)//B3-LYP	G3-RAD	G3-RAD(5 <i>d</i>)
Geometry	UMP2(fu)/6-31G(<i>d</i>)	B3-LYP/6-31G(<i>d</i>)	B3-LYP/6-31G(<i>d</i>)	B3-LYP/6-31G(<i>d</i>)	B3-LYP/6-31G(<i>d</i>)
Zero-point energy	UHF/6-31G(<i>d</i>) ^a	B3-LYP/6-31G(<i>d</i>) ^b	B3-LYP/6-31G(<i>d</i>) ^b	B3-LYP/6-31G(<i>d</i>) ^c	B3-LYP/6-31G(<i>d</i>) ^c
Single-point energies	UQCISD(T)/6-31G(<i>d</i>)	UQCISD(T)/6-31G(<i>d</i>)	UCCSD(T)/6-31G(<i>d</i>)	URCCSD(T)/6-31G(<i>d</i>)	URCCSD(T)/6-31G(<i>d</i>)
	UMP4/6-31+G(<i>d</i>)	UMP4/6-31+G(<i>d</i>)	UMP4/6-31+G(<i>d</i>)	RMP4/6-31+G(<i>d</i>)	RMP4/6-31+G(<i>d</i>)
	UMP4/6-31G(2 <i>df,p</i>) ^d	UMP4/6-31G(2 <i>df,p</i>) ^d	UMP4/6-31G(2 <i>df,p</i>) ^d	RMP4/6-31G(2 <i>df,p</i>) ^e	RMP4/6-31G(2 <i>df,p</i>) ^e
	UMP2(fu)/G3large ^f	UMP2(fu)/G3large ^f	UMP2(fu)/G3large ^f	RMP2(fu)/G3large ^e	RMP2(fu)/G3large ^f
HLC					
A	6.386	6.760	6.602	6.884	6.450
B	2.977	3.233	3.207	2.747	2.410
C	6.219	6.786	6.449	6.561	6.446
D	1.185	1.269	1.212	1.341	0.996

^aScaled by 0.8929.^bScaled by 0.96.^cScaled by 0.9806.^d(6*d*,7*f*) basis functions.^e(6*d*,10*f*) basis functions.^f(5*d*,7*f*) basis functions.

This allows more flexibility in accommodating the unpaired electron(s) and, in the case of the Hartree–Fock wave function, often leads to a lower-energy description of the electronic structure. However, treating the α and β electrons separately can lead to spin contamination (i.e., mixing of higher spin states) since the wave function is no longer an eigenfunction of $\langle S^2 \rangle$. The level of spin contamination is reflected in the deviation of the $\langle S^2 \rangle$ expectation value from that of a pure spin state (i.e., 0.75 for a doublet, 2.0 for a triplet, etc.).

A further alternative is to remove higher spin states from the unrestricted wave function by means of a spin-projection operator. Spin-projected energies are designated by a P prefix (e.g., PHF, PMP).

It is not clear beforehand which out of R, U, or P is to be preferred. At the HF and MP levels, the differences between them can be very large. However, at the QCISD(T) and CCSD(T) levels, it has been found that the differences between R and U are generally small.¹⁸ While the standard *Gn* procedures use energies determined from unrestricted wave functions, the *Gn*-RAD procedures make use of energies determined from spin-restricted wave functions, and the modified G2 procedures of Morokuma and co-workers use spin-projected energies.

In the present study, *ab initio* molecular orbital calculations¹⁹ were performed using the GAUSSIAN 98,²⁰ ACES II,²¹ and MOLPRO 2000.6 (Ref. 22) computer programs. Unless indicated otherwise, restricted-open-shell reference wave functions (e.g., RHF and RMP2) and the frozen-core (fc) approximation were used. Unrestricted-open-shell calculations are designated with a U prefix, while correlation of all electrons in a molecule is denoted (fu). Because the B3-LYP (Ref. 23) density functional calculations in this study were all carried out using the unrestricted procedure, the U in this case is omitted for simplicity. Zero-point vibrational energy (ZPVE) scaling factors were either standard for the particular method or optimized,²⁴ as noted.

Standard G3 theory⁴ includes a UMP2(fu)/6-31G(*d*) optimized geometry and a UHF/6-31G(*d*) ZPVE (scaled by 0.8929 so as to reproduce fundamental vibrational frequencies). A UQCISD(T)/6-31G(*d*) base energy is corrected to UQCISD(T)(fu)/G3large using a series of additivity corrections at the UMP2 and UMP4 levels. Core-correlation is in-

cluded, by performing the UMP2/G3large single-point calculation with correlation of all electrons (fu). Additionally, a spin-orbit correction is included for atoms. To account for remaining deficiencies, a higher-level correction (HLC) is applied. It has the form $-An_{\beta}-B(n_{\alpha}-n_{\beta})$ for molecules and $-Cn_{\beta}-D(n_{\alpha}-n_{\beta})$ for atoms, where n_{α} and n_{β} are the number of α and β valence electrons, respectively. The values of the HLC parameters in standard G3 are $A=6.386$, $B=2.977$, $C=6.219$, and $D=1.185$ mhartrees. These HLCs were derived to give a best fit to 299 of the 302 energies in the G2/97 test set.⁵ Table I contains a summary of the principal features of the G3 and related procedures.

The G3//B3-LYP procedure⁷ is generally similar to the standard G3 method but makes use of a B3-LYP/6-31G(*d*) geometry and ZPVE (scaled by 0.96 so as to reproduce fundamental vibrational frequencies). The HLC parameters have been redetermined as $A=6.760$, $B=3.233$, $C=6.786$, and $D=1.269$ mhartrees. The G3(CCSD)//B3-LYP procedure⁸ is a modified G3//B3-LYP method in which the UQCISD(T)/6-31G(*d*) energy has been replaced by UCCSD(T)/6-31G(*d*) and the HLC parameters recalculated to account for this difference: $A=6.602$, $B=3.207$, $C=6.449$, and $D=1.212$ mhartrees.

The *Gn*-RAD-type procedures are designed to give improved performance for radicals compared with their standard *Gn* counterparts. The principal features common to all the members of the *Gn*-RAD family include (a) the replacement of all UMP energies by restricted open-shell Møller–Plesset (RMP) energies, (b) using the URCCSD(T) method of MOLPRO rather than UQCISD(T) as the ultimate electron correlation level, and (c) the scaling of vibrational frequencies so as to reproduce ZPVEs. The URCCSD(T) procedure is a spin-unrestricted CCSD(T) calculation performed on a restricted open-shell reference wave function.^{25,26} Additional differences relevant to specific G3-RAD-type procedures are noted below. For all the new methods, we have reoptimized the HLC parameters.

Standard G3-RAD,¹⁷ in addition to incorporating the general features of the *Gn*-RAD-type procedures noted above, differs from standard G3 in that it (a) uses a B3-LYP/6-31G(*d*) optimized geometry and ZPVE (scaled by 0.9806 so as to reproduce ZPVEs),²⁴ (b) evaluates the RMP4/6-31G(2*df,p*) and RMP2(fu)/G3large energies using

TABLE II. Principal features of G3X, G3X(CCSD), G3X-RAD, and G3X-RAD(5*d*).

	G3X	G3X(CCSD)	G3X-RAD	G3X-RAD(5 <i>d</i>)
Geometry	B3-LYP/6-31G(2 <i>df,p</i>)	B3-LYP/6-31G(2 <i>df,p</i>)	B3-LYP/6-31G(2 <i>df,p</i>)	B3-LYP/6-31G(2 <i>df,p</i>)
Zero-point energy	B3-LYP/6-31G(2 <i>df,p</i>) ^a	B3-LYP/6-31G(2 <i>df,p</i>) ^a	B3-LYP/6-31G(2 <i>df,p</i>) ^a	B3-LYP/6-31G(2 <i>df,p</i>) ^a
Single-point energies	UQCISD(T)/6-31G(<i>d</i>) UMP4/6-31+G(<i>d</i>) UMP4/6-31G(2 <i>df,p</i>) ^b UMP2(fu)/G3large ^d UHF/G3Xlarge ^e	UCCSD(T)/6-31G(<i>d</i>) UMP4/6-31+G(<i>d</i>) UMP4/6-31G(2 <i>df,p</i>) ^b UMP2(fu)/G3large ^d UHF/G3Xlarge ^e	URCCSD(T)/6-31G(<i>d</i>) RMP4/6-31+G(<i>d</i>) RMP4/6-31G(2 <i>df,p</i>) ^c RMP2(fu)/G3large ^e RHF/G3Xlarge ^f	URCCSD(T)/6-31G(<i>d</i>) RMP4/6-31+G(<i>d</i>) RMP4/6-31G(2 <i>df,p</i>) ^c RMP2(fu)/G3large ^d RHF/G3Xlarge ^e
HLC				
	<i>A</i>	6.783	6.635	6.894
	<i>B</i>	3.083	3.085	2.719
	<i>C</i>	6.877	6.645	6.655
	<i>D</i>	1.152	1.076	1.351

^aScaled by 0.9854.^b(6*d*,7*f*) basis functions.^c(6*d*,10*f*) basis functions.^d(5*d*,7*f*) basis functions.^e(5*d*,7*f*,9*g*) basis functions.^f(6*d*,10*f*,15*g*) basis functions.

Cartesian (6*d*,10*f*) basis functions,²⁷ and (c) includes our redetermined HLC parameters ($A=6.884$, $B=2.747$, $C=6.561$, and $D=1.341$ mhartrees), optimized to give a best fit to 296 of the 302 energies²⁸ in the G2/97 test set.

G3-RAD(5*d*), introduced for the first time in the present study, differs from standard G3-RAD only in that the RMP2(fu)/G3large calculation is performed using spherical (5*d*,7*f*) basis functions rather than Cartesian (6*d*,10*f*) functions. We have redetermined the HLC parameters to account for this change, yielding $A=6.450$, $B=2.410$, $C=6.446$, and $D=0.996$ mhartrees.

G3X (Ref. 10) is a modified G3 procedure, which makes use of a B3-LYP/6-31G(2*df,p*) geometry and ZPVE (scaled by 0.9854 so as to reproduce ZPVEs). An additional calculation is performed at the UHF level, with a modified G3large basis set (G3Xlarge), to account for deficiencies observed for species containing second-row atoms. The HLC parameters are $A=6.783$, $B=3.083$, $C=6.877$, and $D=1.152$ mhartrees. The G3X(CCSD) method is a modified G3X procedure in which the UQCISD(T)/6-31G(*d*) energy has been replaced by UCCSD(T)/6-31G(*d*) and the HLC parameters redetermined to give $A=6.635$, $B=3.085$, $C=6.645$, and $D=1.076$ mhartrees.¹¹ The principal features of the G3X and related methods are presented in Table II.

G3X-RAD (Ref. 17) follows G3X in using a B3-LYP/6-31G(2*df,p*) geometry and ZPVE (scaled by

0.9854). In addition, like G3-RAD, all energies are evaluated using Cartesian (6*d*,10*f*,15*g*) basis sets. The Hartree–Fock calculation with the G3Xlarge basis set is performed with the restricted-open-shell formalism and we have redetermined the HLC parameters to minimize the mean absolute deviation from experiment for 296 energies²⁸ of the G2/97 test set (yielding $A=6.894$, $B=2.719$, $C=6.655$, and $D=1.351$ mhartrees).

The G3X-RAD(5*d*) procedure, also introduced in the present study, differs from G3X-RAD in that the RMP2(fu)/G3large and RHF/G3Xlarge energies are evaluated using spherical (5*d*,7*f*) and (5*d*,7*f*,9*g*) basis functions, respectively. The HLC parameters are $A=6.522$, $B=2.498$, $C=6.550$, and $D=1.047$ mhartrees.

G3(MP2) (Ref. 6) uses a UMP2(fu)/6-31G(*d*) optimized geometry and a scaled (by 0.8929) UHF/6-31G(*d*) ZPVE. A base energy evaluated at the UQCISD(T)/6-31G(*d*) level is corrected to UQCISD(T)/G3MP2large using an additivity approximation at the UMP2 level. The G3(MP2)//B3-LYP procedure⁷ is generally similar to the standard G3(MP2) method but makes use of a B3-LYP/6-31G(*d*) geometry and ZPVE (scaled by 0.96). The HLC parameters have been redetermined as $A=10.041$, $B=4.995$, $C=10.188$, and $D=2.323$ mhartrees. Table III contains a summary of the principal features of the G3 and G3X procedures based on reduced Møller–Plesset order.

TABLE III. Principal features of G3(MP2), G3(MP2)//B3-LYP, G3(MP2)-RAD, G3X(MP2), and G3X(MP2)-RAD.

	G3(MP2)	G3(MP2)//B3-LYP	G3(MP2)-RAD	G3X(MP2)	G3X(MP2)-RAD
Geometry	UMP2(fu)/6-31G(<i>d</i>)	B3-LYP/6-31G(<i>d</i>)	B3-LYP/6-31G(<i>d</i>)	B3-LYP/6-31G(2 <i>df,p</i>)	B3-LYP/6-31G(2 <i>df,p</i>)
Zero-point energy	UHF/6-31G(<i>d</i>) ^a	B3-LYP/6-31G(<i>d</i>) ^b	B3-LYP/6-31G(<i>d</i>) ^c	B3-LYP/6-31G(2 <i>df,p</i>) ^d	B3-LYP/6-31G(2 <i>df,p</i>) ^d
Single-point energies	UQCISD(T)/6-31G(<i>d</i>) UMP2/G3MP2large ^e	UQCISD(T)/6-31G(<i>d</i>) UMP2/G3MP2large ^e	URCCSD(T)/6-31G(<i>d</i>) RMP2/G3MP2large ^e	UQCISD(T)/6-31G(<i>d</i>) UMP2/G3MP2large ^e UHF/G3Xlarge ^f	URCCSD(T)/6-31G(<i>d</i>) RMP2/G3MP2large ^e RHF/G3Xlarge ^f
HLC					
	<i>A</i>	9.279	10.041	9.413	9.680
	<i>B</i>	4.471	4.995	3.969	4.715
	<i>C</i>	9.345	10.188	9.438	10.039
	<i>D</i>	2.021	2.323	1.888	2.010

^aScaled by 0.8929.^bScaled by 0.96.^cScaled by 0.9806.^dScaled by 0.9854.^e(5*d*,7*f*) basis functions.^f(5*d*,7*f*,9*g*) basis functions.

TABLE IV. Heats of formation for the 29 radicals in the G2/97 test set determined with G3, G3-RAD, G3X, G3X-RAD, and related procedures ($\Delta_f H_{298}$, kJ mol⁻¹).

Radical	$\langle S^2 \rangle^a$	G3 ^b	G3// B3-LYP ^c	G3- RAD(5 <i>d</i>)	G3- RAD	G3X ^d	G3X- RAD(5 <i>d</i>)	G3X- RAD	Expt. ^e
·BeH	0.752	343.9	344.3	345.2	344.7	344.8	345.2	345.0	341.8
·CH	0.756	590.4	589.9	591.2	591.2	589.9	591.3	591.6	596.2
·CH ₂ (³ B ₁)	2.015	386.6	386.2	388.8	389.5	386.6	388.6	389.8	392.0
·CH ₃	0.762	142.3	143.5	144.8	145.8	143.9	144.8	146.0	146.4
·NH	2.014	352.7	351.9	354.1	354.6	351.9	354.1	355.1	356.5
·NH ₂	0.758	186.2	185.4	185.9	187.7	185.4	186.2	188.2	188.7
·OH	0.755	35.1	35.1	35.9	35.8	35.1	36.2	36.5	39.3
·SiH ₂ (³ B ₁)	2.005	355.2	354.8	357.8	359.5	354.4	357.2	359.3	360.7
·SiH ₃	0.754	196.2	195.8	197.3	199.7	194.6	196.6	199.2	200.4
·PH ₂	0.763	136.4	135.6	134.0	135.5	134.7	133.6	135.3	138.5
·CN	1.127	446.4	438.9	440.9	441.9	438.5	441.2	442.6	438.9 ^f
·CHO	0.762	40.6	39.3	40.2	41.4	39.3	40.3	42.0	41.8
·NO	0.768	91.2	90.8	88.2	89.6	90.0	88.5	90.4	90.4
·O ₂	2.037	4.6	-0.4	-7.5	-7.6	0.0	-7.1	-6.2	0.0
·Si ₂	2.013	577.4	577.8	580.2	581.9	576.6	581.2	581.9	585.3
·S ₂	2.029	132.2	133.1	129.8	129.0	130.1	127.0	126.9	128.4
·SO	2.039	7.1	6.3	1.3	1.3	2.9	-1.5	-0.8	5.0
·OCl	0.764	108.4	111.3	114.1	112.3	107.9	110.4	109.4	101.3
·CCH	1.187	570.3	565.3	566.7	566.6	565.7	567.8	568.1	565.3
·CHCH ₂	0.935	295.0	294.1	296.6	296.6	294.6	296.9	297.2	299.6
·COCH ₃	0.764	-10.5	-11.3	-10.1	-9.4	-11.7	-10.3	-9.2	-10.0
·CH ₂ OH	0.759	-16.3	-17.2	-16.4	-14.7	-16.7	-16.2	-14.1	-17.2
·OCH ₃	0.758	20.5	18.4	19.6	20.3	18.4	19.3	20.5	17.2
·OCH ₂ CH ₃	0.760	-10.5	-10.0	-13.3	-13.1	-10.0	-13.6	-12.9	-15.5
·SCH ₃	0.758	121.3	121.3	122.3	122.2	120.5	121.5	121.7	124.7
·CH ₂ CH ₃	0.763	120.1	120.5	121.8	121.9	120.9	121.5	121.8	120.9
·CH(CH ₃) ₂	0.763	90.0	90.0	91.5	90.8	90.4	90.9	90.5	90.0
·C(CH ₃) ₃	0.763	54.4	55.2	56.4	55.7	55.2	55.7	54.3	51.5
·ONO	0.766	33.9	31.4	28.7	32.0	31.0	29.1	33.2	33.1
MAD		3.51	3.18	3.19	2.59	3.18	3.14	2.50	
MD		-0.35	-1.17	-0.88	-0.29	-1.60	-1.10	-0.27	
LD		-7.94	+10.04	+12.86	+11.01	-8.79	+9.14	+8.16	

^aSpin-squared expectation value at the UMP2(fu)/6-31G(*d*) level.^bFrom Ref. 4.^cFrom Ref. 7.^dFrom Ref. 10.^eFrom Ref. 5, unless otherwise noted.^fA value of 441.4 kJ mol⁻¹ is recommended in Ref. 37.

The G3(MP2)-RAD procedure used in the present study is an improved version of the originally reported G3(MP2)-RAD.^{29,30} It continues to make use of a B3-LYP/6-31G(*d*) optimized geometry and ZPVE (scaled by 0.9806). However, the improved version of G3(MP2)-RAD includes newly optimized HLC parameters ($A=9.413$, $B=3.969$, $C=9.438$, and $D=1.888$ mhartrees) that we have obtained through optimization of 301 energies³¹ of the G2/97 test set.

G3X(MP2) (Ref. 10) and G3X(MP2)-RAD (Ref. 17) correspond to modified G3X and G3X-RAD procedures, respectively, with reduced Møller–Plesset order. Like G3X, both of these methods make use of a B3-LYP/6-31G(2*df*,*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. As with the new G3(MP2)-RAD method, we have optimized the HLC parameters for G3X(MP2)-RAD so as to give the best fit to 301 energies³¹ of the G2/97 test set, yielding $A=9.556$, $B=3.992$, $C=9.684$, and $D=1.970$ mhartrees.

G3-RAD, G3-RAD(5*d*), G3X-RAD, G3X-RAD(5*d*), G3(MP2)-RAD, and G3X(MP2)-RAD total energies for all atoms and molecules used in this study are available from an EPAPS document.³²

III. RESULTS AND DISCUSSION

Heats of formation at 298 K for the 29 radicals of the G2/97 test set obtained at the G3, G3//B3-LYP, G3-RAD, G3X, G3X-RAD, G3(MP2), G3(MP2)//B3-LYP, G3(MP2)-RAD, G3X(MP2), G3X(MP2)-RAD and related levels of theory are given in Tables IV and IX, which also include mean absolute deviations (MADs), mean deviations (MDs), and largest deviations (LDs) from experiment. Summaries of the mean absolute deviations from experiment for these methods are given in Tables V, VII, and X. Tables VI, VIII, XI and XII present, for selected methods, calculated energies that show large deviations (≥ 12.5 kJ mol⁻¹) from experiment.

Within the G2/97 test set, the subsets of the 29 heats of formation ($\Delta_f H_{298}$) for radicals, the 88 ionization energies

TABLE V. Summary of mean absolute deviations from experiment (kJ mol^{-1}) for G3, G3-RAD, and related procedures for the G2/97 test set.

	G3 ^a	G3//B3-LYP ^b	G3(CCSD)//B3-LYP ^c	G3-RAD(5d)	G3-RAD
Heats of formation	3.93	3.89	3.91	4.01	3.68
Nonhydrogens	7.20	6.90	6.78	6.75	6.61
Hydrocarbons	2.85	2.38	2.30	2.30	2.51
Subst. hydrocarbons	2.34	2.93	2.71	3.59	2.95
Inorganic hydrides	3.64	3.26	3.05	3.03	2.98
Radicals	3.51	3.18	3.51	3.19	2.59
Ionization energies	4.73	4.60	4.69	4.23	4.34
Electron affinities	4.10	3.97	4.06	3.91	3.90
Proton affinities	5.48	5.10	5.10	5.44	5.52
All	4.26	4.14	4.14	4.10	3.96

^aFrom Ref. 4.^bFrom Ref. 7.^cFrom Ref. 8.

(IEs) and the 58 electron affinities (EAs) will best reflect the performance of the various methods for describing radicals. However, it should be noted that the heats of formation of the closed-shell species will also be affected by the RAD-type modifications since these are derived from atomization

TABLE VI. G3, G3//B3-LYP, G3-RAD(5d), and G3-RAD calculated energies with deviations from experiment of $\geq 12.5 \text{ kJ mol}^{-1}$ for the G2/97 test set.

	Deviation from expt. ^a			
	G3 ^b	G3//B3-LYP ^c	G3-RAD(5d)	G3-RAD
Heats of formation				
C ₂ F ₄	20.5	18.0	18.2	18.0
Na ₂	16.7	18.0	18.7	15.4
CH ₂ =CHCl	15.1	14.2	13.2	14.5
C ₂ Cl ₄	14.2	8.4	4.3	10.3
AlCl ₃	13.8	7.9	4.3	0.8
CS ₂	13.8	12.5	8.9	7.6
SiCl ₄	0.0	-8.4	-13.4	-11.1
SiF ₄	-4.6	-9.2	-8.7	-16.9
·OCl	-7.1	-10.0	-12.9	-11.0
ClF ₃	-8.0	-13.0	-12.4	-9.8
CF ₂ O	-14.2	-14.6	-14.1	-15.0
SO ₂	-15.9	-10.9	-9.7	-12.2
PF ₃	-20.1	-24.3	-22.4	-24.6
Ionization energies				
B ₂ F ₄	29.3	28.9	25.9	24.5
BF ₃	-4.6	-15.9	-13.9	-13.0
BCl ₃	-4.6	-18.4
Be	-13.4	-14.6	-13.6	-14.5
Mg	-13.4	-14.6	-14.0	-15.4
C ₂ H ₅ OH	-14.2	5.8	2.0	1.7
CH ₃ Cl	-16.3	-1.7	0.9	1.2
O ₂	-16.7	-2.1	2.3	2.3
CH ₃ F	-20.9	-15.9	-16.3	-16.3
·CN	-25.5	-27.6	-16.9	-17.0
Electron affinities				
·NH	17.6	18.4	15.7	15.8
·CH ₃	11.7	12.6	11.6	10.4
·Li	-12.1	-13.4	-12.2	-12.3
·Na	-15.1	-16.3	-16.4	-16.2

^aDeviation = Experiment - Theory.^bFrom Ref. 4.^cFrom Ref. 7.

energies that use the calculated energies of the atoms which, for the molecules in the G2/97 test set, are all open-shell.

A. G3-RAD and G3-RAD(5d)

The heats of formation of the 29 radicals in the G2/97 test set, calculated at the G3-RAD(5d) and G3-RAD levels, are compared with G3 and G3//B3-LYP results in Table IV. G3-RAD (MAD = 2.59 kJ mol^{-1}) (Ref. 33) performs slightly better than G3 and G3//B3-LYP (MAD = 3.51 and 3.18 kJ mol^{-1} , respectively) for radical heats of formation, while G3-RAD(5d) (MAD = 3.19 kJ mol^{-1}) shows similar performance to G3//B3-LYP. Baboul *et al.*⁷ have noted that the improved geometries and zero-point energies obtained at B3-LYP/6-31G(d) lead to the better overall performance of G3//B3-LYP compared with standard G3. They find that at G3//B3-LYP, 27 of the 299 energies examined in the G2/97 test set differ by more than 4 kJ mol^{-1} from those obtained at G3. Of these, 18 show improved agreement with experiment at G3//B3-LYP and these include the heats of formation of the ·CN, :O₂, and ·CCH radicals. We similarly note an improved agreement with experiment for G3-RAD and G3-RAD(5d) compared with standard G3 for heats of formation of radicals, partly due to improved geometries and ZPVEs obtained at B3-LYP/6-31G(d).

The largest differences in radical heats of formation between G3-RAD(5d) and G3-RAD on the one hand, and G3//B3-LYP on the other occur for :O₂ ($\sim 7 \text{ kJ mol}^{-1}$), :SO (5.0 kJ mol^{-1}), :SiH₂ (4.7 kJ mol^{-1}), :Si₂ (4.1 kJ mol^{-1}), :S₂ (4.1 kJ mol^{-1}), and ·SiH₃ (3.9 kJ mol^{-1}). For the triplet radicals, :O₂, :SO, and :S₂ quite large differences are observed between the component energies obtained with UMP (as in G3//B3-LYP) and RMP [as in G3-RAD(5d) and G3-RAD]. While there is significant cancellation in the additivity scheme, a residual difference of $\sim 5 \text{ kJ mol}^{-1}$ remains for each of these radicals. The use of the (6d,10f) combination for both the RMP4/6-31G(2df,p) and RMP2(fu)/G3large single-point calculations in G3-RAD generally leads to better agreement with experiment, in particular for :SiH₂, :Si₂, :S₂, and ·SiH₃.

Three of the radicals in the G2/97 test set exhibit significant spin-contamination (·CN, ·CCH, and ·CHCH₂). G3//B3-LYP, G3-RAD(5d), and G3-RAD give similar heats

of formation for these radicals, and show significant improvement over standard G3, largely due to the improved geometry and ZPVE obtained with B3-LYP/6-31G(*d*).

A summary of the overall performance of the G3-RAD(5*d*) and G3-RAD procedures is included in Table V, where they are compared with G3, G3//B3-LYP, and G3(CCSD)//B3-LYP. G3-RAD gives the lowest overall mean absolute deviation from experiment of 3.96 kJ mol⁻¹, while the G3-RAD(5*d*) procedure also performs well with an overall MAD of 4.10 kJ mol⁻¹. Curtiss *et al.*⁴ report that the standard G3 method gives an overall MAD of 4.26 kJ mol⁻¹. In comparison, the G3//B3-LYP (Ref. 7) and G3(CCSD)//B3-LYP (Ref. 8) procedures both give MADs of 4.14 kJ mol⁻¹.

As noted above, G3-RAD performs well for radical heats of formation (MAD=2.59 kJ mol⁻¹). G3-RAD(5*d*) (MAD=3.19 kJ mol⁻¹) performs slightly less well but improves on standard G3 and G3(CCSD)//B3-LYP. Similarly, G3-RAD gives improved overall performance for the heats of formation (MAD=3.68 kJ mol⁻¹) compared with the standard G3 procedures, while G3-RAD(5*d*) does slightly less well (MAD=4.01 kJ mol⁻¹).

G3-RAD(5*d*) and G3-RAD differ only in the use of spherical (5*d*,7*f*) versus Cartesian (6*d*,10*f*) basis functions for the RMP2(fu)/G3large single-point energy. The improved performance of G3-RAD over G3-RAD(5*d*) for heats of formation suggests that the (6*d*,10*f*) combination adds greater flexibility to the underlying *sp* basis. This appears most pronounced for second-row species. The MAD from experiment for the heats of formation of the 50 second-row species for G3-RAD is 5.0 kJ mol⁻¹, while for G3//B3-LYP and G3-RAD(5*d*) a value of 5.6 kJ mol⁻¹ is obtained. One notable exception to this trend is the heat of formation of SiF₄, where G3-RAD gives a significantly poorer result than both G3//B3-LYP and G3-RAD(5*d*) (Table VI). In comparison, the MADs from experiment for the heats of formation of the 98 first-row species for G3//B3-LYP, G3-RAD, and G3-RAD(5*d*) are 2.9, 2.9, and 3.2 kJ mol⁻¹, respectively.

G3-RAD(5*d*) and G3-RAD perform particularly well for ionization energies with MADs of 4.23 and 4.34 kJ mol⁻¹, respectively. Both RAD procedures also show a slight improvement over G3//B3-LYP for electron affinities, with MADs of 3.91 and 3.90 kJ mol⁻¹, respectively, compared with 3.97 kJ mol⁻¹.

Table VI presents energies from the G2/97 test set that show deviations from experiment ≥ 12.5 kJ mol⁻¹ (~ 3.0 kcal mol⁻¹) for one or more of G3, G3//B3-LYP, G3-RAD(5*d*), or G3-RAD. Such deviations from experiment are observed for 19 energies (nine $\Delta_f H_{298}$ values, eight IEs, and two EAs) at G3, 17 energies (six $\Delta_f H_{298}$ values, seven IEs, and four EAs) at G3//B3-LYP, 15 energies (seven $\Delta_f H_{298}$ values, six IEs, and two EAs) at G3-RAD(5*d*) and 14 energies (six $\Delta_f H_{298}$ values, six IEs, and two EAs) at G3-RAD.

Twelve of the thirteen heats of formation with large deviations in Table VI are found for nonhydrogen species. Kedziora *et al.*³⁴ note that scalar relativistic effects can make a significant contribution to the total atomization energy (TAE), particularly for nonhydrogen species containing

second-row atoms. Scalar relativistic effects were found to make a contribution to the TAE of >4 kJ mol⁻¹ for six of the molecules in Table VI (C₂F₄, C₂Cl₄, AlCl₃, SiCl₄, SiF₄, and PF₃). However, with a modified G3 procedure which includes a scalar relativistic correction [G3(rel)], Kedziora *et al.*³⁴ found only a relatively small change in performance between G3(rel) and G3 and concluded that the HLC generally compensates for scalar relativistic effects which tend to be systematic. On the basis of CBS-QB3 calculations, Montgomery *et al.*³⁵ have questioned the experimental heats of formation of C₂F₄, CH₂=CHCl, and CF₂O and the ionization energy of B₂F₄.

The G3//B3-LYP, G3-RAD(5*d*), and G3-RAD energies listed in Table VI are generally very similar and tend to show improvement over standard G3. Significant improvements, related to the better geometries and ZPVEs obtained with B3-LYP/6-31G(*d*), are observed for the heats of formation of C₂Cl₄, AlCl₃, and SO₂, and the ionization energies of C₂H₅OH, CH₃Cl, :O₂, and CH₃F.⁷ However, Baboul *et al.*⁷ note that B3-LYP/6-31G(*d*) poorly describes the Jahn–Teller distorted electronic states of the cations of BF₃, BCl₃, and CH₄, which in turn leads to large deviations from experiment for the ionization energies of these species. The deviations from experiment for IE(BF₃) at G3//B3-LYP, G3-RAD(5*d*) and G3-RAD are -15.9, -13.9, and -13.0 kJ mol⁻¹ and for IE(CH₄) are -11.3, -11.8, and -12.2 kJ mol⁻¹, respectively. These are significantly larger than the deviations with standard G3 (-4.6 and -3.3 kJ mol⁻¹, respectively), which uses MP2/6-31G(*d*) geometries. We are unable to calculate the ionization energy of BCl₃ at the G3-RAD(5*d*) and G3-RAD levels, because of a basis function limit (≤ 256) in ACES II. The B3-LYP/6-31G(*d*) geometry and ZPVE also lead to significantly larger deviations from experiment for G3//B3-LYP, G3-RAD, and G3-RAD(5*d*) values for the heats of formation of SiCl₄, SiF₄, •OCl, ClF₃, and PF₃ than observed with standard G3.

The most significant improvement observed for the G3-RAD(5*d*) and G3-RAD procedures over G3//B3-LYP is for the ionization energy of the •CN radical. As shown in Table IV, all three procedures provide reasonable and quite similar values for the heat of formation of the •CN radical. However, all three procedures give quite poor results for the heat of formation of CN⁺. The G3-RAD(5*d*) and G3-RAD values ($\Delta_f H_0 = 1766.5$ and 1767.7 kJ mol⁻¹, respectively) are in somewhat closer agreement with experiment ($\Delta_f H_0 = 1750.5$ kJ mol⁻¹) (Refs. 36 and 37) than the value obtained at G3//B3-LYP ($\Delta_f H_0 = 1775.5$ kJ mol⁻¹). In comparison, the G3(CCSD)//B3-LYP values for the heats of formation of •CN and CN⁺ are 437.1 and 1766.9 kJ mol⁻¹, respectively, in reasonable agreement with our G3-RAD(5*d*) and G3-RAD values. This suggests that the use of CCSD(T) rather than QCISD(T) in the additivity scheme leads to improved performance by these procedures for the energy of the CN⁺ cation.

As we have noted above, the heats of formation of the closed-shell species will also be affected by the RAD-type modifications since these are derived from atomization energies that use the calculated energies of the atoms, which for

the molecules in the G2/97 test set are all open-shell. We find that the difference between U and R, following additivity, for first-row atoms is generally about 0.5 kJ mol^{-1} while for second-row atoms this increases to $\sim 1.5 \pm 0.5 \text{ kJ mol}^{-1}$.³⁸ The effect of these differences is most evident in the heats of formation of C_2Cl_4 , AlCl_3 , and SiCl_4 . The use of the $(6d,10f)$ combination for the MP2(full)/G3large energy in G3-RAD leads to improvements for the heats of formation of AlCl_3 and CS_2 but larger deviations for C_2Cl_4 and SiF_4 . The replacement of QCISD(T) with CCSD(T) also contributes to the improvement observed for CS_2 .

The improved performance of G3-RAD over standard G3, particularly for radical heats of formation, can be attributed partly to the use of B3-LYP/6-31G(*d*) geometries and ZPVEs, partly to the use of RMP energies versus UMP energies in the additivity scheme and partly to the use of Cartesian $(6d,10f)$ versus spherical $(5d,7f)$ basis functions for the MP2(fu)/G3large single-point energy. The energies obtained with QCISD(T) and CCSD(T) are generally very similar. However, in some specific examples the inclusion of CCSD(T), as in the RAD-type procedures, leads to improved agreement with experiment.

B. G3X-RAD and G3X-RAD(5*d*)

G3X, G3X-RAD(5*d*), and G3X-RAD heats of formation for the 29 radicals in the G2/97 test set are included in Table IV. Curtiss *et al.*¹⁰ report that the MAD from experiment for G3X for the 29 radicals of the G2/97 test set is 3.18 kJ mol^{-1} . G3X-RAD (MAD = 2.50 kJ mol^{-1}) (Ref. 33) shows improved agreement with experiment over G3X while G3X-RAD(5*d*) (MAD = 3.14 kJ mol^{-1}) gives similar performance to G3X. In addition, G3X-RAD and G3X-RAD(5*d*) show a slight improvement over G3-RAD and G3-RAD(5*d*), respectively. The G3X-RAD(5*d*) and G3X-RAD radical heats of formation are generally slightly higher than those determined at G3X.

Not surprisingly, the largest differences between G3X-RAD(5*d*) and G3X-RAD on the one hand, and G3X on the other occur for the same group of radicals as noted in the previous section, $\cdot\text{SiH}_2(^3B_1)$, $\cdot\text{SiH}_3$, $\cdot\text{O}_2$, $\cdot\text{Si}_2$, $\cdot\text{S}_2$, and $\cdot\text{SO}$. Again, the differences observed for $\cdot\text{O}_2$, $\cdot\text{S}_2$, and $\cdot\text{SO}$ are largely due to the use of RMP versus UMP energies in the additivity scheme. As for G3-RAD, the use of the $(6d,10f)$ combination for both the RMP4/6-31G(2*df,p*), RMP2(full)/G3large and RHF/G3Xlarge calculations in G3X-RAD generally leads to improvements over G3X and G3X-RAD(5*d*), in particular for $\cdot\text{SiH}_2$, $\cdot\text{SiH}_3$, and $\cdot\text{Si}_2$.

G3X, G3X-RAD(5*d*), and G3X-RAD give quite similar results for the heats of formation for two of the three highly spin-contaminated radicals, $\cdot\text{CHCH}_2$ and $\cdot\text{CCH}$. The difference for $\cdot\text{CN}$ radical is slightly larger (4.1 kJ mol^{-1}), with the G3X result being in closer agreement with the experimental value used in the G2/97 test set and the G3X-RAD result in closer agreement with the experimental value recommended by Berkowitz *et al.*³⁷

Table VII presents a summary of the mean absolute deviations from experiment for G3X, G3X(CCSD), G3X-RAD(5*d*), and G3X-RAD. The G3X-RAD procedure

TABLE VII. Summary of mean absolute deviations from experiment (kJ mol^{-1}) for G3X, G3X-RAD, and related procedures for the G2/97 test set.

	G3X ^a	G3X(CCSD) ^b	G3X -RAD(5 <i>d</i>)	G3X -RAD
Heats of formation	3.60	3.60	3.60	3.11
Nonhydrogens	6.11	6.11	5.69	4.77
Hydrocarbons	2.47	2.34	2.30	2.47
Subst. hydrocarbons	2.63	2.97	3.10	2.55
Inorganic hydrides	3.39	3.35	2.97	3.14
Radicals	3.18	3.35	3.14	2.50
Ionization energies	4.48	4.60	4.05	4.13
Electron affinities	4.10	4.22	3.74	3.81
Proton affinities	5.06	5.06	5.02	5.07
All	4.02	3.97	3.85	3.65

^aFrom Ref. 10.

^bFrom Ref. 11.

gives the lowest overall mean absolute deviation from experiment of 3.65 kJ mol^{-1} while the G3X-RAD(5*d*) procedure also performs well with an MAD of 3.85 kJ mol^{-1} . Curtiss *et al.*¹⁰ report an overall MAD of 4.02 kJ mol^{-1} for the G3X procedure while the G3X(CCSD) procedure¹¹ gives a value of 3.97 kJ mol^{-1} . G3X-RAD performs particularly well for heats of formation overall with an MAD of 3.11 kJ mol^{-1} , while G3X, G3X(CCSD), and G3X-RAD(5*d*) each give MADs of 3.60 kJ mol^{-1} .

As noted by Curtiss *et al.*,¹⁰ the most significant improvement for G3X compared with G3 is found for the heats of formation of the nonhydrogen species. They find that both the improved geometries obtained with B3-LYP/6-31G(2*df,p*) and the inclusion of the HF/G3X large correction for second-row atoms lead to the improved performance of G3X over standard G3 but that the latter of these is the more important. We also observe significant overall improvement in the heats of formation of the nonhydrogen species in going from G3-RAD and G3-RAD(5*d*) to G3X-RAD and G3X-RAD(5*d*), respectively.

In a similar manner to G3-RAD(5*d*) and G3-RAD, G3X-RAD(5*d*), and G3X-RAD differ only in the use of spherical $(5d,7f)$ or $(5d,7f,9g)$ versus Cartesian $(6d,10f)$ or $(6d,10f,15g)$ basis functions for the single-point energies evaluated at RMP2(fu)/G3large and RHF/G3Xlarge. As in the case of G3-RAD, the improved performance of G3X-RAD for heats of formation suggests that the $(6d,10f,15g)$ combination adds greater flexibility to the underlying sp basis, particularly for species containing second-row atoms. The MAD from experiment for the 50 second-row species is 4.00 kJ mol^{-1} at G3X-RAD while this increases to 4.60 kJ mol^{-1} at G3X-RAD(5*d*) and 4.76 kJ mol^{-1} at G3X. This effect is particularly noticeable in the heat of formation of AlF_3 , for which G3X-RAD shows significant improvement over G3X and G3X-RAD(5*d*) (Table VIII). G3X-RAD also shows improved agreement with experiment for the heats of formation of the 98 first-row species (MAD = 2.75 kJ mol^{-1}) compared with G3X-RAD(5*d*) and G3X (MADs = 3.07 and 3.08 kJ mol^{-1} , respectively).

While we have determined the HLCs for G3X-RAD(5*d*)

TABLE VIII. G3X, G3X-RAD(5*d*), and G3X-RAD calculated energies with deviations from experiment of ≥ 12.5 kJ mol⁻¹ for the G2/97 test set.

	Deviations from expt. ^a		
	G3X ^b	G3X-RAD(5 <i>d</i>)	G3X-RAD
Heats of formation			
Na ₂	18.8	18.6	15.3
C ₂ F ₄	18.0	17.5	15.6
CH ₂ =CHCl	14.2	13.2	14.1
CS ₂	13.8	9.1	8.0
COS	13.4	10.9	7.8
AlF ₃	12.6	11.7	3.3
CF ₂ O	-14.6	-14.7	-16.6
Ionization energies			
B ₂ F ₄	28.9	27.7	26.0
CH ₃ F	-12.1	-12.5	-12.7
Be	-15.1	-13.6	-14.7
Mg	-15.5	-14.1	-15.6
BF ₃	-15.9	-13.4	-12.6
•CN	-27.2	-16.5	-16.3
Electron affinities			
:NH	17.6	15.5	15.4
•CH ₃	13.8	13.6	12.2
•Li	-13.8	-12.4	-12.5
•Na	-17.0	-16.5	-16.4

^aDeviation = Experiment - Theory.^bFrom Ref. 10.

and G3X-RAD using 296 of the energies in the G2/97 test set, we note that Curtiss *et al.*¹⁰ have determined the HLC for G3X using the larger G3/99 test set. However, they have indicated that determination of the HLC parameters for G3X with the G2/97 test set gives almost identical values to those determined with the G3/99 test set. They also report that the overall MAD for G3X for the smaller G2/97 test set is almost the same as that for the larger G3/99 test set on which the HLC was determined.

Table VIII presents energies from the G2/97 test set for G3X, G3X-RAD(5*d*), and G3X-RAD that show the largest deviations from experiment (≥ 12.5 kJ mol⁻¹). Many of the energies with large deviations from experiment listed in Table VI [G3//B3-LYP, G3-RAD(5*d*), and G3-RAD] are also noted to have large deviations at G3X, G3X-RAD, and G3X-RAD(5*d*). However, many of the heats of formation and ionization energies listed in Table VIII show a slight improvement over the corresponding G3//B3-LYP, G3-RAD(5*d*), and G3-RAD values (Table VI). The deviations from experiment in the electron affinities of Table VIII are generally similar to or slightly greater than the corresponding G3//B3-LYP, G3-RAD(5*d*), and G3-RAD values of Table VI.

The largest differences between G3X on the one hand and G3X-RAD(5*d*) and G3X-RAD on the other, for the energies listed in Table VIII, occur for the heats of formation of CS₂, COS, and AlF₃, and the ionization energy of •CN.

The improved values at G3X-RAD, compared with G3X, for the heats of formation of CS₂, COS, and AlF₃ are due largely to the use of the (6*d*,10*f*) combination. Again, the replacement of QCISD(T) with CCSD(T)

also contributes to the improved agreement with experiment for the heat of formation of CS₂ and the ionization energy of •CN.

The G3X-RAD procedure shows improved performance in almost all categories compared with standard G3X, most noticeably for the subset of 29 radical heats of formation. We therefore recommend the G3X-RAD procedure for reliable thermochemical prediction, particularly for radicals but more generally for closed-shell molecules as well. While the performance of G3X-RAD for the prediction of thermochemical values of nonhydrogen species is slightly better than for standard G3X, this remains a category for which occasional large deviations from experiment are observed.

C. G3(MP2)-RAD

Heats of formation for radicals calculated at G3(MP2)-RAD are compared with G3(MP2) and G3(MP2)//B3-LYP values in Table IX. The radical heats of formation obtained with G3(MP2), G3(MP2)//B3-LYP, and G3(MP2)-RAD are generally very similar. However, the use of B3-LYP/6-31G(*d*) geometries, in G3(MP2)//B3-LYP and G3(MP2)-RAD, leads to significant improvements in the values for the heat of formation of •CN, :O₂, and •CCH compared with G3(MP2). The radical heats of formation displaying the largest differences between G3(MP2)-RAD and G3(MP2)//B3-LYP occur for :Si₂, :S₂, and :SO. Again, for :O₂, :SO, and :S₂ quite large differences are observed between the component energies obtained with UMP [as in G3(MP2)//B3-LYP] and RMP [as in G3(MP2)-RAD].

The mean absolute deviations from experiment for the G2/97 test set for G3(MP2)-RAD are compared with the MADs previously reported for G3(MP2),⁶ G3(MP2)//B3-LYP,⁷ and G3(MP2,CCSD)//B3-LYP (Ref. 8) in Table X. G3(MP2)-RAD performs slightly better overall than G3(MP2), G3(MP2)//B3-LYP, and G3(MP2,CCSD)//B3-LYP, with a MAD of 5.17 kJ mol⁻¹. Similar performance to G3(MP2)//B3-LYP and G3(MP2,CCSD)//B3-LYP is observed for heats of formation overall (MAD = 4.73 kJ mol⁻¹). However, significant improvements are observed for electron affinities (MAD = 5.81 kJ mol⁻¹). G3(MP2)-RAD performs slightly better than G3(MP2) for proton affinities (MAD = 3.98 kJ mol⁻¹ versus 4.27 kJ mol⁻¹) but not quite as well as G3(MP2)//B3-LYP or G3(MP2,CCSD)//B3-LYP (MADs = 3.72 kJ mol⁻¹).

Table XI presents energies from the G2/97 test set with deviations from experiment of ≥ 12.5 kJ mol⁻¹ for G3(MP2), G3(MP2)//B3-LYP, and G3(MP2)-RAD. The energies listed are generally very similar. G3(MP2)//B3-LYP and G3(MP2)-RAD show improved performance [compared with G3(MP2)] for the heat of formation of SO₂ and the ionization energies of :O₂ and CH₃F, due largely to the improved B3-LYP/6-31G(*d*) geometry and ZPVE used in these procedures. However, as noted above, B3-LYP/6-31G(*d*) performs poorly for the BCl₃⁺, BF₃⁺, and CH₄⁺ radical cations, leading to poor ionization energies for BCl₃, BF₃, and CH₄.

TABLE IX. Heats of formation for the 29 radicals in the G2/97 test set determined with G3(MP2), G3(MP2)-RAD, G3X(MP2), G3X(MP2)-RAD, and related procedures ($\Delta_f H_{298}$, kJ mol⁻¹).

Radical	$\langle S^2 \rangle^a$	G3(MP2) ^b	G3(MP2)// B3-LYP ^c	G3(MP2)- RAD	G3X(MP2) ^d	G3X(MP2)- RAD	Expt. ^e
•BeH	0.752	353.5	353.5	355.0	354.4	355.4	341.8
•CH	0.756	588.7	587.9	587.8	587.9	588.3	596.2
•CH ₂ (³ B ₁)	2.015	386.2	385.3	386.7	385.8	387.1	392.0
•CH ₃	0.762	143.1	143.9	144.0	144.3	144.2	146.4
•NH	2.014	351.5	349.8	350.4	349.8	351.0	356.5
•NH ₂	0.758	186.2	184.9	184.2	184.9	184.7	188.7
•OH	0.755	34.7	33.9	34.4	34.7	35.2	39.3
•SiH ₂ (³ B ₁)	2.005	348.9	347.3	350.9	346.9	350.6	360.7
•SiH ₃	0.754	192.5	191.6	193.4	190.4	192.5	200.4
•PH ₂	0.763	133.1	131.8	129.9	130.5	129.3	138.5
•CN	1.127	445.2	436.4	437.7	436.0	438.2	438.9 ^f
•CHO	0.762	39.7	37.7	40.0	38.5	40.5	41.8
•NO	0.768	91.6	90.0	90.0	89.5	90.4	90.4
•O ₂	2.037	8.4	1.7	-1.3	2.5	-0.3	0.0
•Si ₂	2.013	573.6	572.8	577.4	572.0	575.7	585.3
•S ₂	2.029	126.4	125.9	119.1	122.6	116.2	128.4
•SO	2.039	9.6	7.1	11.0	2.9	6.4	5.0
•OCl	0.764	110.5	111.7	114.7	108.8	111.2	101.3
•CCH	1.187	568.2	562.3	562.2	563.2	563.7	565.3
•CHCH ₂	0.935	294.1	292.5	293.1	293.3	293.7	299.6
•COCH ₃	0.764	-10.0	-11.7	-9.1	-11.3	-9.1	-10.0
•CH ₂ OH	0.759	-15.1	-16.3	-15.4	-15.5	-15.0	-17.2
•OCH ₃	0.758	22.2	19.2	20.0	19.7	20.1	17.2
•OCH ₂ CH ₃	0.760	-8.4	-9.2	-12.8	-8.4	-12.7	-15.5
•SCH ₃	0.758	119.7	118.8	119.6	118.4	118.9	124.7
•CH ₂ CH ₃	0.763	120.9	120.9	121.0	121.3	120.9	120.9
•CH(CH ₃) ₂	0.763	90.8	90.4	90.7	90.8	90.3	90.0
•C(CH ₃) ₃	0.763	55.6	55.2	56.9	55.6	55.2	51.5
•ONO	0.766	38.1	34.7	37.2	34.7	37.6	33.1
MAD		5.15	4.94	5.10	5.19	4.67	
MD		-0.40	-2.11	-1.47	-2.31	-1.75	
LD		± 11.72	-13.39	+13.39	-13.81	+13.60	

^aSpin-squared expectation value at the UMP2(fu)/6-31G(d) level.^bFrom Ref. 6.^cFrom Ref. 7.^dFrom Ref. 10.^eFrom Ref. 5, unless otherwise noted.^fA value of 441.4 kJ mol⁻¹ is recommended in Ref. 37.

The largest differences between G3(MP2)//B3-LYP and G3(MP2)-RAD for the energies listed in Table XI are seen for the heats of formation of CS₂, and SO₂ and the ionization energy of •CN. The improvements observed at

G3(MP2)-RAD, compared with G3(MP2)//B3-LYP in $\Delta_f H_{298}(\text{CS}_2)$ and IE(•CN), and the larger deviation from experiment for $\Delta_f H_{298}(\text{SO}_2)$ are largely due to the replacement of QCISD(T) by CCSD(T) in the additivity scheme.

TABLE X. Summary of mean absolute deviations from experiment (kJ mol⁻¹) for G3(MP2), G3(MP2)-RAD, G3X(MP2), G3X(MP2)-RAD, and related procedures for the G2/97 test set.

	G3(MP2) ^a	G3(MP2)//B3-LYP ^b	G3(MP2,CCSD)// B3-LYP ^c	G3(MP2)-RAD	G3X(MP2) ^d	G3X(MP2)-RAD
Heats of formation	4.94	4.73	4.77	4.73	4.64	4.44
Nonhydrogens	8.87	8.33	8.33	8.11	7.74	7.66
Hydrocarbons	2.93	3.14	2.97	3.33	3.01	2.99
Subst. hydrocarbons	3.10	2.93	2.97	3.00	3.01	2.82
Inorganic hydrides	4.31	3.89	3.93	3.48	4.23	3.70
Radicals	5.15	4.94	5.15	5.10	5.19	4.67
Ionization energies	5.90	5.73	5.86	5.70	5.69	5.31
Electron affinities	6.11	6.02	6.15	5.81	6.32	5.86
Proton affinities	4.27	3.72	3.72	3.98	3.30	3.33
All	5.44	5.23	5.31	5.17	5.23	4.92

^aFrom Ref. 6.^bFrom Ref. 7.^cFrom Ref. 8.^dFrom Ref. 10.

TABLE XI. G3(MP2), G3(MP2)//B3-LYP, and G3(MP2)-RAD calculated energies with deviations from experiment of ≥ 12.5 kJ mol $^{-1}$ for the G2/97 test set.

	Deviation from expt. ^a		
	G3(MP2) ^b	G3(MP2)//B3-LYP ^c	G3(MP2)-RAD
Heats of formation			
CS ₂	22.2	21.8	18.0
C ₂ Cl ₄	20.9	19.2	18.7
CH ₂ =CHCl	18.4	18.4	18.6
C ₂ F ₄	18.0	18.8	19.8
COS	14.2	15.5	12.8
Na ₂	13.8	13.4	14.5
CS	13.4	13.8	11.0
AlCl ₃	12.5	10.9	9.7
Li ₂	12.1	12.6	13.4
:SiH ₂ (³ B ₁)	11.7	13.4	9.8
:Si ₂	11.7	12.6	11.0
·OCl	-9.2	-10.5	-13.4
SO ₂	-16.3	-10.5	-14.4
·BeH	-11.7	-11.7	-13.1
CF ₂ O	-16.7	-15.5	-15.5
ClF ₃	-18.0	-19.7	-21.2
PF ₃	-21.8	-23.0	-21.9
Ionization energies			
B ₂ F ₄	29.7	29.3	26.1
:S	15.1	13.4	11.7
·Na	13.4	12.6	13.9
BCl ₃	-3.8	-18.0	...
BF ₃	-3.8	-18.8	-17.9
:O ₂	-16.7	-2.5	-5.4
·CN	-19.7	-24.7	-17.0
Be	-22.6	-23.8	-23.2
CH ₃ F	-22.6	-17.6	-17.0
Electron affinities			
:NH	18.8	18.8	17.4
·B	18.8	18.0	19.6
:C	15.1	14.2	17.3
C ₂	13.0	11.7	11.2
:O	13.8	12.1	13.4
·Na	-27.2	-28.9	-28.3
·Li	-31.4	-32.6	-31.6

^aDeviation = Experiment - Theory.^bFrom Ref. 6.^cFrom Ref. 7.

D. G3X(MP2)-RAD

G3X(MP2) and G3X(MP2)-RAD heats of formation for the 29 radicals in the G2/97 test set are included in Table IX. G3X(MP2)-RAD shows improved agreement with experiment compared with G3X(MP2) (MAD=4.67 versus 5.19 kJ mol $^{-1}$) for the $\Delta_f H_{298}$ values for radicals, in accord with our previous findings.^{17,33} In particular, G3X(MP2)-RAD shows improved agreement with experiment for all three of the highly spin-contaminated radicals in Table IX. In our previous study,¹⁷ we found G3X(MP2)-RAD and G3(MP2)-RAD to give very similar performance. However, for the 29 radicals of the G2/97 test set, G3X(MP2)-RAD shows a significant improvement compared with G3(MP2)-RAD.³⁹ The largest improvements occur for :SO (4.6 kJ mol $^{-1}$) and ·OCl (3.4 kJ mol $^{-1}$), which can be attributed partly to the improved geometries obtained with

B3-LYP/6-31G(2df,p) and partly due to the HF/G3Xlarge correction for second-row atoms.¹⁰

The largest differences between G3X(MP2) and G3X(MP2)-RAD for radical heats of formation occur for :S₂, and ·OCH₂CH₃. As noted for G3(MP2)-RAD, significant differences are observed between the component energies obtained with UMP [as in G3X(MP2)] and RMP [as in G3X(MP2)-RAD] for :O₂, :SO, and :S₂.

A summary of the performance of G3X(MP2) and G3X(MP2)-RAD is included in Table X, along with that for G3(MP2) and related procedures. G3X(MP2)-RAD gives the best overall performance of the procedures listed in Table X, with a mean absolute deviation from experiment of 4.92 kJ mol $^{-1}$. Improvements compared with G3X(MP2) are observed for heats of formation (MAD=4.44 kJ mol $^{-1}$), ionization energies (MAD=5.31 kJ mol $^{-1}$) and electron affinities (MAD=5.86 kJ mol $^{-1}$). The MAD for proton affinities (3.33 kJ mol $^{-1}$) is close to that observed for G3X(MP2). It is pleasing to see the significant improvement in the radical heats of formation, with an MAD of 4.67 kJ mol $^{-1}$. G3X(MP2)-RAD performs better than G3(MP2)-RAD for almost all the categories in Table X.

Table XII presents energies from the G2/97 test set with deviations from experiment of ≥ 12.5 kJ mol $^{-1}$ for G3X(MP2) and G3X(MP2)-RAD. Large deviations from experiment are observed for 29 energies at G3X(MP2) (13 $\Delta_f H_{298}$ values, eight IEs, and eight EAs) but just 20 energies at G3X(MP2)-RAD (nine $\Delta_f H_{298}$ values, six IEs, and five EAs).

The largest differences between G3X(MP2) and G3X(MP2)-RAD for the energies listed in Table XII occur for the heat of formation of CS₂, the ionization energies of C₆H₅NH₂ and ·CN, and the electron affinities of ·PO and ·SCH₂CH₃. As noted in the previous section, the inclusion of CCSD(T) in place of QCISD(T) leads to improved values for $\Delta_f H_{298}$ (CS₂) and IE(·CN).

The significant improvement in the ionization energy of C₆H₅NH₂ and the electron affinity of the ·PO radical appears to be due to the use of RMP energies versus UMP energies in the additivity scheme. The $\langle S^2 \rangle$ values for C₆H₅NH₂⁺ and ·PO at the UMP2/6-31G(d) level are 1.153 and 0.855, respectively, reflecting significant spin contamination. The large difference between the previously reported G3X(MP2) value and the current G3X(MP2)-RAD value for EA(·SCH₂CH₃) may be attributed to different states being used for the ·SCH₂CH₃ radical. We have calculated the electron affinity for the A'' ground state of the ·SCH₂CH₃ radical, whereas it appears that it was previously calculated for the higher energy A' state.¹⁰ The deviation from experiment at G3X(MP2) for EA(·SCH₂CH₃) reduces to -4.1 kJ mol $^{-1}$ when calculated for the A'' state, in close agreement with our G3X(MP2)-RAD value.

G3X(MP2)-RAD shows improved performance in almost all categories over the standard G3-type procedures based on reduced Møller-Plesset order, particularly for radical heats of formation. We therefore recommend G3X(MP2)-RAD as an economical procedure for reliable thermochemical prediction, particularly for radicals but more generally for closed-shell molecules as well.

TABLE XII. G3X(MP2) and G3X(MP2)-RAD calculated energies with deviations from experiment of ≥ 12.5 kJ mol⁻¹ for the G2/97 test set.

	Deviation from expt. ^a	
	G3X(MP2) ^b	G3X(MP2)-RAD
Heats of formation		
CS ₂	23.4	19.1
C ₂ Cl ₄	19.7	20.8
CH ₂ =CHCl	18.0	18.6
COS	15.9	12.9
CS	15.1	11.8
C ₂ F ₄	14.6	17.8
:SiH ₂ (³ B ₁)	13.8	10.1
Na ₂	13.8	14.1
:Si ₂	13.4	9.6
Li ₂	13.4	13.4
·BeH	-12.6	-13.6
BF ₃	-13.0	-10.6
CF ₂ O	-18.0	-16.7
Ionization energies		
B ₂ F ₄	30.5	27.8
·Na	13.4	13.7
:S	13.0	11.2
CH ₃ F	-12.6	-12.7
C ₆ H ₅ NH ₂	-13.0	-8.1
BF ₃	-18.0	-17.7
Be	-24.3	-23.7
·CN	-24.3	-16.5
Electron affinities		
:NH	18.8	16.9
·B	18.8	19.4
:C	15.1	17.1
·PO	13.4	3.7
C ₂	13.0	11.6
·SCH ₂ CH ₃	-12.6 ^c	-3.0
·Na	-29.2	-28.7
·Li	-33.0	-32.1

^aDeviation = Experiment - Theory.^bFrom Curtiss *et al.*, Ref. 10.^cThis value refers to the A' state of ·SCH₂CH₃. A deviation of -4.6 kJ mol⁻¹ is obtained for the EA calculated for the ground A'' state of ·SCH₂CH₃ (see text).

IV. CONCLUSIONS

We have developed and assessed modifications of the G3, G3X, G3(MP2), and G3X(MP2) methods with the aim of providing a better description for the thermochemistry of radicals. The principal features of the new methods, designated G3-RAD, G3X-RAD, G3(MP2)-RAD, and G3X(MP2)-RAD, are (a) use of B3-LYP geometries and vibrational frequencies (in place of UHF or UMP2), including the scaling of vibrational frequencies so as to reproduce ZPVEs, (b) use of URCCSD(T) as the highest-level correlation procedure [in place of UQCISD(T)], and (c) use of RMP for basis-set-extension corrections (in place of UMP). The RAD modifications not only affect the results for radicals but also affect the calculated heats of formation for closed-shell molecules because these are determined using atomization energies that involve the open-shell atoms.

The RAD procedures have been assessed using the G2/97 test set. The modified procedures all perform better than their standard G3-type counterparts. Of the stan-

dard RAD methods, best overall results are obtained with G3X-RAD, with a mean absolute deviation (MAD) from experimental results of 3.65 kJ mol⁻¹, followed by G3-RAD (MAD=3.96 kJ mol⁻¹), G3X(MP2)-RAD (MAD=4.92 kJ mol⁻¹) and G3(MP2)-RAD (MAD=5.17 kJ mol⁻¹). G3X-RAD performs particularly well for heats of formation, showing an MAD of 3.11 kJ mol⁻¹. G3X(MP2)-RAD is quite cost effective with an MAD for $\Delta_f H_{298}$ of 4.44 kJ mol⁻¹. G3-RAD and G3X-RAD give good results for radical heats of formation, with MADs of 2.59 and 2.50 kJ mol⁻¹, respectively, while the MADs for G3(MP2)-RAD and G3X(MP2)-RAD are 5.10 and 4.67 kJ mol⁻¹, respectively. The G3-RAD(5d) and G3X-RAD(5d) procedures, which use spherical Gaussians (5d,7f) or (5d,7f,9g) in the G3large or G3Xlarge calculations rather than the Cartesian Gaussians (6d,10f) or (6d,10f,15g) that are used in G3-RAD or G3X-RAD, perform less well for the calculation of heats of formation than the latter methods.

ACKNOWLEDGMENTS

The authors gratefully acknowledge generous allocations of computing time on the Compaq Alphaserver of the National Facility of the Australian Partnership for Advanced Computing, Australian National University Supercomputer Facility, and the support of the Australian Research Council.

- ¹For recent reviews, see for example, J. M. L. Martin, in *Computational Thermochemistry*, ACS Symp. Ser., edited by K. K. Irikura and D. J. Frurip (American Chemical Society, Washington, D.C., 1998), Vol. 677; L. A. Curtiss and K. Raghavachari, in *Computational Thermochemistry*, ACS Symp. Ser., edited by K. K. Irikura and D. J. Frurip (American Chemical Society, Washington, D.C., 1998), Vol. 677; G. A. Petersson, in *Computational Thermochemistry*, ACS Symp. Ser., edited by K. K. Irikura and D. J. Frurip (American Chemical Society, Washington, D.C., 1998), Vol. 677; L. A. Curtiss and K. Raghavachari, in *Encyclopedia of Computational Chemistry*, edited by P. v R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, New York, 1998); L. A. Curtiss, P. C. Redfern, and D. J. Frurip, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (Wiley-VCH, New York, 2000), Vol. 15; T. Helgaker, W. Klopper, A. Halkier, K. L. Bak, P. Jørgensen, and J. Olsen, in *Quantum-Mechanical Prediction of Thermochemical Data*, edited by J. Cioslowski (Kluwer Academic, Dordrecht, The Netherlands, 2001); K. Raghavachari and L. A. Curtiss, in *Quantum-Mechanical Prediction of Thermochemical Data*, edited by J. Cioslowski (Kluwer Academic, Dordrecht, The Netherlands, 2001); G. A. Petersson, in *Quantum-Mechanical Prediction of Thermochemical Data*, edited by J. Cioslowski (Kluwer Academic, Dordrecht, The Netherlands, 2001); J. M. L. Martin and S. Parthiban, in *Quantum-Mechanical Prediction of Thermochemical Data*, edited by J. Cioslowski (Kluwer Academic, Dordrecht, The Netherlands, 2001).
- ²D. J. Henry and L. Radom, in *Quantum-Mechanical Prediction of Thermochemical Data*, edited by J. Cioslowski (Kluwer Academic, Dordrecht, The Netherlands, 2001).
- ³L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991); L. A. Curtiss, K. Raghavachari, and J. A. Pople, *ibid.* **98**, 1293 (1993); **103**, 4192 (1995); L. A. Curtiss, P. C. Redfern, B. J. Smith, and L. Radom, *ibid.* **104**, 5148 (1996); B. J. Duke and L. Radom, *ibid.* **109**, 3352 (1998).
- ⁴L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **109**, 7764 (1998).
- ⁵L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **106**, 1063 (1997); L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, *ibid.* **109**, 42 (1998).
- ⁶L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).

- ⁷A. G. Baboul, L. A. Curtiss, P. C. Redfern, and K. Raghavachari, *J. Chem. Phys.* **110**, 7650 (1999).
- ⁸L. A. Curtiss, K. Raghavachari, P. C. Redfern, A. G. Baboul, and J. A. Pople, *Chem. Phys. Lett.* **314**, 101 (1999).
- ⁹L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *J. Chem. Phys.* **112**, 7374 (2000).
- ¹⁰L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, *J. Chem. Phys.* **114**, 108 (2001).
- ¹¹L. A. Curtiss, P. C. Redfern, K. Raghavachari, and J. A. Pople, *Chem. Phys. Lett.* **359**, 390 (2002).
- ¹²L. A. Curtiss and K. Raghavachari, *Theor. Chem. Acc.* **108**, 61 (2002).
- ¹³C. W. Bauschlicher and H. Partridge, *J. Chem. Phys.* **103**, 1788 (1995).
- ¹⁴A. M. Mebel, K. Morokuma, and M. C. Lin, *J. Chem. Phys.* **101**, 3916 (1994).
- ¹⁵A. M. Mebel, K. Morokuma, and M. C. Lin, *J. Chem. Phys.* **103**, 7414 (1995).
- ¹⁶C. J. Parkinson, P. M. Mayer, and L. Radom, *Theor. Chem. Acc.* **102**, 92 (1999).
- ¹⁷D. J. Henry, C. J. Parkinson, and L. Radom, *J. Phys. Chem. A* **106**, 7927 (2002).
- ¹⁸J. F. Stanton, *J. Chem. Phys.* **101**, 371 (1994).
- ¹⁹W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986); F. Jensen, *Introduction to Computational Chemistry* (Wiley, New York, 1999).
- ²⁰M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98 (Gaussian, Inc., Pittsburgh, PA, 1998).
- ²¹J. F. Stanton, J. Gauss, J. D. Watts *et al.*, ACES II, Quantum Theory Project (University of Florida, Gainesville, 1992).
- ²²H.-J. Werner, P. J. Knowles, R. D. Amos *et al.*, MOLPRO 2000.6 (University of Birmingham, Birmingham, 1999).
- ²³A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993); P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).
- ²⁴A. P. Scott and L. Radom, *J. Phys. Chem.* **100**, 16502 (1996).
- ²⁵P. J. Knowles, C. Hampel, and H. J. Werner, *J. Chem. Phys.* **99**, 5219 (1993); **112**, 3106 (2000).
- ²⁶J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
- ²⁷In the standard G3 procedures, energies evaluated with the 6-31G(2df,p), G3large, and G3Xlarge basis sets use (6d,7f), (5d,7f), and (5d,7f,9g) basis functions, respectively.
- ²⁸The ionization energies for BCl₃, CH₂=C=CH₂, C₆H₅CH₃, C₆H₅OH, and C₆H₅NH₂ and the electron affinity of CH₂=C=C: were not included.
- ²⁹D. J. Henry, C. J. Parkinson, P. M. Mayer, and L. Radom, *J. Phys. Chem. A* **105**, 6750 (2001).
- ³⁰G3(MP2)-RAD was used in Ref. 29 without reoptimizing the HLCs.
- ³¹The ionization energy for BCl₃ was not included.
- ³²See EPAPS Document No. E-JCPSA6-118-301311 for BINHEX WORD 2001 text files containing the total energies at the G3-RAD, G3-RAD(5d), G3X-RAD, G3X-RAD(5d), G3(MP2)-RAD and G3X(MP2)-RAD levels of theory for all atoms and molecules used in this study. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from ftp.aip.org in the directory/epaps/. See the EPAPS homepage for more information.
- ³³The mean absolute deviations from experiment for G3-RAD, G3X-RAD, G3(MP2)-RAD, and G3X(MP2)-RAD differ slightly from the values in our recent assessment (Ref. 17). This is due to the use of a slightly different test set, and the use in the previous study of theoretical values for the heats of formation of the Be and Si atoms and more recent experimental values for several species. In the present study, we have used the same experimental heats of formation for atoms and molecules as employed in the original G3 investigations so as to facilitate comparisons.
- ³⁴G. S. Kedziora, J. A. Pople, V. A. Rassolov, M. A. Ratner, P. C. Redfern, and L. A. Curtiss, *J. Chem. Phys.* **110**, 7123 (1999).
- ³⁵J. A. Montgomery, Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.* **112**, 6532 (2000).
- ³⁶Calculated from the heat of formation [$\Delta_f H_0(\cdot\text{CN}) = 438.5 \text{ kJ mol}^{-1}$] and ionization energy [$\text{IE}(\cdot\text{CN}) = 1312.0 \text{ kJ mol}^{-1}$] for the $\cdot\text{CN}$ radical reported by Berkowitz *et al.* (Ref. 37).
- ³⁷J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- ³⁸For example, the difference in total energy (minus HLC) between G3//B3-LYP (UMP energies) on the one hand, and G3-RAD(5d) and G3-RAD (RMP energies) on the other for the C, O, and F atoms lie between 0.4 and 0.5 kJ mol⁻¹. However, the difference between G3//B3-LYP and G3-RAD(5d) for Al, Si, S, and Cl atoms are 1.4, 1.1, 1.9, and 1.5 kJ mol⁻¹, respectively, while for G3-RAD these values become 1.5, 1.2, 2.0, and 1.6 kJ mol⁻¹, respectively.
- ³⁹The differences in the MADs for G3(MP2)-RAD and G3X(MP2)-RAD in the present study is due largely to the improved values obtained with G3X(MP2)-RAD for the heats of formation of $\cdot\text{SO}$ and $\cdot\text{OCl}$ which were not included in the test set used in our previous study.