Benchmark Study of Isotropic Hyperfine Coupling Constants for Hydrogen: Influence of Geometry, Correlation Method, and Basis Set

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Received: December 5, 2002; In Final Form: May 2, 2003

Isotropic hyperfine coupling constants (iHFCCs) can be easily measured by electron spin resonance spectroscopy in solution, but they have proven difficult to calculate from first principles. We test the performance of the newly developed (aug-)cc-pVXZ-t5s basis sets for hydrogen with Dunning's (aug-)cc-pVXZ and -pCVXZ basis sets for non-hydrogen atoms. Correlation is included by CCSD and CCSD(T) using UHF and ROHF references. A two-point extrapolation of cc-pVDZ:cc-pVDZ-t5s-a5 and cc-pVTZ:cc-pVTZ-t5s-a6 hydrogen iHFCCs is found to be very useful. Diffuse functions have nearly no influence on extrapolated iHFCCs. We also explore the dependence of the calculated iHFCCs on the level of theory used in optimizing the geometries. For this purpose, we optimized geometries up to the UHF-CCSD/cc-pCVQZ and UHF-CCSDT/cc-pCVTZ levels and extrapolated to the "complete basis set" limit. The calculated iHFCCs are compared to reference values, which are experimental numbers corrected for solvent and the most important vibrational effects. Our test molecules are the $CH_3^\bullet$, $C_2H_3^\bullet$, and $H_2CN^\bullet$ radicals. At the highest level of theory, the largest deviations from the reference values are smaller than 3.5 G and 6%. The rms errors are below 2.1 G and 4%. The cc-pVXZ:cc-pVXZ-t5s basis set combinations perform better than the EPR-n and the Chipman [631|41] basis set. All of them are better than similarly sized basis sets that were not developed for iHFCCs. The calculated iHFCCs are influenced most strongly by the choice of basis set, the perturbative inclusion of connected triple excitations, and the choice of reference wave function and the level of theory in geometry optimization. Core correlation is necessary for the computation of iHFCCs for non-hydrogen atoms but has very little influence on the iHFCCs of hydrogen atoms. A good compromise between the cost and accuracy of hydrogen iHFCCs seems to be reached by two-point extrapolated ROHF-CCSD(T)-fc iHFCCs at UHF-MBPT(2)-fc/cc-pVTZ geometries. ROHF-MBPT(2)-fc or UHF-CCSD-fc/cc-pVTZ geometries are necessary when single excitations are not negligible.

Introduction

There has been considerable interest[1−4,7−10] in ab initio calculations of magnetic hyperfine interactions in free radicals. The interaction of nuclear and electronic magnetic moments produces hyperfine splitting in the ESR spectrum. The magnitude of the hyperfine splitting is proportional to the hyperfine coupling constant (HFCC). The hyperfine coupling constant can be factored into an isotropic part and an anisotropic part. The isotropic hyperfine coupling constants (iHFCCs) of molecules provide a direct measure of the net spin density at the various nuclei in a molecule, and the anisotropic coupling constants provide a measure of the asymmetry of the spin density. The isotropic HFC constant $A_{iso}(N)$ at a magnetic nucleus N is determined by the Fermi contact interaction and is given in units of the magnetic flux required to obtain resonance by

$$A_{iso}(N) = \frac{8\pi}{3}\left(\frac{g_e}{g_0}\right) g_N \beta_N \rho_S(r_N) \qquad (1)$$

where g_e and g_0 are the g values of the electron in the radical and the free electron, respectively. For most organic free radicals, the ratio (g_e/g_0) may be taken as unity. The nuclear g factor g_N and the nuclear magneton β_N are known constants. The essential quantity to be calculated is therefore $\rho_s(r_N)$, which is the electronic spin density at the location of the nucleus, r_N.

Reviews agree that isotropic hyperfine coupling constants (iHFCCs) are among the properties that are difficult to calculate accurately.[1−4] Both solvent effects and vibrational averaging change the values for the nonvibrating gas-phase molecule by a few percent. In exceptional cases, solvent effects may reach 10%, and the effect of large-amplitude motions may be as large as 37%.[5] Not many gas-phase measurements are available, and the few calculations of vibrational averaging are often limited to large-amplitude motions. Because errors related to the correlation method and basis set cannot easily be distinguished, systematic studies increasing the amount of correlation and the completeness of the basis set are needed. Basis sets for the calculation of iHFCCs require extremely tight s functions and need to be more flexible in the inner valence and core regions than conventional basis sets. Correlation is important, and core correlation is necessary for atoms heavier than helium. At the Hartree−Fock level, iHFCCs are often wrong by 100%. The fact that the spin density arises from the subtraction of two comparably sized α- and β-electron densities may increase problems caused by both overly contracted basis sets and insufficient correlation. More details about the calculation of spin densities and reasons for the basis set requirements for calculating iHFCCs are given in the preceding article.[6]

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10.1021/jp0276348 CCC: $25.00

Several research groups have attempted the calculation of quantitatively accurate HFC constants of organic radicals using a variety of methods and basis sets. Chipman[2] developed a method that is closely related to ROHF-CIS and considers mainly spin polarization effects. With basis sets designed for this method,[7] the deviation of calculated iHFCCs from experiment was usually smaller than 25%. The success of this relatively inexpensive method is due to error cancellation.[1,2] The results can be improved by multireference CI calculations, most commonly MR-CISD. The reference space has to be chosen carefully, and the convergence of iHFCCs with respect to the number of "excited configurations" is slow.[1,4] It is possible to include the effects of (energetically) less important configurations by perturbation theory (MRD-CI/B_K).[1] This procedure drastically improves the results of the underlying MR-CISD calculations and reduces the uncertainties related to the number and selection of "excited configurations". This scheme gives quite accurate results, as do coupled cluster[8-10] methods, if at least single and double excitations are included. A perturbative treatment of triple excitations generally improves the results. B3LYP/EPR-n ($n = 2, 3$) calculations by Barone[3] have been quite successful for organic radicals, but atomic calculations show large errors for EPR-2 (35−65%). B3LYP/EPR-3 has errors of <10% for boron, carbon, and nitrogen, but oxygen and fluorine are still off by ∼30%. This prompts caution for molecules with atoms in "unusual" environments.

Sekino and Bartlett employed finite-field coupled-cluster (CC) methods with double-ζ plus polarization basis sets to calculate moderately accurate hyperfine coupling constants for a range of small radicals.[8] Later, Bartlett et al. developed MBPT- and CC-based methods to evaluate first-order properties analytically.[9] Analytical methods are far more efficient and numerically precise than finite-field methods. The fundamental quantity that evolves from the analytical derivative approach is the relaxed density matrix, which defines all first-order properties, including isotropic and anisotropic hyperfine coupling constants. Perera et al.[9] calculated the iHFCCs of first-row atoms analytically from the coupled-cluster relaxed density with a variety of extended basis sets. The iHFCCs of atoms showed considerable oscillation as the basis set was improved. In CCSD(T) calculations, the Chipman [631|41] basis set performed better than DZP and TZ2P for molecular radicals.[10]

This work will explore the performance of the cc-pVXZ-t5s basis sets[6] for hydrogen with Dunning's cc-basis sets[11] for non-hydrogen atoms in common radicals. To describe the electron density at the hydrogen nucleus, we added five tight s primitives to the parent basis set. Basis sets with one continuous contraction of the tightest s primitives are labeled cc-pVXZ-t5s-cn, with n being the number of s functions. Basis sets with alternating contraction patterns (odd-numbered primitives in one contraction and even-numbered primitives in a second contraction) are named cc-pVXZ-t5s-an, with n being the number of s functions. The higher angular momentum functions remain unchanged. These new basis sets have increased flexibility in the inner valence/cusp region and provide a better description of the electron density close to and at the nucleus. Depending on the degree of contraction, the t5s basis sets' performance is good to excellent for $H^\bullet$, $H_2^{+\bullet}$, and $H_4^{+\bullet}$.[6] The t5s-a(v+3) basis sets (v is the number of s functions in the parent basis set: 2 for cc-pVDZ, 3 for aug-cc-pVDZ and cc-pVTZ, ...) perform as excellently as the uncontracted basis sets, and the t5s-a(v+2) basis sets are very nearly as good. More contracted basis sets such as cc-pVDZ-t5s-c3 and -c2 show larger errors but still remedy the systematic underestimation of isotropic HFCCs exhibited by the parent basis sets.[6]

Although the correlation method, basis set, and geometry are recognized as being important factors (see references cited in ref 1−4), they tend to be investigated separately. We do not know of any systematic study that investigates the dependence of the iHFCCs of organic radicals upon geometry, basis set, and correlation. Here, we do so with an emphasis on the hydrogen iHFCCs. We consider the $CH_3^\bullet$, $C_2H_3^\bullet$, and $H_2CN^\bullet$ radicals. The latter two have β hydrogens where iHFCCs are very difficult to calculate.[2] Experimental iHFCCs corrected for solvent and the most important vibrational effects are available. Such a study can provide us with some insight and an impression of the accuracy that one might expect to reach in the treatment of moderately large organic radicals of chemical interest (e.g., the silacyclobutane radical cation[12]).

We begin our benchmark study by determining highly accurate geometries. We extrapolate to the complete basis set (CBS) limit for several correlation methods in an attempt to approach the full-CI/CBS limit. In the second part, we will calculate isotropic hyperfine coupling constants (iHFCCs) using different correlation-consistent basis sets in a(v+3) contractions, different correlation methods, and reference determinants. We compare to experimental values that have been corrected for solvent and the most important vibrational effects. In the third part, we will explore the geometry dependence of the isotropic hyperfine coupling constants. Finally, we will compare our iHFCCs to results with other contraction patterns and other basis sets.

Radicals

The methyl radical has a planar equilibrium geometry of D_{3h} symmetry. The ground-state electron configuration is $1a'^2 2a'^2 1e^4 1a''$. The $1a''$ SOMO is a p_π orbital localized at the carbon atom. $CH_3^\bullet$ is a π radical. The SOMO has a node in the molecular plane, so direct contributions are zero and the iHFCC arises primarily from spin polarization effects. In the "umbrella" vibrational mode (ν_2, ∼610 cm^{-1})[13] of the radical, the SOMO changes from a pure p orbital to an sp hybrid. The s character of the hybrid orbital then allows for a significant direct contribution of the SOMO to the iHFCC. Because of symmetry, the change in iHFCCs is the same at both turning points of the vibration, and the cancellation of opposite changes is reduced. Easily accessible higher vibrational states enhance this effect. The vibrational effect on the carbon iHFCC is among the largest known. The hyperfine splitting of $CH_3^\bullet$ is well known.[2,5,8,10,14-19]

$H_2CN^\bullet$ was first detected by Adrian and co-workers, who obtained its electron spin resonance spectrum in an argon matrix.[20] Yamamoto and Saito reported the microwave spectrum of $H_2CN^\bullet$ in the $^2B_2$ electronic ground state in the gas phase.[21] The unpaired electron is in a b_2 orbital localized mainly at the nitrogen atom. Such radicals, where the electron density of the SOMO is nonzero in the plane of symmetry (here the plane including the hydrogens), are called σ radicals. Yamamoto and Saito predicted values for the C═N distance and the HCH angle from the corrected rotational constants based on three assumed values for the C−H distance. For C−H distances of 1.08, 1.11, and 1.14 Å, the derived C═N distances and the HCH angles were 1.260 Å/122.3°, 1.247 Å/116.7°, and 1.232 Å/112.2°, respectively. The C═N bond distance was significantly shorter than the normal C═N bond distance of imines. Jacox reported the vibrational and electronic spectra measured in solid argon.[22] Bair et al. reported on the uncertainty in the equilibrium geometry of the $H_2CN^\bullet$ radical.[23] The reported values for the

TABLE 1: Optimized, Approximated, and Extrapolated Bond Lengths (Å) of $CH_3^\bullet$

	DZ	TZ	QZ	CBS3^a
UMBPT(2)-fc/	1.0896	1.0744	1.0731	1.0727
UCCSD-fc/	1.0937	1.0776	1.0764	1.0761
UCCSD(T)-fc/	1.0946	1.0788	1.0777	1.0774
UCCSDT-fc/	1.0949	1.0790	1.0778^b	1.0776
UCCSD(TQ)-fc/	1.0945	1.0784	1.0773^b	1.0770
UCCSD-fc/A	1.0920	1.0781	1.0767	1.0761
UCCSD(T)-fc/A	1.0932	1.0795	1.0780	1.0775
UMBPT(2)/C	1.0880	1.0730	1.0716	1.0712
UCCSD/C	1.0921	1.0762	1.0749	1.0745
UCCSDT/C	1.0933	1.0777	1.0764^c	1.0760
UCCSD(TQ)/C^d	1.0929	1.0770	1.0758	1.0755
RMBPT(2)-fc/	1.0895	1.0746		
RCCSD-fc/^{e}	1.0936	1.0775	1.0763	1.0760
RCCSD(T)-fc/^{e}	1.0946	1.0788	1.0776	1.0773
RMBPT(2)/C	1.0880			
RCCSD(T)/C	1.0931			

[a] Ref 37. [b] Approximation C. [c] Approximation C′ (all geometries optimized including core correlation). [d] Approximation D. [e] Ref 28.

C=N bond length ranged from 1.10 to 1.36 Å. The ab initio results were in a narrower but significant range, 1.23 Å (MBPT4/6-31G**)[24] to 1.268 Å (GVB-CI/[321|31].[23] There have been a number of previous theoretical studies on $H_2CN^\bullet$.[10,15,16,23−27]

The vinyl radical $C_2H_3^\bullet$ is another example of a σ radical. The $^2A'$ ground state is planar with an electron configuration of $1a'^2...6a'^2 1a''^2 7a'$. The 7a′ orbital occupied by the unpaired electron is an in-plane sp hybrid. Not even an approximate experimental structure has been reported for the vinyl radical. The geometry recommended by Peterson and Dunning[28] (CCSD(T)/cc-pVQZ + corrections) is r(C1C2) = 1.3102 Å, r(C1H1) = 1.0773 Å, r(C2H2) = 1.0830 Å, r(C2H3) = 1.0881 Å, a(C2C1H1) = 137.0°, a(H2C2C1)=122.0°, and a(H3C2C1) = 121.3° (H2 is trans to H1). There have been several previous attempts to calculate the iHFC constants of $C_2H_3^\bullet$.[2,8,10,15−18] The iHFCCs of β hydrogens ($H_2CN^\bullet$ and H4 and H5 in $C_2H_3^\bullet$) have been exceptionally difficult to calculate.[2]

Computational Details

All calculations were performed with ACES II[29] using spherical d, f, and g functions. Geometries were optimized at MBPT(2), CCSD, CCSD(T), CCSD(TQ), and CCSDT with the correlation-consistent basis sets of Dunning et al.[11] up to cc-pVQZ. Later on, cc-pVXZ, cc-pCVXZ, and aug-cc-pVXZ will be abbreviated as XZ, CXZ, and AXZ. The frozen-core approximation was used only when core correlation functions were absent. Because there is no ROHF implementation of CCSD(TQ), many calculations use UHF references. The references are indicated by the prefixes R and U. A tighter convergence criterion was used for optimizations (rms force ≤ 10^{-5} au). At that stage, geometry changes were smaller than 5 × 10^{-3} pm or deg and up to 2 orders of magnitude smaller in most cases.

The isotropic hyperfine coupling constants (iHFCCs) are calculated from analytic spin densities at CCSD and CCSD(T). The required constants are taken from ref 30. The regular cc-basis sets were used at carbon and nitrogen with cc-pVXZ-t5s basis sets[6] (see above) at hydrogen. We also used DZP,[31] TZ2P,[32] Chipman's [631|41],[7] IGLOn (n = 2−4),[33] EPR-n (n = 2, 3),[3,34] 6-31G(d,p),[35] and 6-311+G(2df,p)[36] basis sets to calculate iHFCCs.

Complete basis set (CBS) extrapolations were performed with an equation given by Peterson, Woon, and Dunning:[37]

$$A_X = A_\infty + Be^{-(x-1)} + Ce^{-(x-1)^2} \tag{2}$$

Because computational limitations made it impossible to calculate iHFCCs for $C_2H_3^\bullet$ with QZ basis sets, we used a two-parameter version of eq 1 for coupling constants:

$$A_X = A_\infty + Be^{-(x-1)} \tag{3}$$

Later, these extrapolations will be called CBS3 and CBS2. All extrapolations used full numerical accuracy; the tabulated values were rounded afterward. One way to check the accuracy of the extrapolation schemes is to extrapolate both the cc-pVXZ and the aug-cc-pVXZ series to the complete basis set limit. Because for X → ∞ both basis sets become equivalent, the extrapolated CBS values should be identical.[38]

Geometries

Because of the rapidly increasing computational demands, we chose not to optimize some geometries but to approximate them. Table S1 (Supporting Information) contains the differences in geometry parameters optimized with basis sets up to QZ, CQZ, and AQZ and the CBS3 extrapolated values. The difference between QZ and TZ geometry parameters is quite constant. This suggests approximating QZ geometry parameters by adding the difference in QZ and TZ geometry parameters computed at a lower level of theory to the TZ geometry parameter optimized at the current level of theory. We tried three approximations: adding the difference in MBPT(2)-fc/QZ and -TZ geometry parameters (A, see ref 39), adding the

TABLE 2: Optimized, Approximated, and Extrapolated Geometry Parameters (Å and deg) of $H_2CN^\bullet$

	rCN				rCH				aNCH			
	DZ	TZ	QZ	CBS3^a	DZ	TZ	QZ	CBS3^a	DZ	TZ	QZ	CBS3^a
UMBPT(2)-fc/	1.2254	1.2132	1.2102	1.2086	1.1067	1.0926	1.0919	1.0920	121.45	121.24	121.18	121.15
UCCSD-fc/	1.2622	1.2470	1.2429	1.2406	1.1081	1.0928	1.0922	1.0924	121.37	121.17	121.13	121.10
UCCSD(T)-fc/	1.2654	1.2508	1.2468	1.2446	1.1100	1.0951	1.0947	1.0949	121.44	121.23	121.18	121.15
UCCSDT-fc/	1.2683	1.2536	1.2496^b	1.2474	1.1102	1.0951	1.0946^b	1.0947	121.43	121.23	121.18^c	121.15
UCCSD(TQ)-fc/	1.2630	1.2486	1.2447^b	1.2425	1.1087	1.0936	1.0931^b	1.0932	121.33	121.15	121.11^c	121.08
RMBPT(2)-fc/	1.2621	1.2487			1.1051	1.0909			121.06	120.86		
RCCSD(T)-fc/	1.2678	1.2533	1.2493	1.2471	1.1101	1.0951	1.0947	1.0948	121.42	121.21	121.16	121.13
UMBPT(2)/C	1.2236	1.2109			1.1054	1.0916			121.45	121.24		
UCCSD/C	1.2600	1.2436	1.2398	1.2378	1.1066	1.0918	1.0908	1.0907	121.37	121.18	121.13	121.10
UCCSDT/C	1.2662	1.2504	1.2467^d	1.24484	1.1088	1.0942	1.0932^d	1.09312	121.43	121.24	121.18^c	121.15
UCCSD(TQ)/C^e	1.2608	1.2451	1.2416	1.2397	1.1072	1.0926	1.0917	1.0916	121.33	121.17	121.11	121.08
RMBPT(2)/C	1.2601				1.1037				121.06			
RCCSD(T)/C	1.2656				1.1087				121.42			

[a] Ref 37. [b] Approximation C. [c] Approximation B. [d] Approximation C′ (all geometries optimized including core correlation). [e] Approximation D.

TABLE 3: Optimized, Approximated, and Extrapolated Bond Lengths and Bond Angles of $C_2H_3^{\bullet}$[a]

Bond Lengths (Å)

		DZ	TZ	QZ	CBS3[b]		DZ	TZ	QZ	CBS3[b]
UMBPT(2)-fc/	(a)	1.2975	1.2811	1.2778	1.2762	(b)	1.0919	1.0758	1.0747	1.0746
UCCSD-fc/		1.3294	1.3111	1.3073	1.3054		1.0947	1.0776	1.0766	1.0765
UCCSD(T)-fc/		1.3326	1.3146	1.3109[c]	1.3091		1.0962	1.0794	1.0784[c]	1.0783
UCCSDT-fc/		1.3357	1.3177[d]	1.3141[c]	1.3122		1.0964	1.0796[d]	1.0786[c]	1.0785
UCCSD(TQ)-fc/		1.3309	1.3129	1.3092[c]	1.3073		1.0958	1.0786	1.0775[c]	1.0775
MBPT(2)/C		1.2948	1.2782				1.0903	1.0747		
UCCSD/C		1.3266	1.3075	1.3037[e]	1.3018		1.0931	1.0765	1.0755[e]	1.0754
UCCSD(T)/C		1.3298	1.3107[f]	1.3070[e]	1.3051		1.0946	1.0781[f]	1.0771[e]	1.0769
UCCSDT/C		1.3330	1.3138[f]	1.3101[e]	1.3082		1.0949	1.0783[f]	1.0773[e]	1.0772
UCCSD(TQ)/C		1.3281[g]	1.3093[g]	1.3055[g]	1.3037		1.0942[g]	1.0774[g]	1.0764[g]	1.0763
RMBPT(2)-fc/		1.3270	1.3106				1.0927	1.0766		
RCCSD-fc/[h]		1.3301	1.3121	1.3084	1.3065		1.0947	1.0776	1.0766	1.0765
RCCSD(T)-fc/[h]		1.3350	1.3172	1.3136	1.3118		1.0963	1.0795	1.0786	1.0786
RMBPT(2)/C		1.3242					1.0911			
RCCSD(T)/C		1.3325					1.0947			
UMBPT(2)-fc/	(c)	1.1007	1.0867	1.0859	1.0859	(d)	1.0959	1.0818	1.0810	1.0810
UCCSD-fc/		1.1034	1.0883	1.0875	1.0876		1.0983	1.0831	1.0824	1.0824
UCCSD(T)-fc/		1.1052	1.0904	1.0897[c]	1.0897		1.0997	1.0849	1.0841[c]	1.0842
UCCSDT-fc/		1.1054	1.0906[d]	1.0899[c]	1.0899		1.0999	1.0850[d]	1.0843[c]	1.0843
UCCSD(TQ)-fc/		1.1044	1.0889	1.0882[c]	1.0882		1.0991	1.0839	1.0831[c]	1.0831
UMBPT(2)/C		1.0993	1.0856				1.0944	1.0807		
UCCSD/C		1.1019	1.0871	1.0864[e]	1.0864		1.0967	1.0820	1.0813[e]	1.0813
UCCSD(T)/C		1.1037	1.0890[f]	1.0883[e]	1.0883		1.0982	1.0835[f]	1.0828[e]	1.0828
UCCSDT/C		1.1040	1.0892[f]	1.0885[e]	1.0885		1.0984	1.0837[f]	1.0829[e]	1.0829
UCCSD(TQ)/C		1.1028[g]	1.0878[g]	1.0871[g]	1.0871		1.0975[g]	1.0828[g]	1.0820[g]	1.0820
RMBPT(2)-fc/		1.1008	1.0868				1.0960	1.0818		
RCCSD-fc/[h]		1.1034	1.0881	1.0874	1.0875		1.0983	1.0831	1.0823	1.0823
RCCSD(T)-fc/[h]		1.1051	1.0901	1.0894	1.0894		1.0998	1.0850	1.0843	1.0843
RMBPT(2)/C		1.0994					1.0945			
RCCSD(T)/C		1.1038					1.0983			

Bond Angles (deg)

		DZ	TZ	QZ	CBS3[b]		DZ	TZ	QZ	CBS3[b]
UMBPT(2)-fc/	(e)	136.50	137.71	137.91	138.01	(f)	121.12	121.06	120.98	120.93
UCCSD-fc/		135.85	136.94	137.04	137.07		121.34	121.34	121.29	121.25
UCCSD(T)-fc/		135.79	136.93	137.04[e]	137.06		121.32	121.31	121.26[e]	121.22
UCCSDT-fc/		135.72	136.85[d]	136.96[e]	136.99		121.33	121.32[d]	121.27[e]	121.23
UCCSD(TQ)-fc/		136.04	137.20	137.30[e]	137.33		121.33	121.36	121.31[e]	121.27
UMBPT(2)/C		136.61	137.85				121.10	121.06		
UCCSD/C		135.92	137.05	137.15[e]	137.18		121.32	121.34	121.29[e]	121.25
UCCSD(T)/C		135.87	137.00[f]	137.10[e]	137.13		121.31	121.33[f]	121.27[e]	121.24
UCCSDT/C		135.79	136.91[f]	137.01[e]	137.04		121.31	121.33[f]	121.28[e]	121.24
UCCSD(TQ)/C[g]		136.11	137.31	137.42	137.44		121.31	121.36	121.31	121.27
RMBPT(2)-fc/		135.95	137.10				121.04	121.03		
RCCSD-fc/[h]		135.92	136.98	137.07	137.09		121.33	121.34	121.27	121.22
RCCSD(T)-fc/[h]		135.79	136.91	137.02	137.06		121.33	121.34	121.30	121.27
RMBPT(2)/C		136.04					121.02			
RCCSD(T)/C		135.86					121.31			
UMBPT(2)-fc/	(g)	121.99	122.08	122.15	122.20					
UCCSD-fc/		121.87	121.92	121.98	122.02					
UCCSD(T)-fc/		121.90	121.95	122.01[e]	122.04					
UCCSDT-fc/		121.89	121.94[d]	122.00[e]	122.04					
UCCSD(TQ)-fc/		121.88	121.89	121.95[e]	121.98					
UMBPT(2)/C		122.00	122.13							
UCCSD/C		121.88	121.97	122.03[e]	122.07					
UCCSD(T)/C		121.91	122.00[f]	122.06[e]	122.10					
UCCSDT/C		121.90	121.99[f]	122.05[e]	122.09					
UCCSD(TQ)/C[m]		121.89	121.94	122.00	122.04					
RMBPT(2)-fc/		121.71	121.77							
RCCSD-fc/[h]		121.86	121.89	121.99	122.06					
RCCSD(T)-fc/[h]		121.85	121.88	121.98	122.05					
RMBPT(2)/C		121.72								
RCCSD(T)/C		121.89								

[a] (a) C1C2, (b) C1H3, (c) C2H4, (d) C2H5, (e) CCH3, (f) CCH4, (g) CCH5. [b] Ref 37. [c] Approximation C. [d] Approximation b. [e] Approximation B. [f] Approximation b′. [g] Approximation D. [h] Ref 28.

difference in CCSD-fc/QZ and -TZ geometry parameters (B), and adding the difference in CCSD-fc/QZ and -TZ geometry parameters, scaled by the ratio of the TZ-DZ differences in geometry parameters optimized at the current level of theory and CCSD-fc (C). The right side of Table S1 shows how much the CBS3 geometry parameters change because of approximated

TABLE 4: CBS2 and CBS3 Extrapolations of IHFCCs at RCCSD(T)//CCSDT/CBS3 in G and Reference Values

	$CH_3^\bullet$		$H_2CN^\bullet$			$C_2H_3^\bullet$					rmsd[a]	
	C	H	N	C	H	C1	C2	H3	H4	H5	G	%[b]
cc-pCVDZ:cc-pVDZ-t5s-a5	24.3	−27.7	5.4	−28.7	78.6	−7.3	109.7	11.8	60.0	35.5	3.5	15.4
cc-pCVTZ:cc-pVTZ-t5s-a6	24.5	−25.9	8.4	−28.3	78.7	−6.5	109.9	13.6	60.0	36.0	2.9	7.2
cc-pCVQZ:cc-pVQZ-t5s-a7	26.1	−25.3	9.1	−28.3	79.0							
CBS2	24.7	−24.8	10.1	−28.1	78.8	−6.0	110.0	14.6	60.1	36.4	2.8	5.9
CBS3	27.2	−25.0	9.6	−28.3	79.1							
cc-pVDZ:cc-pVDZ-t5s-a5[c]		−27.8			78.6			11.5	59.9	35.5	3.1	13.0
cc-pVTZ:cc-pVTZ-t5s-a6[c]		−26.0			78.9			13.5	60.2	36.0	2.3	6.9
cc-pVQZ:cc-pVQZ-t5s-a7[c]		−25.4			79.1			14.1	60.3	36.4	2.1	5.3
CBS2[c]		−24.9			79.0			14.7	60.3	36.3	2.0	4.0
CBS3[c]		−25.0			79.3			14.4	60.4	36.6	2.0	4.6
reference (see text)	30.0	−24.9	9.6	−28.5	81.5	−7.4	115.2	15.6	63.8	35.4		

[a] rmsd of hydrogen iHFCCs. [b] As a percentage of the reference value. [c] Frozen core.

QZ geometries. We see that approximation B gives the best overall results. Approximation C is slightly superior for bond lengths if all optimizations use the same family of basis sets (all with or all without core-correlation functions). The largest changes in CBS3 geometry parameters are 0.06 pm and 0.07° for approximation B. In the rest of the paper, we will use approximation B and, if basis set families do not change, approximation C for bond lengths.

The geometry changes due to the inclusion of core correlation (e.g., CCSD/CDZ − CCSD-fc/DZ) are somewhat regular and of the magnitude of the QZ−TZ differences. The difference due to core correlation does not change monotonically when the valence basis set is increased (Supporting Information, Table S2). The difference at CBS3 is closer to the difference at DZ than to the difference at TZ. The differences due to core correlation at CBS3 and DZ differ by less than 0.06 pm. Increasing the level of correlation beyond CCSD causes the difference due to core correlation to change by less than 0.03 pm or deg. It therefore appears possible to approximate UCCSD(TQ)/CXZ geometries by adding the difference in UCCSD/CXZ and UCCSD-fc/XZ geometries to UCCSD(TQ)-fc/XZ geometries (approximation D[39]).

The optimized bond lengths of $CH_3^\bullet$ are given in Table 1, together with values extrapolated by the CBS3 equation. $CH_3^\bullet$ does not need much correlation. The largest connected single and double excitations (T1 and T2 amplitudes)[40] are 0.01 and 0.04 at UCCSD/CDZ. Going to UCCSDT/CDZ changes the largest T amplitudes by less than 0.003. Adding correlation beyond CCSD increases the CH bond length by less than 0.15 pm (Supporting Information, Table S3). The inclusion of core-correlation functions reduces the bond length by ∼0.15 pm. The CBS3 values derived from XZ and AXZ optimizations are virtually identical. There is nearly no difference between UHF- and ROHF-based calculations. Our best geometries, UCCSDT/CBS3 and UCCSD(TQ)/CBS3, have CH bond lengths of 1.0760 and 1.0755 Å, respectively. This is in the range predicted by Peterson and Dunning[28] (1.0760 ± 0.0005 Å). Both equilibrium distances are slightly shorter than Herzberg's value for the average distance in the vibrational ground state[41] ($r_0 = 1.079_0$ Å) and much longer than the equilibrium distance determined by Špirko and Bunker[42] ($r_e = 1.0581$ Å).

$H_2CN^\bullet$ is a more difficult molecule. Its equilibrium geometry is very dependent on method/basis set combinations.[23] This is, in our opinion, due to the need for high levels of correlation. At UCCSD/CDZ, the largest T1 and T2 amplitudes are 0.16 and 0.14, respectively. At UCCSDT/CDZ, they are 0.17 and 0.16, respectively, a change of ∼15%. ROHF references significantly reduce the largest T1 amplitude (0.07 at RCCSD/CDZ) but leave the largest T2 amplitude nearly unchanged. The large T2 amplitudes suggest that connected quadruple excitations are desirable to augment the unconnected quadruple excitations (T2*T2, among others[40]) incorporated by the exponential ansatz of the CC wave function. The optimized geometry parameters are given in Table 2. Our best geometries, UCCSDT/CBS3 and UCCSD(TQ)/CBS3 (in parentheses), have $r_{CN} = 1.2448(1.2397)$ Å, $r_{CH} = 1.0931(1.0916)$ Å, and $a_{NCH} = 121.16(121.08)°$. The changes due to larger valence basis sets (Supporting Information, Table S4) are quite regular. The difference between QZ and TZ geometry parameters is $\sim{}^1/_4$ of the TZ−DZ difference for the CN distance and the NCH angle but only ∼5% for the CH distance. Some difference in the basis set trends is seen between MBPT(2) and the CC methods and, to a smaller degree, between frozen-core and core-correlated optimizations. The geometry changes due to different correlation methods (Supporting Information, Table S5) are quite constant for basis sets larger than DZ, but even the changes at DZ and CBS3 usually differ by less than 0.1 pm or deg. The changes in geometry due to core-correlation functions are nearly equal at CCSD and CCSDT. There seems to be a roughly linear trend for TZ, QZ, and CBS3 with the DZ difference out of the trend but similar to that for CBS3.

$C_2H_3^\bullet$, too, is a difficult molecule. The largest T1 and T2 amplitudes are 0.15 and 0.14 at CCSD/CDZ but 0.17 and 0.16 at CCSDT/CDZ, respectively, a change of ∼17%. As in $H_2CN^\bullet$, ROHF references strongly reduce the largest T1 but not the largest T2 amplitudes. The optimized geometry parameters are given in Table 3. The UCCSDT/CBS3 and UCCSD(TQ)/CBS3 (in parentheses) geometries have $r_{CC} = 1.3082(1.3037)$ Å, $r_{CH3} = 1.0772(1.0763)$ Å, $r_{CH4} = 1.0885(1.0871)$ Å, $r_{CH5} = 1.0829(1.0820)$ Å, $a_{CCH3} = 137.04(137.44)°$, $a_{CCH4} = 121.24(121.27)°$, and $a_{CCH5} = 122.09(122.04)°$. The differences in the structure recommended by Peterson and Dunning[28] are largest in r_{CC} (−0.20/−0.65 pm) and a_{CCH3} (0.04/0.44°). The larger differences of the CCSD(TQ)/CBS3 structure suggest that connected quadruple excitations are especially important in the double bond and at the location of the unpaired electron. The changes due to larger valence basis sets (Supporting Information, Table S6) are quite regular. The difference between QZ and TZ geometry parameters is $\sim{}^1/_5$ of the TZ−DZ difference for the CC distance but only 5−10% for the CH distance. The CCH3 bond angle increases by more than 1° when going from DZ to TZ optimizations, but the other bond angles change by less than 0.1°. The difference between bond angles optimized with QZ and TZ basis sets usually is 0.1° or less. Some difference in the basis set trends is seen between MBPT(2) and the CC methods and, to a smaller degree, where core-correlation functions are present. The geometry changes due to different correlation methods (Supporting Information, Table S7) are quite constant for basis sets larger than DZ, but even the changes at DZ and CBS3 usually differ by less than 0.1 pm and 0.1°. The changes in geometry due to core-correlation functions (Table S7) are nearly equal at CCSD and CCSDT.

Isotropic Hyperfine Coupling Constants at the UCCSDT/CBS3 Geometry

Including all effects that influence an experimental measurement is computationally very demanding. The influence of vibrational motion on the iHFCCs can be as large as 37%[5,34] of the static value (large-amplitude motions), although differences are usually much smaller.[2] The solvent effect on iHFCCs is reported to be relatively small, up to 10% in extreme cases.[2] To save computational effort, we will compare to experimental values corrected for solvent and vibrational effects where such corrections are available. These reference values are collected in Table 4. For $CH_3^•$, we use the values of Fessenden[5] (liquid methane, 96 K) and the corrections of Rega et al.[34] (umbrella motion, toluene). For $H_2CN^•$, we combine the gas-phase values of Yamamoto and Saito[21] (173 K) with the scaled vibrational correction of Chipman et al.[25] Other experiments by Kasai and Ericson[43] (Ar matrix, 4 K) and McManus et al.[25] (aqueous solution, ~291 K) result in hydrogen iHFCCs that are 3−4 G (3−5%) larger than the gas-phase values. For $C_2H_3^•$, we combine the values of Fessenden[5] and Fessenden−Schuler[44] (liquid ethene/ethane, 93−95 K) with the corrections of Rega et al.[34] (C═CH in-plane bending, toluene). Other values for the hydrogen iHFCCs were derived by Adrian et al. (Ar matrix, 4 K; ref 48 in ref 44) and Kasai[45] (Ar matrix, 4 K). The result of Kasai is more similar to that of Fessenden−Schuler with differences smaller than 2.6 G and 7%. Given the differing number of uncorrected vibrational modes, the accuracy of the reference values probably decreases from $H_2CN^•$ over $CH_3^•$ to $C_2H_3^•$.

To get an idea of the accuracy that we can achieve, we calculated iHFCCs with RCCSD(T) and the CDZ:DZ-t5s-a5, CTZ:TZ-t5s-a6, and CQZ:QZ-t5s-a7 basis set combinations and used the CBS3 extrapolation. Because the CQZ:QZ-t5s-a7 calculations are very demanding—in fact, too demanding for $C_2H_3^•$—we will also test the CBS2 extrapolation with only DZ and TZ values. A complete comparison of the CBS2 and CBS3 extrapolated hydrogen iHFCCs is possible when using the frozen-core approximation and basis sets without core-correlation functions. Table 4 shows that the iHFCCs generally become more similar to the reference values with larger basis sets. The rms deviation decreases from DZ over TZ to QZ. Both the CBS2 and CBS3 extrapolations give better results than TZ calculations. The extrapolated iHFCCs differ by less than 0.3 G for hydrogen but up to 2.5 G for non-hydrogen atoms. Also, somewhat against expectations, the hydrogen iHFCCs agree better with the reference values if the frozen-core approximation is used. We attribute this difference in behavior to the fact that the hydrogen basis sets were developed for the calculation of iHFCCs but the cc-pCVXZ basis sets were not. A similar conclusion about the cc-pCVXZ basis sets has been reached by Helgaker et al.[46] They calculated NMR coupling constants—in their case, dominated by the Fermi contact term—and found that uncontracting s functions and adding tight s primitives are necessary to achieve good results. But, even using the cc-pCVXZ basis sets, the CBS2 extrapolated non-hydrogen iHFCCs differ by less than 5.2 G and 18% from the reference values. The CBS2 extrapolated hydrogen iHFCCs are much more accurate, with the largest deviations being 3.7 G and 3%.

For a more complete exploration of the dependence of the hydrogen iHFCCs on the details of the calculation, we calculated iHFCCs at the UCCSDT/CBS3 geometry with CCSD(T) and four basis set combinations. We used CDZ:DZ-t5s-a5, ACDZ:ADZ-t5s-a6, CTZ:TZ-t5s-a6, and ACTZ:ATZ-t5s-a7 and applied the CBS2 extrapolation. We also used the frozen-core approximation and basis sets without core-correlation functions as well as UHF and ROHF reference functions. Figure 2 (Supporting Information, Table S8) shows that the presence of core-correlation functions and the choice of reference wave function change the hydrogen iHFCCs in $CH_3^•$ by 0.2 G or less. Perturbative inclusion of connected triple excitations changes the hydrogen iHFCCs by 0.5 to 1.1 G. CBS2 extrapolation improves the iHFCCs from both the XZ and the AXZ calculations. The CBS2−DZ difference is 2.4 to 3.0 G and about half that for CBS2−ADZ. The extrapolated UCCSD(T) and RCCSD(T) values are within 0.2 G of the reference value. The carbon iHFCCs (Table 5) change little with the increasing size of the basis set, but the presence of diffuse functions causes a 2 G difference in the CBS2 extrapolated values. This, as well as the relatively large difference between UHF- and ROHF-based CCSD values, suggests that the core/inner-valence region of the carbon basis sets is not flexible enough.[6,46]

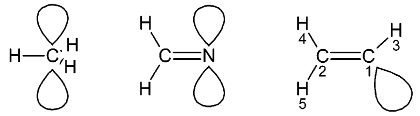

Figure 1. Structures of the radicals.

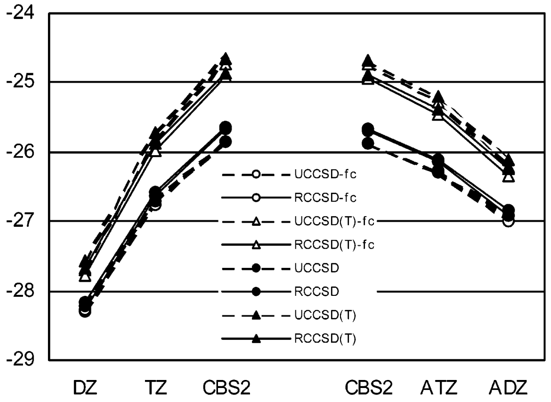

Figure 2. Hydrogen iHFCCs of $CH_3^•$ at the UCCSDT/CBS3 geometry. The reference value is −24.9 G.

The hydrogen iHFCCs of $H_2CN^•$ (Figure 3; Supporting Information, Table S9) change by 0.2 G or less in the presence of core-correlation functions. Using an ROHF reference changes them by just 0.2 G at the CCSD level but by 1.0 to 1.3 G at CCSD(T). The perturbative introduction of connected triple excitations changes the hydrogen iHFCCs by 1.9 to 2.6 G for ROHF references and by about half that value for UHF references. Extrapolating the XZ and AXZ values tends to reduce the iHFCCs slightly (CBS2-(A)(C)DZ = −1.3 to 0.4 G). An extrapolation using DZ and ADZ values will not yield the CBS2 value for a given method. The extrapolated iHFCCs fall between 93% (CCSD) and 97% (RCCSD(T)) of the reference value. The carbon iHFCCs (Table 6) change little with increasing basis set size, but the choice of reference function causes a 2 G difference in the CCSD(T) values, which is not present at the CCSD level. The nitrogen iHFCCs depend strongly on the size of the basis set, but the choice of both reference functions and perturbative triples and the presence of diffuse functions have little influence.

The hydrogen iHFCCs of $C_2H_3^•$ (Figure 4; Supporting Information, Table S10) follow the same general pattern, except

TABLE 5: Carbon Isotropic Hyperfine Coupling Constants of $CH_3^\bullet$ at the CCSDT/CBS3 Geometry[a]

C H	DZ DZ-t5s-a5	TZ TZ-t5s-a6	 CBS2[b](XZ)	ADZ ADZ-t5s-a6	ATZ ATZ-t5s-a7	 CBS2[b](AXZ)
UCCSD/C	25.3	25.9	26.3	24.2	24.3	24.3
RCCSD/C	24.1	24.5	24.8	22.9	22.8	22.8
UCCSD(T)/C	24.5	24.6	24.6	23.4	22.9	22.6
RCCSD(T)/C	24.3	24.5	24.7	23.2	22.9	22.7

[a] The reference value is 30.0 G. [b] Equation 4.

TABLE 6: Isotropic Hyperfine Coupling Constants of $H_2CN^\bullet$ at the CCSDT/CBS3 Geometry[a]

	C, N: H:	DZ DZ-t5s-a5	TZ TZ-t5s-a6	 CBS2[b] (XZ)	ADZ ADZ-t5s-a6	ATZ ATZ-t5s-a7	 CBS2[b](AXZ)
(a)	UCCSD/C	−28.9	−28.5	−28.2	−28.6	−27.9	−27.6
	RCCSD/C	−29.0	−28.7	−28.6	−28.7	−28.3	−28.0
	UCCSD(T)/C	−27.4	−26.6	−26.2	−27.1	−26.2	−25.7
	RCCSD(T)/C	−28.7	−28.3	−28.1	−28.4	−27.9	−27.6
(b)	UCCSD/C	5.6	8.6	10.3	7.6	9.1	9.9
	RCCSD/C	5.3	8.2	9.9	7.1	8.7	9.5
	UCCSD(T)/C	5.1	7.9	9.5	7.1	8.4	9.1
	RCCSD(T)/C	5.4	8.4	10.1	7.4	8.9	9.7

[a] (a) Carbon, (b) nitrogen. The reference values are −28.5 and 9.6 G [b] Equation 4.

TABLE 7: Isotropic Hyperfine Coupling Constants of $C_2H_3^\bullet$ at the CCSDT/CBS3 Geometry[a]

	C: H:	DZ DZ-t5s-a5	TZ TZ-t5s-a6	 CBS2[b] (XZ)	ADZ ADZ-t5s-a6	ATZ ATZ-t5s-a7	 CBS2[b] (AXZ)
(a)	UCCSD/C	−7.2	−6.2	−5.7	−6.8	−4.7	−3.4
	RCCSD/C	−7.7	−6.9	−6.4	−7.3	−6.5	−6.1
	UCCSD(T)/C	−5.7	−4.4	−3.7	−5.3	−2.1	−0.3
	RCCSD(T)/C	−7.3	−6.5	−6.0	−7.0	−6.2	−5.7
(b)	UCCSD/C	111.6	112.3	112.7	108.6	109.0	109.2
	RCCSD/C	111.4	112.1	112.6	108.3	110.4	111.6
	UCCSD(T)/C	108.5	108.1	107.9	105.2	103.7	102.8
	RCCSD(T)/C	109.7	109.9	110.0	106.5	108.1	109.1

[a] (a) C1, (b) C2. The reference values are −7.4 and 115.2 G [b] Equation 4.

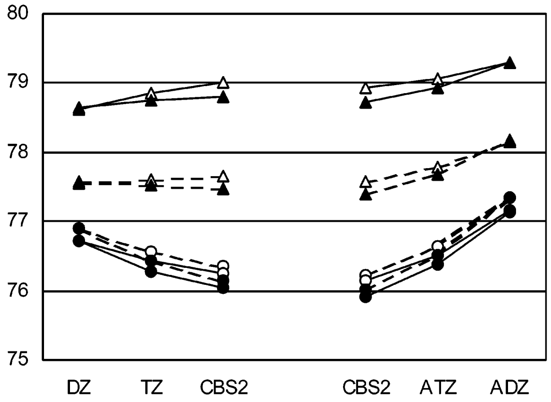

Figure 3. Hydrogen iHFCCs of $H_2CN^\bullet$ at the CCSDT/CBS3 geometry in G. See Figure 2 for the legend. The reference value is 81.5 G.

for those calculated with UHF references and the ACTZ:ATZ-t5s-a7 basis set combination. They will be excluded from further analysis. The iHFCCs calculated by other methods change by less than 0.3 G when core orbitals are frozen. Using an ROHF reference brings changes of up to 0.7 G at CCSD and 1.2 to 1.7 G at CCSD(T). Perturbative inclusion of triple excitations causes differences of up to 2.1 G, independent of the reference function. CBS2 extrapolation increases the iHFCCs at H3 by 2.5 to 3.6 G for the XZ and by about $^2/_3$ that much for the AXZ basis sets. The changes at H4 and H5 are smaller than 1 G. The rms error is 2.3 G at RCCSD(T)/CBS2 and 2.1 G when the frozen-core approximation is applied. At the other levels of theory, the rms error is 2.9 to 3.5 G. When the error is expressed as a percentage of the reference value, both RCCSD(T) methods keep the largest error smaller than 7%. The carbon iHFCCs (Table 7) do not vary too much with the increasing size of the basis set. However, with UCCSD(T), they tend to be smaller—for some basis sets, much smaller—than expected from the RCCSD(T) values. To a smaller degree, this can also be observed in the UCCSD/ACXZ iHFCCs. The problems at UCCSD and UCCSD(T)/ACXZ may be related to those found for hydrogen iHFCCs, but not all of them occur in the same calculations. They appear to be related to the simultaneous presence of large T1 amplitudes in UHF-based calculations and both diffuse and core-correlation functions in the ACXZ basis sets.

Generally, a CBS2 extrapolation of RCCSD(T) hydrogen iHFCCs (with or without the frozen-core approximation) gives the best results. The presence of diffuse functions does not improve the extrapolated values. Core correlation is of little importance for the hydrogen iHFCCs. The choice of reference function makes some difference for $H_2CN^\bullet$ and $C_2H_3^\bullet$ where the T1 amplitudes may be large. Perturbative triple excitations are useful, and perturbative quadruple excitations might further improve the iHFCCs for $H_2CN^\bullet$ and $C_2H_3^\bullet$ where the T2 amplitudes are large. The non-hydrogen iHFCCs are less accurate. Even with CBS2 extrapolation, relative errors may be large. The choice of reference function has more influence than with hydrogen iHFCCs. ROHF-based CCSD and CCSD(T) are better for our three radicals, but that may not be the case in general. Better basis sets are needed for quantitative calculations of non-hydrogen iHFCCs. Those of Barone et al.[3] or Helgaker et al.[46] are promising.

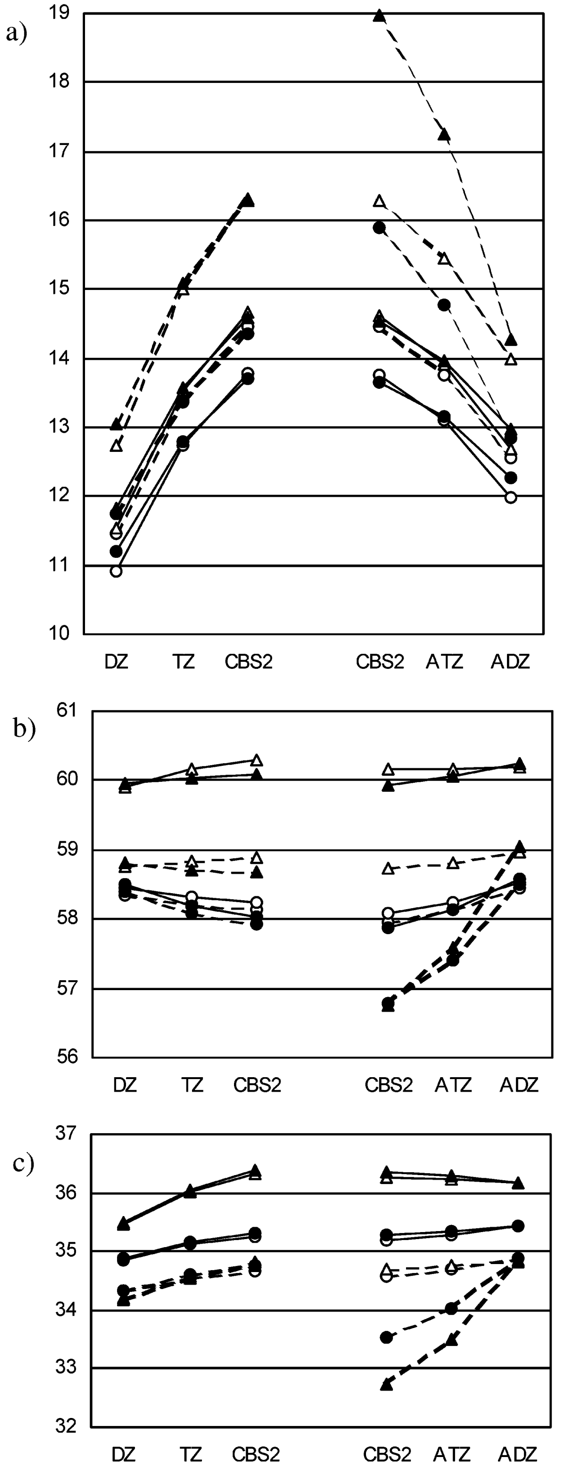

Figure 4. Hydrogen iHFCCs of $C_2H_3^{\bullet}$ at the UCCSDT/CBS3 geometry in G. See Figure 2 for the Legend. (a) H3, (b) H4, and (c) H5. The reference values are 15.6, 63.8, and 35.4 G.

Effects of Hydrogen Basis Set Contraction

To explore the influence of contraction of the t5s basis sets for hydrogen, we calculated iHFCCs for all three radicals at RCCSD(T)-fc//CCSDT/CBS3 with the (A)XZ:(A)XZ-t5s basis sets. The results are given in Table S11 (Supporting Information). Table 8 summarizes the deviations of CBS2 extrapolated hydrogen iHFCCs obtained with contracted basis sets from those calculated with uncontracted basis sets. The t5s-a(v+3) basis sets (see the end of the Introduction) give results that are virtually identical to those of the uncontracted basis sets. The t5s-a(v+2) basis sets are nearly as good, with the largest deviations being smaller than 0.2 G and 0.6%. The continuously contracted basis sets perform a little worse than those with alternating contractions for v+3 and v+2. For v+1, the continuously contracted basis sets are better, but the largest errors rise to 0.9 G and 3.7%.

TABLE 8: Error of CBS2 Extrapolated IHFCCs at RCCSD(T)-fc//CCSDT/CBS3, Caused by Contraction of the Hydrogen Basis Sets

	XZ-t5s-a	AXZ-t5s-a	XZ-t5s-c	AXZ-t5s-c	XZ-t5s-a	AXZ-t5s-a	XZ-t5s-c	AXZ-t5s-c
	rms (error in G)				rms (error in %)			
v+3	0.0	0.0	0.1	0.1	0.0	0.0	0.2	0.1
v+2	0.1	0.1	0.2	0.1	0.3	0.2	0.6	0.3
v+1	0.8	1.3	0.6	0.5	1.6	2.5	2.0	1.1
	|max error in G|				|max error in %|			
v+3	0.0	0.0	0.1	0.1	0.0	0.0	0.4	0.1
v+2	0.2	0.2	0.3	0.2	0.6	0.3	1.1	0.3
v+1	1.7	2.1	0.9	0.9	2.8	3.7	3.7	1.1

Geometry Dependence of Hydrogen Isotropic Hyperfine Coupling Constants

Isotropic HFCCs depend on the geometry at which they are calculated. To get an impression of the accuracy that can be expected for geometries optimized at various levels of theory, we determined iHFCCs at RCCSD(T) with the CDZ:DZ-t5s-a5 and CTZ:TZ-t5s-a6 basis set combinations and CBS2 extrapolation. As can be seen in Figure 5 (Supporting Information, Table S12), improving the basis set used in the optimization generally leads to smaller errors (differences from the reference values) in the iHFCCs. In our opinion, the UHF-based MBPT-(2) geometries of $H_2CN^{\bullet}$ and $C_2H_3^{\bullet}$ do not follow this trend because the method does not include relatively large single-excitation effects. Going from DZ to TZ optimizations reduces the maximum absolute error by ∼30%. Using the CBS3 geometry lowers the absolute error by another 12% of the DZ error. Similar effects are seen for the relative errors (Figure 5b; Supporting Information, Table S13) of CCSD and CCSD(T) optimized geometries. CBS3 extrapolation including core correlation reduces the largest and rms absolute errors, but the largest relative error is lowered only for the CCSDT geometries. Improving the correlation method beyond CCSD makes the hydrogen iHFCCs a little worse.[47] The best compromise between accuracy and cost appears to be UMBPT(2)-fc/TZ where T1 amplitudes are small and RMBPT(2)-fc/TZ or UCCSD-fc/TZ otherwise. At the UCCSD-fc/TZ geometry, the largest errors are 4 G and 7%. All geometries for $CH_3^{\bullet}$ (where correlation effects are small) reproduce the reference iHFCCs to better than 0.2 G and 1%. A comparison of iHFCCs at the CCSD(T)-fc geometries suggests that ROHF-based optimizations are not generally superior to UHF-based optimizations.

A comparison of the hydrogen iHFCCs computed for the Peterson−Dunning (PD) recommended equilibrium structure[28] and the CCSD(TQ)/CBS3 structure of $C_2H_3^{\bullet}$ shows very similar rms absolute errors with the largest errors of 4.0 G for the PD structure and 3.1 G for our structure (Supporting Information, Table S12). However, the relative errors for the PD structure are smaller by $\sim{}^{1}/_{3}$.

Comparison with Other Basis Sets

Figure 6 (Table 9; Supporting Information, Figure S1) shows the error (difference from reference values) in hydrogen iHFCCs computed at the UCCSDT/CBS3 geometry with RCCSD(T)-fc

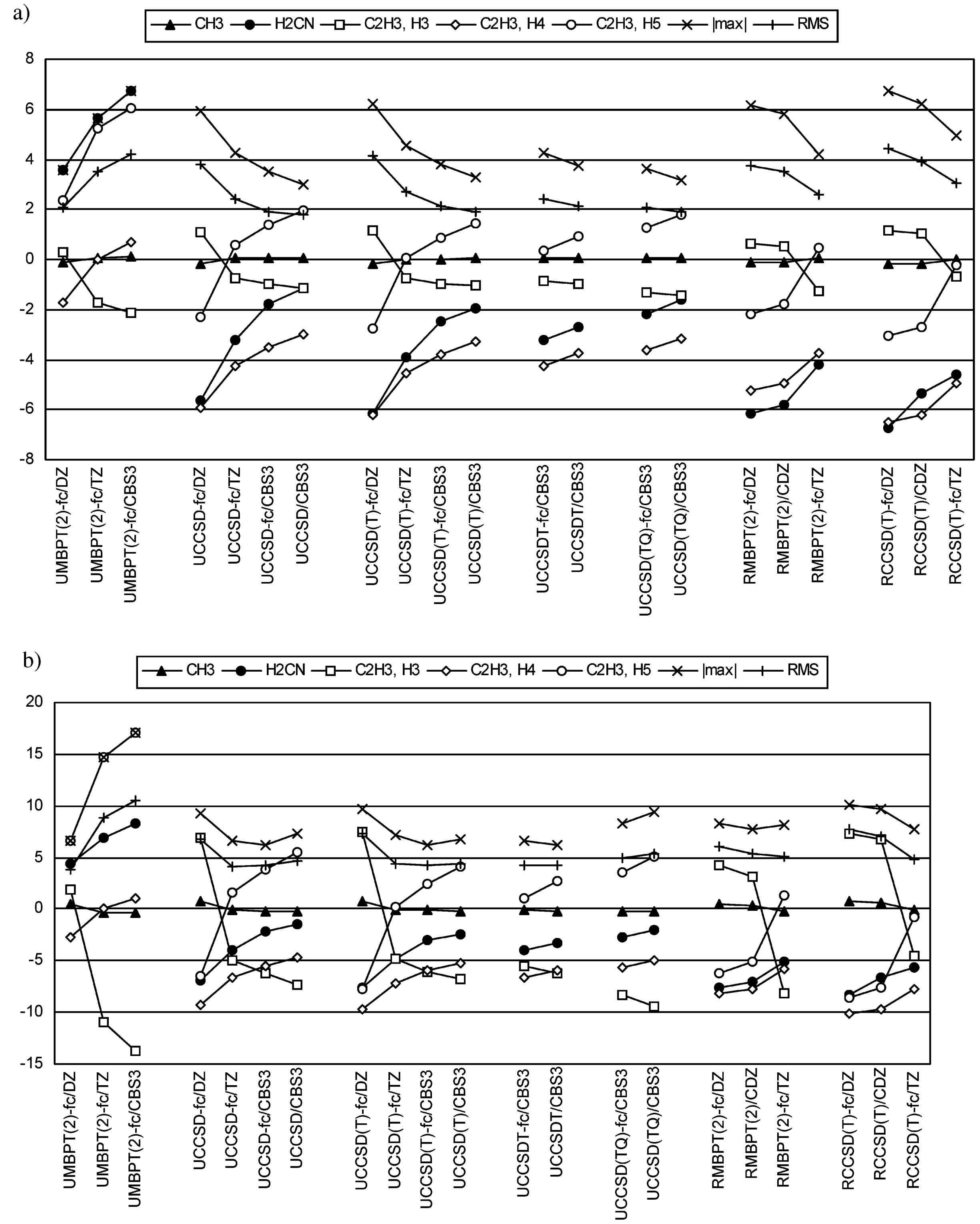

Figure 5. Error in hydrogen iHFCCs at the RCCSD(T)/CBS2 level for different optimized geometries: (a) in G, (b) as a percentage of the reference value.

and various basis sets. The basis sets designed for the calculation of (hydrogen) iHFCCs, XZ:XZ-t5s, EPR-n, and Chipman's [631|41] basis sets give rms absolute errors from 2 to 4 G. The other basis sets have rms errors of 4 to 6 G and will not be discussed further. The largest errors are 4 G for XZ:XZ-t5s, 5 G for EPR-n, and 6 G for Chipman. Generally, enlarging the valence basis set reduces both absolute and relative errors. This leads to a different grouping of these basis sets for relative errors (Figure 6b, Table 10; Supporting Information, Figure S2): DZ: DZ-t5s-a6, EPR-2, and Chipman basis sets show rms errors of ∼12%, and the TZ:TZ-t5s-a6 and EPR-3 basis sets have rms errors of ∼8%. The two-point extrapolation of XZ:XZ-t5s iHFCCs gives the best results, with relative errors of <6% and absolute errors of <4 G. The rms errors are 4% and 2 G.

A closer look at the EPR-n and XZ:XZ-t5s results shows that they lie close to each other, except for $CH_3^•$ and H3 of $C_2H_3^•$. Because each of the XZ-t5s (X = D, T, Q) basis sets gives excellent results for $H^•$, $H_2^{+•}$, and $H_4^{+•}$, the larger spread of

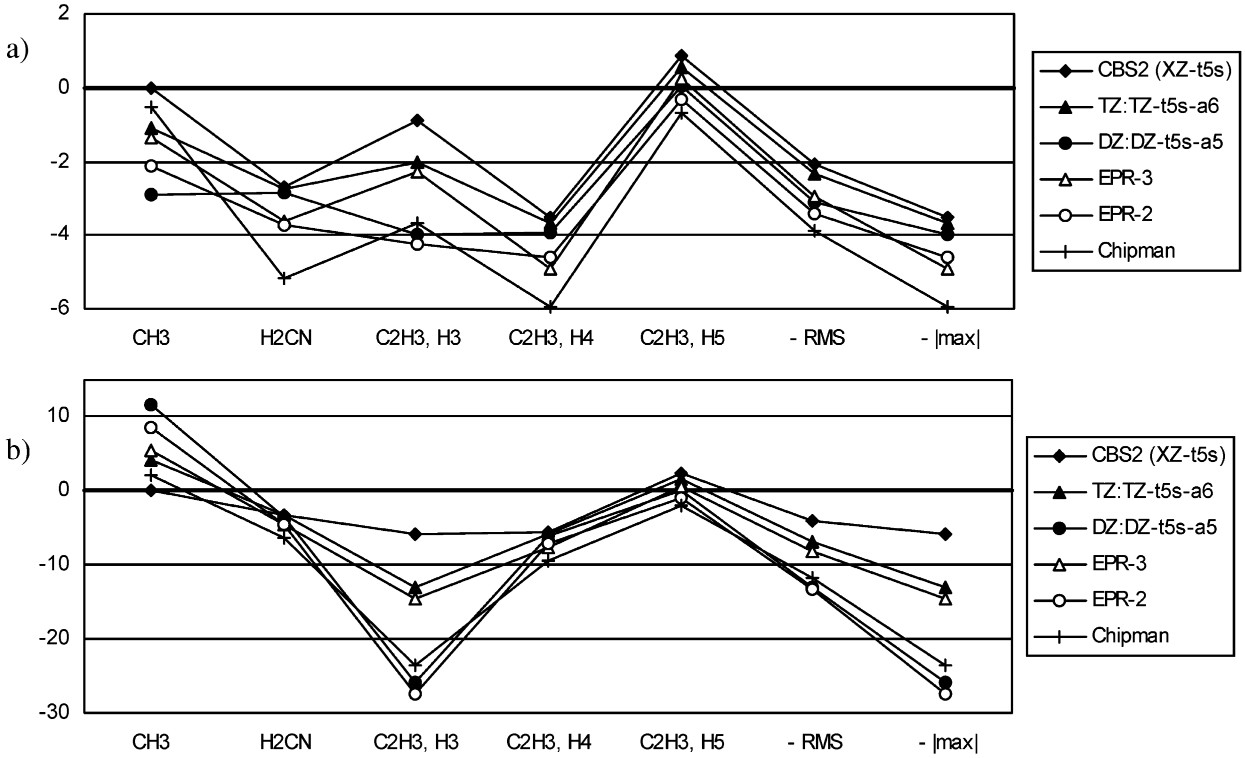

Figure 6. Error in hydrogen iHFCCs at the RCCSD(T)-fc//UCCSDT/CBS3 level for various basis sets: (a) in G, (b) as a percentage of the reference value.

TABLE 9: Influence of Basis Sets[a]

	$CH_3^•$	$H_2CN^•$	$C_2H_3^•$, H3	$C_2H_3^•$, H4	$C_2H_3^•$, H5	rms	|max|
CBS2 (XZ-t5s)[b]	0.0	−2.7	−0.9	−3.5	0.9	2.1	3.5
TZ:TZ-t5s-a6	−1.1	−2.8	−2.0	−3.7	0.6	2.3	3.7
DZ:DZ-t5s-a5	−2.9	−2.9	−4.0	−3.9	0.1	3.1	4.0
EPR-3	−1.4	−3.6	−2.3	−4.9	0.3	3.0	4.9
EPR-2	−2.1	−3.7	−4.3	−4.6	−0.3	3.4	4.6
Chipman	−0.5	−5.1	−3.7	−6.0	−0.7	3.9	6.0
TZ2P	0.5	−5.6	−3.6	−6.4	−1.0	4.2	6.4
DZP	−2.1	−8.6	−5.5	−9.2	−2.1	6.3	9.2
iglo4	0.8	−8.0	−2.6	−8.0	−1.8	5.2	8.0
iglo3	0.9	−5.7	−3.2	−7.6	−1.3	4.5	7.6
iglo2	−2.1	−8.4	−6.4	−8.2	−1.7	6.1	8.4
6-311+G(2df,p)	0.5	−8.0	−2.8	−8.0	−1.6	5.3	8.0
6-31G(d,p)	−5.2	−4.7	−6.5	−6.7	−1.3	5.3	6.7

[a] Deviation (in G) from reference values of the RCCSD(T)-fc//CCSDT/CBS3 isotropic hyperfine coupling constants for hydrogen. [b] Equation 4: Two-point extrapolation of DZ:DZ-t5s-a5 and TZ:TZ-t5s-a6 iHFCCs.

iHFCCs for these atoms might be due to the carbon basis sets that are more contracted and were optimized for the atomic ground state.

Summary and Conclusions

We explored the behavior of hydrogen isotropic hyperfine coupling constants (iHFCCs) with respect to the level of theory used in geometry optimizations and the correlation method and basis set used in iHFCC calculations. For iHFCCs, we combine correlation-consistent basis sets for non-hydrogen atoms with newly developed basis sets for hydrogen (DZ:DZ-t5s-a5 means cc-pVDZ-t5s-a5 for hydrogen and cc-pVDZ otherwise). We compare to experimental values corrected for solvent influence and, where available, vibrational effects. Our test molecules are $CH_3^•$, $H_2CN^•$, and $C_2H_3^•$. Whereas $CH_3^•$ needs little correlation, $H_2CN^•$ and $C_2H_3^•$ have the largest double excitations (T2 amplitudes) of ∼0.15 and need high levels of correlation. The largest single excitations (T1 amplitudes) are slightly larger with UHF references but strongly reduced (∼0.05) with ROHF references.

Tests show that a two-point extrapolation (CBS2) of DZ:DZ-t5s-a5 and TZ:TZ-t5s-a6 values is very useful for hydrogen iHFCCs. With differences of less than 0.5 G and 0.5%, it is nearly as good as a three-point extrapolation (CBS3) including QZ:QZ-t5s-a7 values. The non-hydrogen (especially carbon) iHFCCs calculated including core correlation are less accurate, and the difference between CBS2 and CBS3 extrapolated values is larger. This is probably due to the non-hydrogen basis sets, which were not optimized for the calculation of iHFCCs. A comparison of iHFCCs computed at the UCCSDT/CBS3 geometry shows that both CBS2 extrapolation and perturbative inclusion of connected triple excitations are important. ROHF references are superior for $H_2CN^•$ and $C_2H_3^•$ where they reduce large T1 amplitudes. The frozen-core approximation has little

TABLE 10: Influence of Basis Sets[a]

	$CH_3^•$	$H_2CN^•$	$C_2H_3^•$, H3	$C_2H_3^•$, H4	$C_2H_3^•$, H5	rms	|max|
CBS2 (XZ-t5s)[b]	0.1	−3.3	−5.8	−5.5	2.5	4.0	5.8
TZ:TZ-t5s-a6	4.3	−3.4	−13.1	−5.8	1.6	6.9	13.1
DZ:DZ-t5s-a5	11.6	−3.5	−25.8	−6.2	0.1	13.0	25.8
EPR-3	5.5	−4.4	−14.6	−7.7	0.7	8.0	14.6
EPR-2	8.5	−4.5	−27.4	−7.2	−0.9	13.4	27.4
Chipman	2.2	−6.3	−23.6	−9.3	−2.0	11.8	23.6
TZ2P	−1.8	−6.9	−22.9	−10.1	−2.7	11.7	22.9
DZP	8.3	−10.5	−35.1	−14.4	−5.8	18.2	35.1
iglo4	−3.4	−9.8	−16.6	−12.5	−5.1	10.6	16.6
iglo3	−3.7	−7.0	−20.6	−11.9	−3.8	11.3	20.6
iglo2	8.4	−10.3	−41.0	−12.8	−4.9	20.2	41.0
6-311+G(2df,p)	−1.9	−9.9	−18.0	−12.5	−4.5	11.0	18.0
6-31G(d,p)	21.1	−5.8	−41.9	−10.4	−3.8	21.7	41.9

[a] Relative deviation (in %) from reference values of the RCCSD(T)-fc//CCSDT/CBS3 isotropic hyperfine coupling constants for hydrogen.

[a] Equation 4: Two-point extrapolation of DZ:DZ-t5s-a5 and TZ:TZ-t5s-a6 iHFCCs.

influence on the hydrogen iHFCCs. Overall, the best method considered for the calculation of hydrogen iHFCCs is RCCSD(T)-fc.

The RCCSD(T)/CBS2 iHFCCs for $CH_3^•$ are excellent and nearly independent of the level of theory used in the geometry optimization. For $H_2CN^•$ and $C_2H_3^•$, the iHFCCs depend mainly on the basis set used in the optimization. At DZ geometries, the largest absolute error is 6 to 7 G. TZ geometries reduce the largest error by ∼1.8 G. CBS3(fc) geometries take off ∼0.8 G more, and the inclusion of core correlation lowers the largest error by another ∼0.5 G. The largest relative errors are 8 to 10% at DZ and 6 to 8% at TZ and CBS3(fc) geometries. The largest and rms relative errors tend to increase when core correlation is included in the optimization. This is due to the iHFCCs of H3 and H5 in $C_2H_3^•$. UHF-based MBPT(2) fails for $H_2CN^•$ and $C_2H_3^•$ where single excitations (T1 amplitudes)[40] are too large to be neglected. See the ROHF-MBPT(2) results for the CN radical compared to the much poorer UHF-MBPT(2) values.[48] This matches the recent results of Byrd, Sherrill, and Head-Gordon.[49] However, iHFCCs calculated at UCCSD(T) geometries have slightly smaller errors than those calculated at the corresponding RCCSD(T) geometries. Somewhat surprisingly, the absolute error of hydrogen iHFCCs is lowest at the UCCSD/CBS3 geometry. Perturbative or full inclusion of connected triple excitations either makes the geometries worse or, more likely, reduces the degree of error cancellation in the comparison between computed and reference iHFCCs. The maximum relative error is lowest at the UCCSD-fc and UCCSD(T)-fc/CBS3 geometries.

The best hydrogen iHFCCs at RCCSD(T)-fc//CCSDT/CBS3 were calculated with the XZ:XZ-t5s basis sets. Their largest error is <4 G. The EPR-n basis sets have errors of <5 G, and the Chipman basis set has errors of <6 G. The Chipman, DZ:DZ-t5s-a5, and EPR-2 basis sets have relative errors of <28%. The relative errors are smaller for the TZ:TZ-t5s-a6 and EPR-3 basis sets (<15%). CBS2 extrapolation reduces the relative error to less than 6%. Generally, the flexibility of the basis set is more important for relative errors than for absolute errors. Because all of the XZ-t5s basis sets perform excellently for $H^•$, $H_2^{+•}$, and $H_4^{+•}$, we think that the stronger basis set dependence of the hydrogen iHFCCs of H3 in $C_2H_3^•$ and $CH_3^•$ is caused by the non-hydrogen basis sets. This suggests the possibility of using the sequence DZ:DZ-t5s, TZ:DZ-t5s, QZ:DZ-t5s for extrapolations because DZ-t5s-a5 and -a4 are quadruple-ζ basis sets with respect to the functions in the valence space (primitives present in the cc-pVDZ basis set).

Hydrogen isotropic HFCCs calculated at RCCSD(T)-fc/CBS2 with XZ:XZ-t5s basis sets at good geometries (e.g., CCSD-fc/CBS3 or CCSD(T)-fc/CBS3) differ by less than 3 G and 6% from the reference values. These errors may be due to incompletely accounting for vibrational or solvent effects or neglecting higher excitation levels or the non-hydrogen basis sets. The XZ-t5s basis sets are probably not the reason because they perform excellently for $H^•$, $H_2^{+•}$, and $H_4^{+•}$. As a compromise between accuracy and cost, we recommend RCCSD(T)-fc/CBS2 coupling constants at UHF- or ROHF-based MBPT(2)-fc/TZ geometries, depending on the size of the largest T1 amplitudes. UHF-based CCSD-fc/TZ geometries are better, especially if multiple-bond distances are considered to be important. If iHFCCs at non-hydrogen atoms are desired, then CCSD(T)-fc geometries might be more appropriate. ROHF-based methods may be more appropriate in cases with extremely large T1 amplitudes. At these levels of theory, we found absolute errors <5 G (rms <3 G) and relative errors <8% (rms <5%). Because two of our test molecules require high levels of correlation, we expect the largest and rms errors to be in the upper part of the scale. CBS2 extrapolation is essential to reducing the relative errors. For iHFCCs calculated with just the DZ:DZ-t5s-a5 basis set at TZ geometries, we found maximum errors of up to 5 G and 25%.

Acknowledgment. This work was supported by the U.S. DoD under grant DAAD19-02-1-0176, managed by the U.S. Army Research Office. A.R.A.D. is indebted to the William Fulbright Foreign Scholarship Board (grant no. 24319).

Supporting Information Available: Differences in geometry parameters due to larger valence basis sets, CBS3 extrapolation, diffuse or core-correlation functions, and correlation methods for all molecules. Hydrogen iHFCCs with various methods and basis sets at the CCSDT/CBS3 geometries. Effect of contraction of t5s basis sets on calculated iHFCCs. Absolute and relative deviation of iHFCCs from reference values as a function of geometry. Complete color graphics of absolute and relative deviation of iHFCCs from reference values as a function of basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) Examples for the approximations.

$$\text{a:}\ \ \mathrm{r(CCSDT{-}fc/TZ)} \approx \mathrm{r(CCSDT{-}fc/DZ)} + [\mathrm{r(MBPT(2){-}fc/TZ)} - \mathrm{r(MBPT(2){-}fc/DZ)}]$$

$$\text{b:}\ \ \mathrm{r(CCSDT{-}fc/TZ)} \approx \mathrm{r(CCSDT{-}fc/DZ)} + [\mathrm{r(CCSD{-}fc/TZ)} - \mathrm{r(CCSD{-}fc/DZ)}]$$

$$\text{A:}\ \ \mathrm{r(CCSDT{-}fc/QZ)} \approx \mathrm{r(CCSDT{-}fc/TZ)} + \mathrm{r(MBPT(2){-}fc/QZ)} - \mathrm{r(MBPT(2){-}fc/TZ)}$$

$$\text{B:}\ \ \mathrm{r(CCSDT{-}fc/QZ)} \approx \mathrm{r(CCSDT{-}fc/TZ)} + \mathrm{r(CCSD{-}fc/QZ)} - \mathrm{r(CCSD{-}fc/TZ)}$$

$$\text{C:}\ \ \mathrm{r(CCSDT{-}fc/QZ)} \approx \mathrm{r(CCSDT{-}fc/TZ)} + \frac{\mathrm{r(CCSDT{-}fc/TZ)} - \mathrm{r(CCSDT{-}fc/DZ)}}{\mathrm{r(CCSD{-}fc/TZ)} - \mathrm{r(CCSD{-}fc/DZ)}} * (\mathrm{r(CCSD{-}fc/QZ)} - \mathrm{r(CCSD{-}fc/TZ)})$$

$$\text{D:}\ \ \mathrm{r(CCSDT/CXZ)} \approx \mathrm{r(CCSDT{-}fc/XZ)} + [\mathrm{r(CCSD/CXZ)} - \mathrm{r(CCSD{-}fc/XZ)}]$$

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