

Accuracy of Calculated Chemical Shifts in Carbon 1s Ionization Energies from Single-Reference *ab Initio* Methods and Density Functional Theory

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 Supporting Information

ABSTRACT: A database of 77 adiabatic carbon 1s ionization energies has been prepared, covering linear and cyclic alkanes and alkenes, linear alkynes, and methyl- or fluoro-substituted benzenes. Individual entries are believed to carry uncertainties of less than 30 meV in ionization energies and less than 20 meV for shifts in ionization energies. The database provides an unprecedented opportunity for assessing the accuracy of theoretical schemes for computing inner-shell ionization energies and their corresponding chemical shifts. Chemical shifts in carbon 1s ionization energies have been computed for all molecules in the database using Hartree–Fock, Møller–Plesset (MP) many-body perturbation theory of order 2 and 3 as well as various approximations to full MP4, and the coupled-cluster approximation with single- and double-excitation operators (CCSD) and also including a perturbational estimate of the energy effect of triple-excitation operators (CCSD(T)). Moreover, a wide range of contemporary density functional theory (DFT) methods are also evaluated with respect to computing experimental shifts in C1s ionization energies. Whereas the top *ab initio* methods reproduce the observed shifts almost to within the experimental uncertainty, even the best-performing DFT approaches meet with twice the root-mean-squared error and thrice the maximum error compared to CCSD(T). However, a number of different density energy functionals still afford sufficient accuracy to become tools in the analysis of complex C1s photoelectron spectra.

1. INTRODUCTION

Experimental inner-shell ionization energies and electron structure theory are closely linked.¹ On the one hand, the ability to reproduce experimental energies may provide a stringent test for theoretical methods, for instance in the context of deriving new, improved energy density functionals. On the other hand, as experimentalists target increasingly complex molecules, theoretical ionization energies play an important role in assigning and interpreting photoelectron spectra. Using *m*-xylene as an example, the carbon 1s photoelectron spectrum consists of five closely spaced peaks originating from the five chemically inequivalent carbon atoms. Although it is possible to assign this spectrum unambiguously and hence obtain ionization energies corresponding to each of the unique atoms strictly on the basis of the recorded spectrum, one gains confidence in the results upon discovering that the experimentally derived ionization energy shifts are in good agreement with those predicted by theory.²

A more critical situation that demands reliable theoretical prediction arises with 1-pentyne, which can exist in two different conformers. In this case, the interest lies in determining the relative populations of the conformers. In this molecule, there are five inequivalent carbon atoms, with the possibility that the carbon atoms in one conformer have different ionization energies from those in the other. There are, thus, potentially 10 different peaks in the spectrum. In this case, it has been essential to have good theoretical predictions of relative ionization energies in order to obtain a reliable analysis of the spectrum.³

Many procedures have been proposed for estimating ionization energies and/or shifts in ionization energies: potential models, Koopmans' theorem, the equivalent-cores approximation, transition-state models, and hole-state calculations of various degrees of sophistication.^{4–6} In several previous studies,^{2,7–11} we found that useful results can be obtained with a Δ SCF approach, which involves separate self-consistent field calculations for initial and final states, with the effect from the singly ionized core on the valence electrons simulated by an effective core potential (ECP). The great advantage of this approach is that it is facilitated by the use of most *ab initio* or density functional theory (DFT) methods as implemented in standard electronic-structure codes, for the calculation of shifts in K-shell ionization energies for closed-shell molecules. The main disadvantage of the ECP approach is that it does not explicitly include the ionized and hence singly occupied core orbital. Similar to what is the case for the equivalent-cores approximation, this leads to an almost constant energy offset for the ionized state and precludes the calculation of absolute ionization energies. It does, however, allow for the calculation of chemical shifts, since the unknown energy offset very closely cancels in the subtraction. The errors associated with this simplified description are explored and quantified in this work by comparison to calculations that include an explicit, self-consistent core-hole orbital.

Received: September 20, 2011

Published: November 14, 2011

The Δ SCF/ECP approach implemented in terms of the hybrid density functional theory method B3LYP and polarized triple- ζ basis sets is reasonably economical in regard to computational resources; it can handle large molecules and has been found to give good predictions of relative carbon 1s ionization energies for a wide variety of compounds. Nonetheless, this approach has some specific failures. First, although the method reliably predicts the order of ionization energies for chemically inequivalent carbon atoms, it tends to overestimate the shifts by as much as 20%.^{2,7–10,12} Second, the method works well if we are comparing carbon atoms with the same hybridization but is less reliable if we compare the ionization energies of carbon atoms with different hybridization.

A number of comparative studies have been carried out in order to identify energy density functionals with superior performance in the calculation of ionization energies for a selected class of core states.^{4,13–18} Unfortunately, the comparison between theory and experiment is often complicated by rather small sets of experimental energies or data of either mixed, unknown, or low accuracy.⁶ To improve upon this situation, we have invested considerable effort into measuring carbon 1s ionization energies of small and medium-sized organic molecules as accurately as possible with present day electron spectrometers and third generation synchrotron light sources. The usefulness of this data set was demonstrated by Takahata and co-workers,¹⁹ who used our experimental energies to explore the accuracy of one particular choice of exchange (Perdew–Wang 1986) and correlation (Perdew–Wang 1991) functionals to the calculation of C1s ionization energies. As applied to shifts in 89 adiabatic C1s energies in F- and CH₃-substituted benzenes (relative to benzene), their favored approach gave an average absolute deviation (AAD) from the experimental values of 0.039 eV, which is marginally better than for the B3LYP/ECP approach described above (0.041 eV). The deviation was found to increase somewhat, to an AAD = 0.056 eV, as the chemical diversity was increased.¹⁹ This data set is still heavily biased however with 70% of the entries referring to F- and CH₃-substituted benzenes.

In order to provide a broader and more systematic basis for comparing theoretical methods with experimental results and with each other, we have compiled a database of 77 accurate adiabatic C1s ionization energies for 27 hydrocarbons and fluorohydrocarbons. Included are compounds containing carbon with sp, sp², and sp³ hybridization; aliphatic and aromatic compounds; and compounds with conjugated systems of double bonds. We have measured these experimental values with uniform accuracy at third generation synchrotron facilities. Most of these results have been previously published, but we include also 17 new experimental values, which have been measured using the same procedures that have been previously described. To serve the stated purpose, it is essential to establish the accuracy of the data set, as has been done in the course of the experiments.^{8,9,20} However, estimating the accuracy of an experiment is not easy, and in particular systematic errors may appear unnoticed. Here, the issue of experimental uncertainty is revisited by means of theory, working from the hypothesis that as the theory is systematically improved, the agreement with experimental results should approach the uncertainty of the experimental numbers.

The first part of this work is devoted to comparing experimental shifts in C1s ionization energies with calculated values obtained using a number of wave function-based *ab initio* methods of increasing sophistication, all in the spin-restricted

formalism. These methods include Hartree–Fock theory (HF), Møller–Plesset (MP) many-body perturbation theory of orders 2 and 3 as well as various approximations to full MP4, and coupled-cluster theory with the cluster operator containing single and double excitations (CCSD) and also including a perturbative estimate of the energy contribution from uncoupled triples (CCSD(T)). Apart from Hartree–Fock, these methods have in common that electron correlation is accounted for in terms of determinants that are excited relative to a single reference wave function, namely, the Hartree–Fock state. Formally, the computational cost of HF and B3LYP scales as the fourth power of the number of basis functions N , the corresponding scaling laws for the other methods being N^5 for MP2; N^6 for MP3, MP4D, MP4DQ, MP4SDQ and CCSD; and N^7 for CCSD(T). The methods that scale as the sixth power of N are listed in order of increasing proportionality factor, where the jump between MP3 and MP4SDQ represents a factor of about 3 and the subsequent jump to CCSD is much larger due to the iterative nature of the latter. CCSD(T) and several of the truncated MP4 approaches will be shown to provide highly reliable predictions of C1s shifts (within a few percent), essentially validating the experimental uncertainty estimates. Particular attention is paid to the presence of systematic departure from the general behavior when comparing carbon atoms of different hybridization.

Next, the present compilation of accurate core-level ionization energies will be used as a testing ground for energy density functionals. More specifically, 138 different energy functionals are assessed on their ability to reproduce shifts in C1s energies, covering all main classes of contemporary DFT functionals. An important part of this study is to compare 10 exchange and 10 correlation functionals, respectively, by systematically testing the 100 combination functionals to which they give rise. The comparison of experimental and calculated shifts confirms our previous experience that B3LYP tends to overestimate chemical shifts in C1s ionization energies. There are a number of better alternatives among the DFT functionals, one notable example being the exchange functional proposed by Becke and Roussel (BRx) combined with any of a number of different gradient-corrected correlation functionals.

2. COMPUTATIONAL

The Gaussian 03 set of programs²¹ was used with the B3LYP method to calculate optimized geometries, vibrational frequencies, and zero-point energies for the neutral molecules and the carbon-1s-ionized species. For these calculations, we used atom-centered Gaussian-type functions contracted to triple- ζ quality²² and augmented by polarization functions,²³ leading to C: [5s, 3p, 1d] and H: [3s, 1p]. We refer to this basis set as the TZP basis. For the core-ionized carbon atom, the corresponding nitrogen basis was used with all exponents scaled by a common factor of 0.9293, obtained by minimizing the energy of core-ionized methane.²⁴ The core of the ionized carbon atom was represented by the effective core potential (ECP) of Stevens et al.,²⁵ scaled to account for only one electron in the 1s shell.²⁶ Further details on these procedures can be found in refs 24 and 12. While relativistic effects contribute about 0.05 eV to the C1s ionization energy,²⁷ this converts into less than 0.04% in a chemical shift and is thus not considered further in this work.

With the optimized geometries determined as outlined above, single-point calculations were carried out using the HF, MP2,

Table 1. Experimental Adiabatic C1s Ionization Energies and Experimental and Theoretical (CCSD(T)/TZP) Shifts in C1s Ionization Energies, Relative to That of Methane (All Energies in eV)

molecule	atom	IE	shift		ref
		exptl	exptl	CCSD(T)	
methane	C1	290.689	0.000	0.000	20
ethane	C1	290.545	−0.144	−0.173	20
ethene	C1	290.695	0.006	0.024	20
ethyne	C1	291.128	0.439	0.451	20
propane	C1	290.345	−0.344	−0.332	24
	C2	290.473	−0.216	−0.250	
propene	C1	290.136	−0.553	−0.520	8
	C2	290.612	−0.077	−0.066	
	C3	290.671	−0.018	−0.019	
propyne	C1	290.226	−0.463	−0.443	39
	C2	290.778	0.089	0.117	
	C3	291.610	0.921	0.900	
butane	C1	290.266	−0.423	−0.395	24, 40
	C2	290.312	−0.377	−0.415	
1,3-butadiene	C1	290.060	−0.629	−0.607	8
	C2	290.683	−0.006	0.043	
1-butyne	C1	290.057	−0.632	−0.580	41
	C2	290.554	−0.135	−0.064	
	C3	291.410	0.721	0.702	
	C4	290.673	−0.016	0.003	
2-butyne	C1	291.291	0.602	0.574	41
	C2	290.012	−0.677	−0.671	
1-pentyne	C1	289.979	−0.710	−0.645	3
anti	C3	291.213	0.524	0.518	
1-pentyne	C1	290.017	−0.672	−0.641	3
gauche	C3	291.219	0.530	0.524	
2-pentyne	C1	291.229	0.540	0.541	41
	C2	289.919	−0.770	−0.777	
	C3	289.792	−0.897	−0.825	
	C4	291.120	0.431	0.406	
	C5	290.462	−0.227	−0.221	
1,3-pentadiene	C1	289.762	−0.927	−0.903	8
	C2	290.501	−0.188	−0.142	
	C3	290.247	−0.442	−0.408	
	C4	290.093	−0.596	−0.579	
	C5	290.565	−0.124	−0.114	
trans-3-hexene	C1	290.256	−0.433	−0.421	42
	C2	290.386	−0.303	−0.308	
	C3	289.879	−0.810	−0.745	
3-hexyne	C1	290.442	−0.247	−0.239	41
	C2	291.086	0.397	0.380	
	C3	289.726	−0.963	−0.909	
cyclohexane	C1	290.123	−0.566	−0.557	12
cyclohexene	C1	289.908	−0.781	−0.727	12
	C3	290.321	−0.368	−0.365	
	C4	290.257	−0.432	−0.427	
1,4-cyclo-	C1	290.086	−0.603	−0.559	12
hexadiene	C3	290.556	−0.133	−0.147	
benzene	C1	290.241	−0.448	−0.438	43

Table 1. Continued

molecule	atom	IE	shift		ref
		exptl	exptl	CCSD(T)	
toluene	C1	290.296	−0.393	−0.413	2
	C2	289.970	−0.719	−0.694	
	C3	290.101	−0.588	−0.585	
	C4	290.030	−0.659	−0.661	
	CH ₃	290.493	−0.196	−0.180	
<i>m</i> -xylene	C1	290.134	−0.555	−0.546	2
	C2	289.716	−0.973	−0.922	
	C4	289.779	−0.910	−0.896	
	C5	289.956	−0.733	−0.713	
	CH ₃	290.407	−0.282	−0.258	
<i>p</i> -xylene	C1	290.054	−0.635	−0.623	2
	C2	289.842	−0.847	−0.830	
	CH ₃	290.395	−0.294	−0.268	
fluorobenzene	C1	292.734	2.045	2.071	9
	C2	290.505	−0.184	−0.171	
	C3	290.592	−0.097	−0.068	
	C4	290.375	−0.314	−0.275	
1,3-difluoro- benzene	C1	293.082	2.393	2.449	9
	C2	290.781	0.092	0.107	
	C4	290.624	−0.065	−0.014	
	C5	290.914	0.225	0.293	
1,4-difluoro- benzene	C1	292.867	2.178	2.226	9
	C2	290.838	0.149	0.188	
4-fluorotoluene	C1	290.425	−0.264	−0.255	10
	C2	290.305	−0.384	−0.336	
	C3	290.363	−0.326	−0.326	
	C4	292.485	1.796	1.832	
	CH ₃	290.644	−0.045	−0.009	

MP3, MP4D, MP4DQ, MP4SDQ, CCSD, and CCSD(T)^{28–31} methods as well as an extensive set of density-functional methods as detailed in Figures 4 and 5, all in conjunction with the same basis sets as used during geometry optimization.

In a limited test of basis-set sensitivity in the computed core-level shifts, additional shift calculations were performed for all *ab initio* and DFT methods with the cc-pVTZ basis set³² for both ground and core-ionized states. The core of the ionized carbon atom was represented by the same ECP as in the B3LYP/TZP calculations, with the valence electrons described in the regular cc-pVTZ carbon set augmented by tight CV(2s,2p) functions.³³ Additionally, analogous calculations with the cc-pVDZ sets were carried out for all DFT functionals in the study and used together with cc-pVTZ in an extrapolation procedure toward the complete basis-set limit. For selected functionals, additional tests were performed with the large cc-pVQZ basis. In all cases, the relative ionization energies include zero-point-energy contributions as obtained from the vibrational frequencies calculated at the B3LYP/TZP level of theory.

To explore the accuracy of the ECP description of the ionized core, we compare results at the HF level of accuracy obtained with the ECP approximation and also with an explicit representation of the core hole. These calculations were performed using the DALTON code³⁴ and both TZP and cc-pVTZ basis sets.

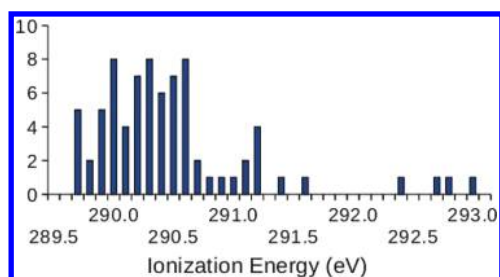


Figure 1. Distribution of experimental C1s ionization energies, in the database, cf. Table 1.

Table 2. Statistical Parameters Derived from Comparison of Experimental and Calculated Carbon 1s Ionization Energies Using *ab Initio* and DFT Methods Combined with the TZP Basis (Uncertainties in the Last Digit Indicated in Parentheses, Energies Given in meV)

method	ME ^b	RMSE ^c	MaxE ^d	slope ^{a,e}	intercept ^{a,e}	RMSD ^{a,f}
HF	−67	115	−309	0.885 (15)	37 (9)	62
MP2	124	140	305	1.040 (15)	−108 (7)	52
MP3	45	62	156	1.022 (11)	−36 (5)	40
MP4D	38	54	108	1.033 (10)	−27 (5)	35
MP4DQ	33	52	140	1.026 (9)	−23 (5)	33
MP4SDQ	8	29	98	1.007 (7)	−2 (3)	24
CCSD	12	33	95	1.015 (8)	−5 (4)	28
CCSD(T)	18	32	72	1.022 (7)	−11 (3)	24
B3LYP	−74	96	−265	0.926 (13)	46 (8)	52
G96B95	−69	95	−262	0.928 (14)	41 (8)	56
BRxP86	0	55	−214	0.928 (11)	−18 (6)	45
BRxKCIS	29	70	217	0.925 (14)	−44 (7)	53
SVWN	47	86	304	0.973 (19)	−56 (10)	72

^a Excluding carbon atoms directly bonded to fluorine. ^b Mean error; theoretical − experimental shift. ^c Root-mean-squared error. ^d Maximum error in any single datum. ^e Best-fit line, experimental vs theoretical shifts. ^f Root-mean-squared deviation between best-fit line and experimental shifts.

3. RESULTS AND DISCUSSION

3.1. The Database. Table 1 provides accurate measurements of 77 adiabatic C1s ionization energies for a wide range of hydrocarbons as well as four fluorine-containing organic molecules, spanning the range from 289.7 eV (in 3-hexyne) to 293.1 eV (in 1,3-difluorobenzene) and with a strong emphasis toward the low end of the interval, cf. Figure 1. The ionization energies are given with uncertainties of 30 meV, of which the larger part is associated with the internal calibration compound used, which in most cases is carbon dioxide. The relative ionization energies, i.e., chemical shifts, are believed^{8,9,20} to carry uncertainties of 10–20 meV, the reality of which is addressed in the present study by comparison with theory.

For cases such as ethyne where vibronic coupling of symmetry-related (localized) hole states leads to significant splitting and delocalization of the core–hole state, Table 1 lists the average of the core ionization energies originating from the indicated atoms. This is done in order to simplify a comparison to computed 1s ionization energies, which usually is conducted within the localized-hole formalism. The emphasis in this work lies on

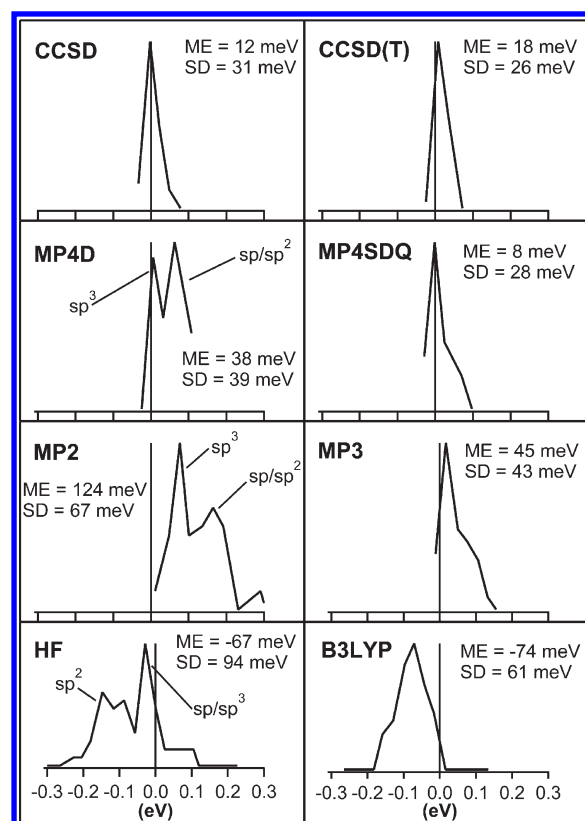


Figure 2. Error distribution in shifts in C1s ionization energies as computed with various electronic structure methods in conjunction with TZP basis sets. The mean error (ME) and standard deviation (SD) are included. Based on $N = 76$ energy shifts relative to methane.

chemical shifts in C1s ionization energies, and Table 1 shows also the shifts relative to methane as measured and as computed at the CCSD(T) level of theory. The corresponding data obtained for a wide range of other theoretical methods are provided as Supporting Information (SI).

3.2. Chemical C1s Shifts from *ab Initio* Methods and B3LYP. We will first compare the following single-reference *ab initio* models, HF, MP2, MP3, MP4D, MP4DQ, MP4SDQ, CCSD, and CCSD(T) with respect to how well they reproduce the experimental chemical shifts as measured by the mean error (ME), root-mean-squared error (RMSE), and the largest error (in magnitude) for any data point (MaxE), cf. top sections of Table 2, and with detailed statistical distributions in Figure 2. We also include B3LYP here, for comparison with previous work as well as a reference when making a wider screening of DFT functionals.

Referring to Table 2, HF and B3LYP give C1s shifts relative to methane that on the average are too low by about 0.07 eV (see also bottom panels of Figure 2). The error for the MP2 method is almost twice as large and of opposite sign, and MP2 comes across as a poor choice for computing chemical shifts in ionization energy. The mean error drops below 0.05 eV at the third order of many-body perturbation theory and is further reduced as fourth-order diagrams are added to the perturbation expansion. At the MP4SDQ, CCSD, and CCSD(T) levels of theory, the mean error is down to 0.01–0.02 eV. A similar development is found in the root-mean-squared error (RMSE), which levels off at 0.03 eV for the best *ab initio* methods. It is noteworthy that the more

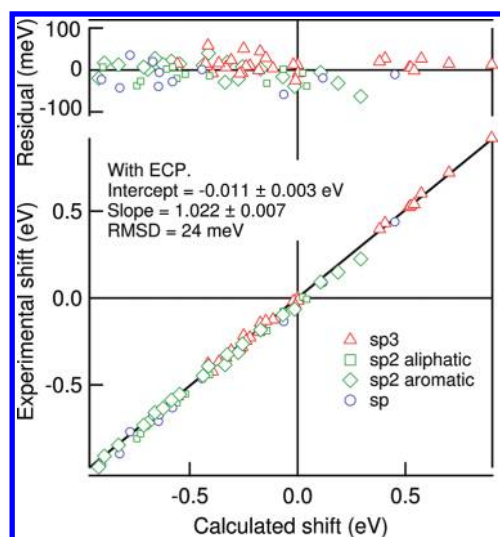


Figure 3. Experimental carbon 1s ionization-energy shifts (relative to methane) versus calculated values based on CCSD(T)/TZP with the core hole simulated by an effective core potential. The solid lines show least-squares fits to the data, and the graph labeled “Residual” shows the deviations of the points from the lines. Based on $N = 72$ data points (fluorocarbons excluded).

time-affordable SDQ approximation to full MP4 performs equally as well as the much more expensive coupled-cluster method CCSD(T).

The importance of triple excitations shows up in one statistical parameter: the largest error in any single shift value, MaxE. This number is 0.07 eV for CCSD(T) and 0.10 eV for CCSD and MP4SDQ and increasing in magnitude to +0.31 and −0.31 eV for MP2 and HF, respectively. Assuming that the errors are normally distributed around the mean, one may compute the standard deviation (SD) as $(\text{RMSE}^2 - \text{ME}^2)^{1/2}$. These values are quoted in Figure 2, to be discussed below. The maximum errors (MaxE) reported in Table 2 are consistent with errors that are normally distributed with the mean and standard deviation as stated, showing that neither the experimental values nor the computed ones contain outliers in the statistical sense.

In order to provide a more complete picture of the errors, we now discuss the error distributions for the different methods in Figure 2 in more detail. For the simpler methods, the error distribution is quite structured and indicates that there are systematic errors associated with subclasses of ionization sites. Closer scrutiny of the error distributions reveals that for HF, the peak near −0.05 eV is strongly dominated by sp^3 -hybridized carbon atoms, whereas errors between −0.1 and −0.2 eV represent sp^2 -hybridized carbon atoms exclusively. The error distribution is bimodal also in the case of MP2 and MP4D, but for these methods the large-error peak includes all sp and the vast majority of the sp^2 carbons, leaving sp^3 -hybridized carbon atoms for the low-error peak. The error distribution of B3LYP is similar to that of HF, albeit with a reduced difference between the two groups described for HF. The error distributions lose structure as the theoretical level is improved, and the distributions may be characterized compactly by the standard deviation (SD) about the mean error.

In Figure 3, we plot the shifts obtained experimentally for the 72 carbon atoms not directly bonded to fluorine, vs shift values calculated at the CCSD(T) level of theory. The four CF carbons,

i.e., carbon atoms directly bonded to fluorine, were omitted in this as well as subsequent analyses in order to avoid an undue bias caused by the four fluorinated carbon atoms at very high ionization energy, cf. Figure 1. The data are shown with symbols indicating the type of hybridization. A least-squares fit of a straight line to the data is indicated by the solid line, and the deviations of the points from the line (residuals) are shown in the upper part of the figure. As can be seen from the regression parameters included in Figure 3 and listed in Table 2, the line passes very close to the origin and has a slope close to 1 (1.022 ± 0.007).

Assuming that the linear fit is able to account for systematic errors in the computed chemical shifts, the remaining deviation represents an upper bound to the mean random error in the experimental shift values. In the case of CCSD(T), the root-mean-squared deviation (RMSD) of the points from the line is 24 meV, which is almost at the level of the expected error in the experimental shift values of 10–20 meV. Results for similar fits for all of the *ab initio* methods considered here are included in the right half of Table 2. CCSD and MP4SDQ group together with CCSD(T) in terms of low residual RMSD, a small intercept, and a slope very close to unity, with MP4D and MP4DQ trailing closely on all accounts, followed by MP3. The RMSD exceeds 0.05 eV for MP2, B3LYP, and HF, and while the intercept is particularly large for MP2, the slope is conspicuously off unity for HF and the hybrid DFT method. The latter statistics show that HF and B3LYP tend to overestimate the chemical shifts for hydrocarbons by about 10%.

3.3. Chemical C1s Shifts from Density Functional Theory.

The computational cost of advanced *ab initio* methods may be too high for routine calculation of chemical shifts for molecules with more than 10 non-hydrogen atoms, and it is clearly desirable to identify cheaper methods that can provide shifts with comparable accuracy. A large number of functionals have been proposed during the past 20 years, covering both hybrid and pure density functionals as well as combination functionals consisting of separate exchange and correlation functionals as well as integrated exchange-correlation functionals. To explore the accuracy in core-level shifts to be expected from different functionals, theoretical estimates of the 76 experimental C1s shifts accounted for above were obtained using a total of 138 different density functionals detailed as 100 combination functionals and an additional 30 hybrid functionals and eight pure functionals.

First, we consider the 100 energy density functionals obtained by combining 10 exchange functionals and 10 correlation functionals in all possible ways. The exchange functionals are denoted S (Slater), B (Becke1988), PW91 (Perdew–Wang1991), G96 (Gill1996), PBE (Perdew–Burke–Ernzerhof), PBEh (hybrid version of PBE), O (OPTX, by Handy–Cohan), BRx (Becke–Roussel1989), PKZB (Perdew–Kurth–Zupan–Blaha), and TPSS (Tao–Perdew–Staroverov–Scuseria), where simplified author lists are included within parentheses to provide a rationale for the acronyms. The acronyms are consistent with those in the Gaussian 09 user manual, which provides full references to the original publication of each functional. The corresponding list of correlation functionals is as follows: VWN (Vosko–Wilk–Nusair), PL (Perdew, local), LYP (Lee–Yang–Parr), P86 (Perdew, 1986), PW91 (Perdew–Wang, 1991), PBE (Perdew–Burke–Ernzerhof), B95 (Becke, 1995), PKZB (Perdew–Kurth–Zupan–Blaha), and KCIS (Krieger–Chen–Iafrate–Savin).

In Figure 4, the root-mean-squared error (RMSE) as computed for the 100 combination functionals is presented in a heat

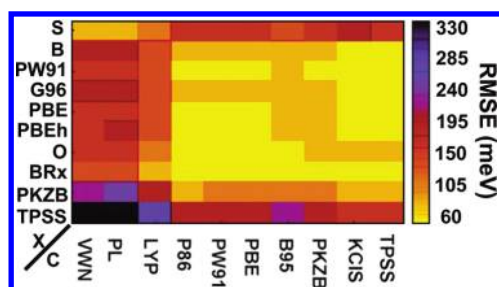


Figure 4. Root-mean-squared error (RMSE) in the C1s chemical shifts relative to methane predicted by selected exchange (X) and correlation (C) functionals and experimental results using the TZP basis. Based on 76 data points.

diagram, with exchange (correlation) functionals labeling rows (columns). It is immediately clear that the local correlation functionals (VWN and PL) lead to inferior results compared to the gradient-corrected ones, even though useful accuracy may be obtained in combination with the simple Slater exchange term, due to error cancellation between the local correlation and exchange functionals. Of the nonlocal correlation functionals, LYP stands out in the negative sense, with PKZB and B95 also performing worse than average. In the case of B95, the error is quite systematic, and a competitive RMSD value is obtained after applying a linear correction as described in the previous section. The difference in RMSE among the remaining functionals is quite small.

Turning to the exchange functionals labeling the rows in Figure 4, surprisingly large errors are found for PKZB and TPSS, irrespective of which correlation functional they are teamed up with. Apart from BRx, the other gradient-corrected exchange functionals group together with quite similar performance. BRx stands out with very small RMSE if combined with a gradient-corrected correlation functional different from LYP. This holds true also for the mean (signed) error, and for the root-mean-squared deviation (RMSD) from a best linear fit to the experimental data. According to Table 2, the lowest RMSE of 55 meV is obtained when BRx is combined with the P86 functional; this is comparable to our results for MP4D but much less accurate than the best *ab initio* methods. The RMSD value is slightly worse than for MP3: 45 vs 40 meV for 72 data points, as is the case for the largest error in any single data point (MaxE), -0.21 eV for BRxP86 and $+0.16$ eV for MP3. This is less accurate than hoped for, and we extended the study by 38 additional functionals of various origins, including the M06 functionals by Truhlar and co-workers (M06, M06HF, M062X, and M06L) and a number of hybrid functionals (B3LYP, B3P86, B3PW91, B1LYP, B1B95, O3LYP, X3LYP, mPW1PW91, mPW1LYP, mPW1PBE, mPW3-PBE, B98, B971, B972, PBE1PBE, BHandH, BHandHLYP, tHCTHhyb, HSEh1PBE, HSE2PBE, PBEh1PBE, ω B97XD, ω B97, ω B97X, TPSSh, LC- ω PBE, and CAM-B3LYP) as well as seven additional pure functionals (VSXC, HCTH, HCTH93, HCTH147, HCTH407, tHCTH, and B97D).

The root-mean-squared errors (RMSE) for the additional functionals are presented in Figure 5 along with data for five of the combination functionals to facilitate a comparison. Seventeen of the 43 functionals included in the figure have very similar RMSE values below 65 meV, i.e., at level with or better than MP3, but none is improving on the BRxP86 functional. The RMSE increases steadily through the next 12 functionals, before leveling out just below 100 meV.

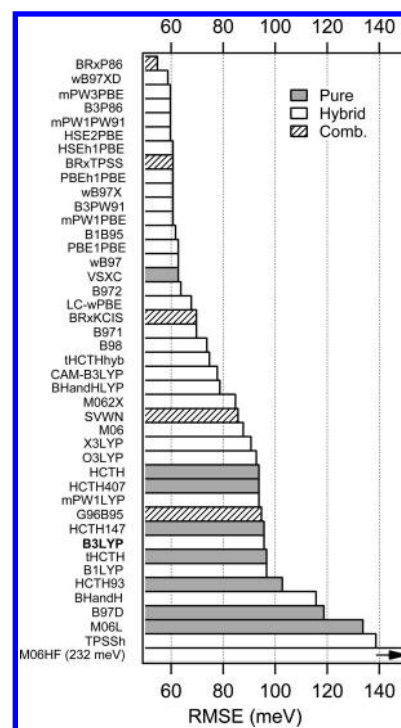


Figure 5. Root-mean-squared error (RMSE) in chemical shifts predicted by pure and hybrid functionals and experimental results using the TZP basis. Five combination functionals are included for comparison. Based on 76 data points.

In general, it is difficult to spot any correlation between performance and how the functionals were constructed, except that PBE and LYP are clearly over- and under-represented, respectively, in the high-performance group of functionals. A small class of functionals shows clearly inferior performance, led by M06L, M06HF, and the hybrid TPSSh functional. B3LYP, which is highlighted in the figure, is performing below average and for instance shows a higher RMSE than the local SVWN functional. Admittedly, the error is more systematic for B3LYP than for SVWN, as evident from the significantly lower RMSD after applying a linear-fit correction, cf. the rightmost column in Table 2.

A recent study by Takahata et al. shows that the PW86x-PW91c functional is able to predict carbon 1s ionization energies with high accuracy,¹⁹ as indicated by an average absolute deviation of 45 meV and a maximum absolute deviation of 130 meV from experimental values. The largest error was actually found for methane (130 meV) and with substantial negative errors for some of the multiply fluorinated benzenes and 1,3-pentadiene. In effect, a fairly large maximum error of 236 meV arises in their computed chemical shift for C1 in 1,3-pentadiene, using methane as the reference compound. For comparison, the corresponding numbers for the BRxP86 functional in conjunction with TZP bases are 36 meV (AAD) and 214 meV (MaxE). In fact, whereas more than 20 of the DFT functionals considered here display average absolute deviations of 45 meV or better, the maximum absolute deviation does not drop below 200 meV. The largest errors in our study were found for 1,3-difluorobenzene, 1,3-pentadiene, and 1-butyne, of which the latter was not included in ref 19.

3.4. Core-Hole Description and Basis Set Effects. It is thus clear that, even the best of the theoretical models is unable to

Table 3. Results of a Linear-Fit Comparison of C1s Shifts Computed at the Hartree–Fock/TZP Level of Theory, Using an Explicit Core–Hole Model and an Effective Core Potential (ECP) Model for the Ionized Core

data set	slope, s^a	intercept, μ (meV) ^a	RMSE (meV)
all	0.999	−16	24
sp ³	1.009	−8	11
sp ²	0.998	−9	14
aliphatic	0.983	−22	15
aromatic	1.004	−4	14
sp	0.984	−59	53

^a core hole shift = $s \times (\text{ECP shift}) + \mu$.

predict the shifts in C1s ionization energy better than to within an RMSE of about 30 meV, which is approaching but still larger than the estimated uncertainty in the experimental results of 10 to 20 meV. It is, therefore, of interest to explore whether the accuracy is limited by the treatment of electron correlation, or possibly by approximations common to the various methods such as the molecular geometries or the use of an effective core potential to describe the ionized core. A partial answer to this question comes from the statistical data already presented. The root-mean-squared error (RMSE) listed in Table 2 is clearly lowest for the high-level methods, MP4SDQ–CCSD(T), largely due to a corresponding reduction in mean error, i.e., a method-dependent uniform shift, as is evident from Figure 2. The standard deviation (SD) about the mean error is seen to be about 30 meV for the high-end methods, with a rapidly increasing SD value as the correlation treatment becomes less complete. However, a standard deviation of 30 meV is still 50% higher than the estimated experimental uncertainty, and the latter is then either too optimistic or there is a source of random error common to the (high-end) computational methods. One possible candidate for such an error is the approximate scheme used to describe the ionized atomic core, to be explored next.

3.4.1. ECP vs Explicit Core Hole. All of the calculations described above used a one-electron effective core potential (ECP) to simulate the effects of the ionized core on the valence electrons. To investigate the possible errors arising from this approximation, all of the chemical shifts in the database were recomputed at the Hartree–Fock level of theory using an explicit and self-consistent core-hole description. These results will now be compared with a similar set of calculations using the ECP, keeping molecular geometries and the basis set the same. A convenient way to analyze these results is by relating the core-hole-based shifts to those obtained with an ECP through a linear regression model, cf. Table 3. Importantly, the two sets of chemical shifts agree closely, as is evident from a slope of 0.9985 and an intercept of −16 meV for the correlation line, meaning that the shift data computed by means of the ECP lie 16 meV higher than those obtained using an explicit core hole. While this average picture applies equally well to sp³ and aromatic sp² carbons, larger errors occur for carbons with triple bonds and to some extent also to aliphatic sp² carbons. For sp-hybridized carbon atoms, the intercept triples to −59 meV and the slope drops to 0.984.

The observation that the ECP model faces limitations in the case of triply bonded carbon atoms is not completely unexpected, as the short C–C distance in the acetylenic moiety should induce stronger orbital relaxation effects in the core orbital of sp carbons

than other carbons. On the other hand, the short C–C distance also implies a stronger tendency to delocalize the core hole over the triply bonded pair of atoms, which is not at all well described at the self-consistent-field level of theory. Hence, an ECP description may still offer the best choice, and the question is whether it is possible to improve upon this model by simple means. One step in this direction is to assume that the change to the C1s shift due to inclusion of an explicit core hole is transferable between electronic-structure methods. If true, this implies that the chemical shift obtained with a given method may be corrected according to

$$\Delta\text{IE}(\text{M, corrected}) = \Delta\text{IE}(\text{M, ECP}) + \Delta\text{IE}(\text{HF, corehole}) - \Delta\text{IE}(\text{HF, ECP}) \quad (1)$$

where “M” refers to any electronic-structure method such as MP2 or CCSD(T). However, if this correction is applied to our CCSD(T)/TZP data, the root-mean-squared error (RMSE) drops only slightly, from 32 to 26 meV. The standard deviation about the mean error remains the same within 1 meV, as is the case also for the root-mean-squared deviation (RMSD) about a best-fit line. Hence, it appears that the use of an effective potential to represent the ionized core induces a very small systematic error in the computed C1s shifts, primarily associated with sp carbons. Correcting by reference to proper hole-state calculations appears relevant only for the most accurate of *ab initio* methods. The possible coupling between the ECP–core-hole correction and choice of basis set is commented upon below.

3.4.2. Basis Set Effects. The default basis set used in the calculations reported thus far is of triple- ζ plus polarization quality and based on the Dunning–Huzinaga set. To explore the impact of the basis set on the quality of the theoretical chemical shifts, the full set of calculations was repeated using the same methods and molecules as previously but now employing the cc-pVTZ basis. This basis set is better than TZP in terms of the polarization space and total number of basis functions, but it is fully contracted in the core orbital space. For this reason, two sets of tight s and p functions were added to the carbon atom undergoing core ionization. We note that the use of this basis set was advocated by Cavagliasso and Chong,¹³ with the slight difference that they apply the addition of compact core functions to all non-hydrogen atoms and also in the initial state. We have confirmed that this difference has negligible impact on the computed relative ionization energies.

The new C1s shifts obtained with the cc-pVTZ basis were compared with the experimental shifts, as reported in Table 4, and the RMSE values of selected methods are compared for the two basis sets. Except for MP2, the introduction of cc-pVTZ leads to poorer agreement with experimental results for all methods. For MP4SDQ and CCSD(T), the RMSE values increase by about 10 meV, while much larger changes are found for most of the DFT methods as well as HF. Quite uniformly for the DFT methods, the mean error is shifted toward lower values by about 50 meV upon changing from TZP to cc-pVTZ. The deviation from a linear best fit to experimental shift values also deteriorates with cc-pVTZ, resulting in RMSD values that typically increase by 20–30 meV. Exceptions to this trend are primarily functionals that represent exchange interaction only through the Slater term; they systematically give too high C1s shifts and hence benefit from the general reduction in shift values observed for cc-pVTZ. Moreover, functionals that include the KCIS correlation functional display less basis-set sensitivity, as illustrated by the representative examples in Table 4.

Table 4. Basis-Set Dependency of the Agreement between Experimental and Theoretical Shifts in Carbon 1s Ionization Energies As Measured by the Root-Mean-Squared Error (RMSE, in meV, based on 77 Data Points)^a

method	basis set					
	TZP	cc-pVTZ	cc-pVDZ	cc-pVQZ	X3(D,T)	X3(T,Q)
HF	115	151				
MP2	140	117				
MP4SDQ	29	39				
CCSD(T)	32	40				
B3LYP	96	149	262	139	105	132
G96B95	95	139	228		108	
BRxP86	55	98	188		74	
BRxKCIS	70	85	177	72	72	66
SVWN	86	91	167		72	

^aIn addition to the TZP and cc-pVnZ ($n = D, T$, and Q) basis sets, the leftmost part of the table reports on energies obtained with a two-point extrapolation method X3(n,m), where n and m are ordinals for cc-pVnZ bases.

The inferior results obtained with the cc-pVTZ basis beg for an explanation. The TZP basis is state adapted in the sense that different orbital exponents are used for the neutral and core-ionized carbon atom.³⁵ In more detail, the basis set used for the core-ionized carbon atom starts from the corresponding nitrogen basis, but with the orbital exponents uniformly scaled by a factor chosen to minimize the energy of core-ionized methane.²⁴ Hence, the TZP basis tends to give a low C1s energy for methane and presumably an energy penalty that increases with departure from a methane-like core. Possibly even more important for TZP outperforming cc-pVTZ is the fact that the scaling factor used for the ionized-carbon basis was optimized in the presence of the effective core potential.

Table 4 also reports on shift data obtained with selected DFT methods in conjunction with the double(D)- and quadruple(Q)- ζ bases cc-pVnZ, where $n = 2, 3$, and 4 corresponds to D, T, and Q, as well as those obtained in a single-parameter extrapolation based on two consecutive members of the correlation-consistent basis sets. The infinite-basis limit is estimated as³⁶ $E_{\infty} = ((1 + n^{-1})^3 E_{n+1} - E_n) / ((1 + n^{-1})^3 - 1)^{-1}$. Employment of the D and T terms in this extrapolation scheme produces shift data that approach the accuracy of those obtained with the TZP basis. For the BRxKCIS functional, extrapolation based on the T and Q data produces chemical C1s shifts that are marginally better than those computed with TZP. Hence, the TZP basis appears to be a very efficient tool for obtaining accurate shift estimates.

3.5. Corrected Shifts. The results discussed above show that if used with TZP bases, MP4DQ, MP4SDQ, CCSD, and CCSD(T) all provide chemical shifts in C1s ionization energies with a root-mean-squared error (RMSE) of about 30 meV or less for a mixed-hybridization set of atoms. Inclusion of a core-hole–ECP correction term does not change this picture. The less costly of the computational methods examined here, Hartree–Fock and density functional theory, lead to RMSEs from 55 meV in the best case (BRxP86) to more than 300 meV in the most unfavorable case, cf. Figure 4. It would be useful to be able to obtain reliable predictions of ionization energies from lower-level calculations. One approach is to remove a large part of the systematic errors in the computed numbers by invoking a linear correction, calibrated toward

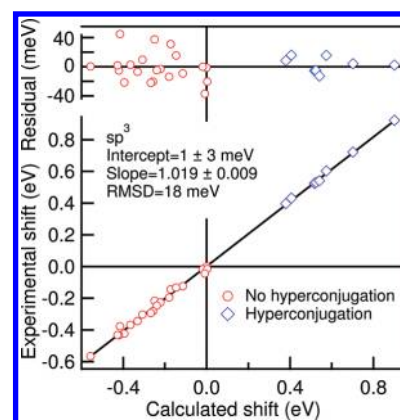


Figure 6. Shifts in carbon 1s ionization energies relative to that of methane for sp^3 -hybridized carbon atoms. Horizontal axis: Calculated using the CCSD(T)/TZP level of theory. Vertical axis: Experimental shifts. The solid line shows a least-squares fit to the data.

experimental shift data. This implies the construction of semi-empirical predictions to experimental shifts, by way of $\Delta I_{\text{exp,pred}} = m \times \Delta I_{\text{theo}} + b$, where regression parameters are exemplified in Table 2 together with root-mean-squared deviation (RMSD) between experimental and corrected-computational shift data. The RMSD from the fit line is down to half of the RMSE for HF, B3LYP, and MP2, with significant improvements also for the other methods. The lowest RMSD value among the DFT methods (41 meV, cf. SI) is obtained for BRx in combination with LYP or either of the two local correlation functionals included in the study (VWN, PL), thus competing well with MP3 but still clearly inferior to the truly high-end *ab initio* methods.

Still higher accuracy is possible at the cost of losing generality if the linear correction is calibrated for subsets of carbon atoms of specific hybridization. In the next section, we consider this approach for CCSD(T), in order to examine the estimated uncertainty in the experimental ionization energies of 10–20 meV.

3.6. A Systematic View on the Basis of Hybridization. That predicting correctly the changes of ionization energies with changes in hybridization represents a challenge to computational models can be seen clearly in the series ethane, ethene, and ethyne, for which the carbon 1s ionization energy increases monotonically. The CCSD(T)/TZP model overestimates this increase by 5% and underestimates it by 3% if the ECP–hole-state correction mentioned in section 2 is included. Previous HF calculations³⁷ show that the predicted shift between ethane and ethene is sensitive to the choice of basis set and that the sign of the shift can be either positive or negative, depending on the basis set. The difference, ethene – ethane, arises from a cancellation of an initial-state effect of 0.32 eV^{5,37} by a comparable relaxation energy in the final state, and the theoretically calculated ionization energy is, therefore, sensitive to the details of the calculation.

The preceding paragraph indicates that even our most accurate computational approach, CCSD(T)/TZP, suffers from systematic errors in computed C1s energy shifts involving carbon atoms of different hybridization. To bypass this problem in order to establish upper bounds to the unsystematic error in the experimental shift values, we explore in some detail the agreement between computed and experimental values for subsets of atoms that share the formal hybridization.

A comparison of experimental and calculated ionization energies for 29 sp^3 hybridized carbon atoms is shown in Figure 6 for

Table 5. Comparison of Experimental Shifts^a in C1s Ionization Energies to Those Computed with CCSD(T) in Combination with TZP and cc-pVTZ Bases, Respectively (Uncertainties in the Last Digit Indicated in Parentheses, Energies Given in meV)

	ME ^b	RMSE ^c	slope	intercept	RMSD ^d
TZP basis					
all hybridizations	18	32	1.022 (7)	−11 (3)	24
sp ³ all (N = 28) ^e	−1	20	1.019 (9)	1 (3)	18
CH ₃ (N = 16) ^e	7	21	1.030 (11)	−6 (4)	16
CH ₂ (N = 12) ^e	−12	19	1.007 (10)	12 (4)	15
sp ² all (N = 33) ^{e,f}	26	33	0.989 (11)	−31 (6)	21
aliphatic (N = 12) ^e	35	38	1.011 (20)	−30 (9)	17
aromatic (N = 21) ^{e,f}	21	30	0.978 (13)	−30 (7)	20
sp all (N = 11) ^e	37	46	1.011 (21)	−32 (13)	29
cc-pVTZ basis					
all hybridizations	4	40	1.021 (11)	0 (6)	40
sp ³ all (N = 28)	−3	16	1.021 (1)	4 (3)	14
sp ² all (N = 33)	−10	35	1.034 (2)	25 (10)	33
sp all (N = 11)	76	81	0.984 (2)	−83 (12)	28

^aME and RMSE are based on 76 shift values, whereas slope, intercept, and RMSD are based on 72 shifts (fluorocarbons excluded). ^bMean error in the theoretical shifts. ^cRMSE between theoretical and experimental shifts. ^dRMSD from fit line. ^eThe number of data points used in the regression. ^fAn additional four data points representing CF carbons were included in ME and RMSE.

the CCSD(T) calculations. The solid line shows a least-squares fit of a straight line to the data, and the parameters of this line are listed in the second line of numbers in Table 5. We see that the slope and intercept are nearly the same as for the overall comparison, but that the root-mean-squared deviation (RMSD) is much smaller. From the residuals, plotted in the upper portion of Figure 6, we see that there is no systematic deviation of the points from the line. The root-mean-squared difference (RMSE) between experiment and theory is 20 meV compared with 32 meV for the overall comparison, and the RMS difference from the trend line is only 18 meV compared with 24 meV for the overall comparison. These differences, 20 and 18 meV, are comparable to the estimated uncertainties in the experimental data, indicating that the CCSD(T) calculations are describing these shifts within the experimental uncertainties. This is a strong indication that, at least for sp³ carbons, the estimated uncertainty in the experimental data, of 10–20 meV, is correct.

The points on the left-hand side of Figure 6 represent sp³-hybridized carbon atoms that are not significantly influenced by hyperconjugation—primarily those in fully saturated alkanes but also carbon atoms in alkenes and alkynes at positions where hyperconjugation does not have an influence. By contrast, those on the right are strongly influenced by hyperconjugation of the type found in propyne, for instance. In propyne, there is significant electron transfer from C3 (the carbon atom with sp³ hybridization) to the C1 carbon via contributions from the mesomeric form HC[−]=C=CH₃⁺. Figure 6 shows that the theoretical calculations provide satisfactory predictions of the effect of hyperconjugation on these ionization energies.

Table 5 also gives regression parameters derived for each hybridization separately and also selected subsets within each hybridization, by comparing the experimental shifts with those

predicted using CCSD(T)/TZP in the same manner as just discussed in detail for sp³. Focusing on sp² carbons, we find that the root-mean-squared error is noticeably greater than that of sp³ carbons, and that this may be traced to a corresponding difference in mean (signed) error. Accordingly, the intercept of the correlation line is significant while the slope remains within a couple of percent from 1. Importantly, the RMSD from the regression line is not much larger than the estimated experimental uncertainties, 21 meV for CCSD(T), and we conclude that an estimated uncertainty of 10–20 meV appears realistic.

For sp hybridization, the errors in the CCSD(T) shifts are somewhat larger than for the other hybridizations. This is evident from an RMSE of 46 meV compared to 33 and 20 meV for the sp² and sp³, respectively. After applying a linear regression model as reported in Table 5, the root-mean-squared deviation from the fit line to experimental shifts is about 30 meV. This number is significantly higher than the estimated uncertainty of 10–20 meV in the experimental energies. From the discussion in section 3.4.1, one realizes that part of this larger error may be ascribed to deficiencies in the effective-potential model (ECP) and possibly also the localized-hole model. Hence, while we are not able to demonstrate that the experimental energies for sp carbons are as accurate as for the other hybridizations, we are not in a position to prove otherwise.

Also included in Table 5 are statistics obtained from computed energies obtained with CCSD(T) in conjunction with cc-pVTZ bases. The RMSE values are similar to those obtained with the TZP basis, except for a much larger mean error and hence larger RMSE for the sp carbons. While this may be corrected for in a linear regression model, the models for the different hybridizations are sufficiently different to give a high overall RMSD of 40 meV for cc-pVTZ, compared to 24 meV for the TZP basis.

4. CONCLUDING REMARKS

A database of 77 adiabatic carbon 1s ionization energies has been prepared, covering linear and cyclic alkanes and alkenes, linear alkynes, and methyl- and fluoro-substituted benzenes. Individual entries are given with uncertainties of less than 30 meV in ionization energies. Comparison to theoretically computed chemical shifts in C1s energies confirms that the uncertainty in the experimental shift values is in the range 10–20 meV, at least for sp³ and sp² carbons. From the perspective of developing and testing new energy density functionals, the database constitutes a potentially useful supplement to existing compilations of accurate experimental data suitable for quantum chemical modeling. For instance, even the GMTKN30 superdatabase,³⁸ which includes data from thermochemistry, molecular structures, reaction kinetics, physical properties, and also proton affinities and valence ionization energies, does not contain core-level ionization energies. While it may be argued that the calculation of core-level energies is a specialized branch of computational chemistry, introduction of the ECP model facilitates the calculation of shifts in K-shell ionization energies on a routine basis.

The comparisons presented here show that the high-end *ab initio* electronic-structure methods MP4SDQ, CCSD, and CCSD(T), when used with scaled, polarized valence triple- ζ bases and an effective potential for the ionized core, are able to predict chemical shifts in carbon 1s ionization energies within a few percent and with an RMSE of about 30 meV. This is for a set

of carbon atoms that include all common hybridizations. There are systematic differences in the ability to reproduce shifts among carbons of sp^3 , sp^2 , and sp hybridizations. The mean and root-mean-squared errors are larger for sp carbons, although some of this discrepancy may be removed if we make a correction for the differences between calculations based on the ECP and those done with an explicit core hole. In general, the use of an effective ionized-core potential provides a very good approximation to the proper hole-state calculation.

Although CCSD(T) stands out as particularly robust and accurate as judged from the smallest worst-error (MaxE), MP4SDQ scales much more favorably in terms of computer time and still has almost as good predictive power with respect to shifts in carbon 1s ionization energies. Hartree–Fock and the hybrid-density-functional method B3LYP significantly overestimate C1s shifts within each single class of carbons that share hybridization as well as across the board, by as much as 15%. Due to the systematic nature of the errors, a linear fit of the computed shifts to the experimental ones provides regression parameters that make it possible to correct the less costly HF, B3LYP, and MP2 calculations to give predictions of shifts that are approaching the experimental uncertainties within each hybridization. For most of the *ab initio* methods, the calculated shifts are in closer agreement with the experimental shifts using the scaled TZP basis set, as compared to the cc-pVTZ basis. This is convenient since the TZP basis is the smaller and less computationally demanding of the two.

After testing 138 contemporary density-functional methods, none is found to compete with the high-end wave-function-based methods with respect to prediction power. The BRx exchange functional in combination with a gradient-corrected correlation functional does represent a cost-efficient alternative if a root-mean-squared error in excess of 50 meV is acceptable, and this is still better than MP3 and similar to MP4DQ. However, the largest error in any single shift datum is consistently found to be significantly larger for the DFT methods, with none getting below 200 meV among the 76 shift values considered here.

■ ASSOCIATED CONTENT

S Supporting Information. Basis sets and molecular geometries for the neutral as well as each core-ionized state are provided as optimized at the B3LYP/TZP level of theory. Electronic and zero-point energies for all neutral and core-ionized states, for all *ab initio* and DFT methods that are considered in the article, using TZP and cc-pVTZ basis sets and, in the case of DFT, also cc-pVDZ and cc-pVQZ (for selected functionals). At the Hartree–Fock level, ionized-state energies are provided on the basis of an explicit core hole as well as an effective-core-potential (ECP) description, while for all other methods, ionized-state energies are obtained with an ECP model. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENT

A.H., L.J.S., and K.J.B. thank the Nordic Research Board (NORDFORSK), the Norwegian High Performance Computing Consortium NOTUR, and the EC Transnational Access to Research Infrastructure Program (TARI) for support.

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