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Thermochemical Properties for Small Halogenated Molecules Calculated by the Infinite Basis Extrapolation Method

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Enthalpies of formation and bond dissociation energies at 298.15 K for molecules containing all four halogen atoms were calculated by CCSD(T) using double- and triple-ζ correlation-consistent basis sets, extrapolated to the complete basis set limit by the infinite basis (IB) method. The small molecules X_2, HX, CH_2X, CH_3X (X = H, F, Cl, Br, I), ClF, BrF, BrCl, IF, ICl, CX (X = H, F, Cl, Br), and CHX (X = H, F, Cl) constituted the benchmark set. The cc-pV(n+d)Z (n = D,T) basis sets were used for chlorine, and two different sequences of conventional basis sets for iodine. The sequence consisting of the smaller SV4P and 6-311G(3df) basis sets for iodine—denoted by (cc)—led to a slightly better performance. The IB extrapolation parameters were obtained by the minimization of the deviation between the zero-point exclusive atomization energies calculated by IB and those calculated by a combined Gaussian/exponential function using a sequence of three cc-pV(n+d)Z basis sets, with n = D, T, Q. All geometry optimizations and vibrational frequency calculations were performed at the MP2/6-311G(d) level of theory. A slight improvement of the calculated bond lengths, vibrational frequencies, and enthalpies of formation for diatomic molecules was achieved by a geometry optimization at levels of theory employing CCSD(T) and complete basis set limits. The calculated thermochemical properties were corrected for spin−orbit effects, and were further improved by the inclusion of core/valence correlation calculated at the CCSD(T)/(cc)-pV(D+d)Z level of theory and scalar relativistic corrections calculated at the MCPF-MVD/(cc)-pV(T+d)Z level. The application of the IB method in a larger set of molecules, including halomethanes $CH_{(4-k)}X_k$ (X = F, Cl; $k = 3, 4$), CH_2XY (X, Y = F, Cl, Br, I), and haloethanes CH_3CH_2X (X = H, F, Cl, Br, I), revealed a systematic failure in molecules containing more than one chlorine atoms, attributed to the inadequacy of the two-point (D,T) extrapolation of correlation energy. The agreement with experimental data was improved by lowering the infinitely extrapolated total energies by the amount $Q(N_{\text{eff}})^{\gamma}$, N_{eff} being the sum of the effective number of electrons for all constituent atoms, defined as the number of valence electrons for H, C, F, Br, I, and the total number of electrons for Cl. The parameters Q and γ were appropriately adjusted by the minimization of the root-mean-square (RMS) deviation from the experimental enthalpies of formation. Thus, by using the parameters $\alpha = 5.02$, $\beta_{\text{CCSD(T)}} = 2.41$, $Q = 9.37 \times 10^{-6}$, and $\gamma = 1.80$, RMS deviations of 5.7 and 6.3 kJ mol^{-1} were obtained for 57 enthalpies of formation and 76 bond dissociation energies, respectively.

Introduction

Enthalpies of formation and bond dissociation energies are among the most useful and widely referenced thermodynamic properties of chemical compounds in the study of gas-phase chemical transformations, such as those occurring in atmospheric and combustion conditions. During the past decades, halogen-containing molecules have attracted a great deal of attention, because of their alarming connection with stratospheric ozone depletion and global warming.[1−4] However, reliable experimental values of the thermodynamic properties for many halogen-containing species are still unavailable, especially for those containing bromine and iodine.[5−9] Fortunately, rapid advances in computer technology combined with the continuous progress made in the development of theoretical model chemistries have enabled the derivation of thermodynamic properties of halogenated molecules by ab initio and density functional theory methods.[10−32] The calculation of thermochemical properties usually constitutes the background for the benchmarking of the model chemistry itself and the starting point of its application in a wider range of compounds and in closely related areas such as the calculation of reaction barriers and the prediction of rate constants. Recent theoretical results using the computationally affordable density functional methods have shown that a single functional capable of uniquely and accurately predicting both enthalpies of formation and bond dissociation energies does not exist.[30] Indeed, the B3P86 functional can accurately predict bond dissociation energies for a variety of compounds,[26,30] while the B3LYP and B3PW91 functionals perform much better in calculations of formation enthalpies.[30,33,34] On the other hand, it has been long established that model chemistries employing post-SCF electron correlation

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methods should treat both one-particle and n-particle problems quite extensively (use of very large basis sets combined with high levels of electron-correlation treatment, respectively), to yield accurate values of thermochemical properties.[28,35−38] Unfortunately, the computational cost of the reliable electron-correlation treatments rises steeply with the size of the molecular system, which limits their application to rather small molecules. Therefore, various efforts have been directed toward a decrease of the cost without sacrificing much of the accuracy, by exploiting the convergence patterns of basis set families.[35−46] Indeed, a number of schemes have been devised which allow the extrapolation to the complete basis set (CBS) limit by a sequence of calculations using less expensive basis sets. Correlation-consistent basis sets have proven to be most appropriate for such a task, owing to their well-defined and systematic convergence properties.[47−50] The combination of correlation-consistent basis sets with coupled cluster theory including single, double, and noniterative triple substitutions, CCSD(T), has proven to be most effective, leading to thermochemical properties possessing errors on the order of only 4 kJ mol^{-1}, for a wide range of molecules containing atoms of the first two rows of the Periodic Table.[36−38,45,46]

In the present work, we have chosen to employ the infinite basis (IB) extrapolation method[43] because of its low computational cost and greater range of applicability. The IB method allows the extrapolation of electronic energies to a complete basis set limit by using only double- and triple-ζ correlation-consistent basis sets. It is based on a separate power-law formulation of the Hartree−Fock $E_{\mathrm{HF}}(n)$ and correlation energy $E_{\mathrm{corr}}(n)$ components of the total correlated electronic energy $E(n)$:

$$E(n) = E_{\mathrm{HF}}(n) + E_{\mathrm{corr}}(n)$$

$$E_{\mathrm{HF}}(n) = E_{\mathrm{HF}}(\infty) + A_{\mathrm{HF}}\, n^{-\alpha}$$

$$E_{\mathrm{corr}}(n) = E_{\mathrm{corr}}(\infty) + A_{\mathrm{corr}}\, n^{-\beta}$$

where n represents the highest angular momentum present in a correlation-consistent basis set (e.g., $n = 2$ and $n = 3$ for double-ζ and triple-ζ, respectively). Index (∞) stands for the infinite basis set limit, A_{HF} and A_{corr} are factors dependent on the molecular system, and the parameters α and β have constant values which depend only on the electron correlation treatment. The parameter α for the Hartree−Fock energy, as well as the parameters β for the MP2, MP4SDTQ, CCSD, and CCSD(T) correlation energies, had been adjusted by using the total electronic energy values for levels of theory employing a sequence of correlation-consistent basis sets (up to cc-pV5Z) in a sample of 29 small molecules and radicals containing atoms of the first two rows of the Periodic Table.[43b] The originally determined values for α and β[43b] were based on calculations using the conventional correlation-consistent cc-pVnZ (n = D,T) basis sets for second-row elements.[48] However, it was realized that these basis sets presented convergence problems for second-row elements, leading to unacceptable errors in properties extrapolated to a complete basis set limit.[37,50] These problems were minimized by several modifications (mostly by adding extra tight d-functions), and thus a new sequence of basis sets was created, cc-pV(n+d)Z (n = D,T,Q,5).[50] The availability of a better convergent sequence of correlation consistent basis sets prompted for a reoptimization of the IB extrapolation parameters. Updated values for these were derived in this work by a fit of the IB-extrapolated zero-point exclusive atomization energies to those obtained by a three-point (D,T,Q or T,Q,5) CBS extrapolation based on a combined Gaussian/exponential function[37,45] for a set of molecules containing H, C, F, Cl, and Br atoms. The performance of the IB extrapolation method in the calculation of thermochemical properties for species containing all four halogen atoms was examined in detail for a benchmark set of small molecules consisting of X_2, HX, CH_2X, CH_3X (X = H, F, Cl, Br, I), ClF, BrF, BrCl, IF, ICl, CX (X = H, F, Cl, Br), CH_2 ($^3B_1$), and CHX ($^1A'$, X = F, Cl), with enthalpies of formation experimentally available.[5−8,51−53] Two different sequences of conventional basis sets for iodine were employed, as well as basis sets augmented with diffuse functions. The dependence of the quality of thermochemical calculations on the level of theory chosen for the geometry optimization of diatomic molecules was also examined. Subsequently, the IB method was applied in a larger set of molecules, including halogenated methanes with more than one halogen atom as well as singly halogenated ethanes, and the calculated properties were compared with experimental values available.[5−8,54−61] All thermochemical properties calculated at 298.15 K were corrected for the first-order spin−orbit coupling in the ^2P state of halogen atoms, the ^3P state of the carbon atom, and the $^2\Pi$ state of methylidynes, as well as for the core/valence correlation and scalar relativistic effects, calculated at the CCSD(T,FU/FC)/(cc)-pV(D+d)Z and MCPF-MVD/(cc)-pV(T+d)Z levels of theory, respectively. Finally, the calculated values were refined by applying a scheme of empirical corrections, to bring them into a closer agreement with experiment.

Computational Details

Most calculations in this work were carried out by the Gaussian94[62] and Gaussian98[63] program suites. Restricted Hartree−Fock (RHF-SCF) and unrestricted Hartree−Fock (UHF-SCF) wave functions were used for the closed and open shell species, respectively. The frozen-core approximation was used in all calculations, except those intended to provide the core/valence corrections. The 3d and 4d electrons of bromine and iodine, respectively, were included in the correlation treatment. The correlation-consistent basis sets for bromine,[49] the updated ones for chlorine,[50] and the 6-311G basis set for iodine[11] were obtained from the Extensible Computational Chemistry Environment Basis Set Database.[64] Since correlation-consistent basis sets for iodine are not available, conventional ones of a corresponding double- and triple-ζ quality were employed. The benchmark calculations were performed using two sequences of basis sets for iodine with different computational requirements. The first sequence contained basis sets with a large number of primitive functions, with contractions of [6s5p3d] and [7s6p4d1f] for the double- and triple-ζ members, respectively,[65] and, correspondingly, [7s6p3d] and [8s7p5d2f] for the diffuse-function augmented variants.[66] The second sequence contained smaller basis sets of a similar ζ-quality to the large ones and the same type of the highest angular momentum function present. It consisted of a double-ζ basis set, SV4P, with a [5s4p3d] contraction,[67] and a triple-ζ basis set, 6-311G(3df), with a [10s9p7d1f] contraction;[11] basis sets using the latter sequence will be collectively denoted as (cc)-pV(n+d)Z (n = D,T). Their augmented variants were constructed by the addition of a set of S and P diffuse functions (with parameters 0.0468 and 0.0286, respectively[11]), and will be denoted as AUG-(cc)-pV(n+d)Z. Pure d- and f-functions were used in all calculations (5D and 7F, respectively). The scalar relativistic corrections were calculated with the MOLCAS program suite, Version 5.2,[68] using single-reference restricted Hartree−Fock wave functions RHF and ROHF, for the closed and open shell species, respectively.

The geometries of all species were optimized, and their vibrational frequencies were calculated at the MP2/6-311G(d) level of theory. Subsequently, single-point energy calculations were performed using Møller−Plesset perturbation theory of second- (MP2)[69] and fourth-order (including single, double, and quadruple substitutions, MP4SDQ, as well as triple substitutions, MP4SDTQ),[70,71] and coupled cluster theory involving single and double substitutions (CCSD),[72,73] and including a quasi-perturbative treatment of triple substitutions, CCSD(T).[74] All calculations for the chlorine-containing species were performed by using both variants of correlation-consistent basis sets, the conventional cc-pVnZ and the improved cc-pV(n+d)Z (n = D,T) ones, to compare their efficiency in the IB extrapolation. However, to avoid confusion, only the results obtained by the improved basis sets will be shown.

The zero-point energies (ZPE) and the thermal corrections to the enthalpy at 298.15 K were calculated by using the harmonic oscillator and rigid rotor approximations, after scaling down all vibrational frequencies by 0.9872.[30] The ZPE and thermal corrections were added to the absolute electronic energies in order to obtain the corresponding total enthalpies at 298.15 K. The molecular enthalpy of formation was computed by using the calculated enthalpy difference of the reverse atomization reaction and the enthalpies of formation of the constituent atoms,[7,8] while the bond dissociation energies were computed from the corresponding total enthalpies calculated for the three participants in a bond fission process.

Results and Discussion

Optimization of the IB Extrapolation Parameters. A variety of approaches were employed for the optimization of the IB extrapolation parameters α and β. These approaches can be primarily divided into two broad types, depending on the property selected: (I) absolute electronic energies, or (II) zero-point exclusive atomization energies. Thus, in each type, the goal was the minimization of the overall RMS deviation (by varying α, β) between the values of the property calculated by the IB method (henceforth denoted as IB[DT]) from those calculated by a three-point CBS extrapolation. The latter was based on a combined Gaussian/exponential function:

$$E(\mathrm{CBS}) = E(n) - b\mathrm{e}^{-(n-1)} - c\mathrm{e}^{-(n-1)^2}$$

This function has been shown to be slightly superior to other forms of three-point CBS extrapolation.[37,45] Therefore, single point energies for the H, C, F, Cl, and Br atoms and all molecules of the benchmark set (excluding iodine-containing ones) were calculated at the CCSD(T)/cc-pV(n+d)Z (n = D,T,Q) levels of theory and were extrapolated to the infinite basis limit, which will be henceforth denoted as CBS[DTQ]. Although a CBS limit based on the cc-pV(n+d)Z (n = T,Q,5) sequence, CBS[TQ5], would be more accurate, the enormous computational requirements of CCSD(T)/cc-pV(5+d)Z limited the calculations to a small subset of the benchmark molecules consisting of H_2, HF, HCl, HBr, F_2, Cl_2, CH, CF, CCl, CBr, CH_2, CHF, CHCl, ClF, CH_3, and CH_4. The absolute differences between the CCSD(T)/CBS[DTQ] and CCSD(T)/CBS[TQ5] electronic energies were almost lower than 1 mH for species containing only H, C, and F atoms, rising to ca. 4 mH for species containing Cl atoms (3.6 mH for Cl_2), and reaching a maximum for the bromine-containing ones (91, 91, and 90 mH for Br, HBr, and CBr, respectively). However, the corresponding differences in the atomization energies were much lower (due to the systematic nature of the above deviations), being ca. 0.6 mH for HBr and CBr, and lower for all other molecules. The results suggested that the CCSD(T)/CBS[DTQ] level of theory would be taken as a sufficiently accurate point of reference for the optimization of the IB extrapolation parameters α and β.

However, it has been pointed out that there is no theoretical foundation for a power law extrapolation of the Hartree−Fock energy (unlike correlation energy),[39,44] and a more accurate treatment could be obtained by an exponential law of the form:

$$E_{\mathrm{HF}}(n) = E_{\mathrm{HF}}(\infty) + B\exp(-\alpha n)$$

where n has its usual meaning (the highest angular momentum present in a correlation-consistent basis set), B depends on the basis set index (n) for each species, and α is an adjustable constant. For a two-point (D,T) extrapolation of the HF energy, the optimal value of parameter α was found to be 1.43 in a set of eight diatomic molecules.[39] Therefore, for each type of the IB parameter optimization, the exponential extrapolation of the HF energy was also considered, and the results were compared with those obtained by the power-law extrapolation since it was shown that the latter performed slightly better.[43b]

The optimization of the α and β parameters by using electronic energies (type I) was performed by individually minimizing the RMS deviations in either (a) the HF and correlation energies or (b) the HF and correlated energies. However, since the differences between the values of β calculated by either approach were only slight, the criterion of theoretical clarity was in favor of the first approach.

Two different procedures were also considered for the parameters optimization by using atomization energies (type II): (a) variation of the parameter α in order to minimize the RMS deviation between the HF/IB and HF/CBS atomization energies and a subsequent variation of β in order to minimize the corresponding RMS deviation in the correlated atomization energies; and (b) simultaneous variation of both α and β in order to minimize the RMS deviation in the correlated atomization energies.

The availability of two different types of IB parameters optimization, each with two different approaches divided further into two ways of accounting for the HF energy extrapolation, led to a total of eight different pathways for the optimization of the parameters by using the CBS[DTQ] calculated limits. Furthermore, for a subset of the benchmark species, the CBS-[TQ5] limits were also attainable, leading to another eight possibilities. The most significant and particularly interesting results are shown in Table 1. A notable fact is that the power-law α parameter is significantly higher than the previous value of 3.39,[43b] which is attributed to the contributions from the individual values of α for Br-containing species, whose average was almost 8, much higher than 3 and 3.2 for species containing F and Cl, respectively. The range of the $\beta_{\mathrm{CCSD(T)}}$ parameters was narrower, with average values of 2.5, 2.7, and 1.6 for species containing F, Cl, and Br atoms, respectively. The data in Table 1 show that the deviations of the absolute energies or atomization energies are almost insensitive to the choice of the Hartree−Fock energy extrapolation (power-law or exponential). A closer examination shows also that the use of parameters obtained by the first type of optimization procedures (entries marked by E_{abs} in the last column of Table 1) led to higher deviations for the CCSD(T)/IB[DT] atomization energies. Therefore, although the optimization of the extrapolation parameters by the procedures of type I is theoretically rigorous and straightforward, it lacks the accuracy needed in practical applications which constitute the targets of the IB method itself. The overall deviation among the optimization procedures in type

TABLE 1: Extrapolation Parameters for the Two-Point (D,T) Infinite Basis Method (α for the Hartree−Fock, *β* for the Correlation Energy)[a]

no. of molecules	α	*β*				RMS deviation (kJ mol^{-1})	Hartree−Fock energy extrapolation	CBS extrapolation basis sets sequence	type of fit for the α, *β* parameters
	HF	MP2	MP4SDTQ	CCSD	CCSD(T)				
29[b,c]	3.39	1.91	2.08	1.94	2.02	9.04	power	TQ5[d]	E_{abs}
29	3.39				2.09	9.00	power	TQ5	AE, separate
29	2.17				2.74	6.86	power	TQ5	AE, simultaneous
26[e,f]	5.30	1.84	1.97	1.94	1.97	9.04	power	DTQ[g]	E_{abs}
26	2.15	1.84	1.97	1.94	1.97	9.04	exponential	DTQ	E_{abs}
26	5.02	2.43	2.41	2.35	2.41	5.33	power	DTQ	AE, separate
26	2.63				3.02	4.62	power	DTQ	AE, simultaneous
26	2.04	2.43	2.41	2.35	2.41	5.33	exponential	DTQ	AE, separate
26	1.06				3.02	4.62	exponential	DTQ	AE, simultaneous
16[e,h]	4.50	1.65	1.85	1.80	1.85	11.01	power	TQ5[i]	E_{abs}
16	4.94	2.45	2.50	2.49	2.50	5.66	power	TQ5	AE, separate
16	2.40				3.47	4.63	power	TQ5	AE, simultaneous

[a] The total RMS deviation from the three-point CBS extrapolated zero-point exclusive CCSD(T) atomization energy is also presented as well as the extrapolation form of the Hartree−Fock energy (power or exponential law), the sequence of basis sets employed in the determination of the three-point CBS limit, and the type of the RMS deviations minimization fit using (a) absolute energies (E_{abs}) with a separate fit of HF energies and correlation energies, or (b) atomization energies (AE) with either a separate or a simultaneous fit of the α, *β* parameters. [b] From reference 43b. [c] Molecules: C_2, CCl, CF, CH, HCN, CO, HCO, CP, CS, CSi, HF, H_2, HCHO, H_2O, HCCH, HCl, N_2, NH, NH_2, NO, O_2, OH, PH, PO, HS, SiH, SiO, SO. [d] Using the sequence of cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets. [e] This work. [f] Molecules: H_2, HF, HCl, HBr, F_2, Cl_2, Br_2, CH, CF, CCl, CBr, CH_2, CHF, CHCl, CHBr, ClF, BrF, BrCl, CH_3, CH_2F, CH_2Cl, CH_2Br, CH_4, CH_3F, CH_3Cl, CH_3Br. [g] Using the sequence of cc-pV(D+d)Z, cc-pV(T+d)Z, and cc-pV(Q+d)Z basis sets. [h] Molecules: H_2, HF, HCl, HBr, F_2, Cl_2, CH, CF, CCl, CBr, CH_2, CHF, CHCl, ClF, CH_3, CH_4. [i] Using the sequence of cc-pV(T+d)Z, cc-pV(Q+d)Z, and cc-pV(5+d)Z basis sets.

II favors the simultaneous optimization of both α and $\beta_{CCSD(T)}$ parameters, with a gain in accuracy of ca. 1 kJ mol^{-1}. However, the separate optimization of α and *β* is theoretically purer and allows the contributions of the HF and correlation energy extrapolations to the overall error of the IB method to be clearly distinguished. Furthermore, since the loss of 1 kJ mol^{-1} is insignificant, the values for α and *β* derived by a separate optimization should be preferred as was also suggested previously.[43b] An inspection of the last three entries in Table 1 reveals that when the electronic or atomization energies at the CBS[TQ5] limit are employed as reference points, the overall deviation of IB[DT] from CBS[TQ5] slightly increases. However, the result is based on a small set of 16 molecules, and it may not be statistically important, although it could be rationalized by considering that IB uses the first two basis sets of the CBS[DTQ] scheme, and thus the IB[DT] values (using the corresponding pair of α, *β* parameters) are closer to CBS[DTQ] than CBS[TQ5]. The final decision on the most appropriate values for the IB extrapolation parameters should compromise theoretical clarity with computational accuracy. Thus, the parameters derived by the separate fit of the IB[DT] Hartree−Fock and correlated atomization energies to the corresponding CBS[DTQ] values are recommended, with $\alpha = 5.02$ or 2.04 for the power-law or exponential extrapolation of the Hartree−Fock energy, respectively. The *β* parameters suggested for MP2, MP4SDTQ, CCSD, and CCSD(T) are 2.43, 2.41, 2.35, and 2.41, respectively.

A comparison among the individual zero-point exclusive atomization energies (neglecting spin−orbit corrections) calculated by CCSD(T) at various infinite basis set limits is shown in Table 2, along with the corresponding deviations from the CCSD(T)/CBS[TQ5] values. As could be expected, there is an excellent agreement between the two CBS extrapolated values, with a maximum deviation of 1.7 kJ mol^{-1} for HBr, unlike the CCSD(T)/IB[DT] atomization energies which were obtained by using various pairs of α and $\beta_{CCSD(T)}$ extrapolation parameters. For CCSD(T)/IB[DT] with $\alpha = 4.50$ and $\beta_{CCSD(T)} = 1.85$ (optimized by separately fitting the HF energy and CCSD(T) correlation energy to their corresponding CBS[TQ5] limits), the deviations for species containing neither Cl nor Br (H_2, CH_2, CHF, CH_3, CH_4) are unacceptably high, which can be lowered by using $\alpha = 5.30$ and $\beta_{CCSD(T)} = 1.97$ (optimized by a fit to the CBS[DTQ] limits). However, the use of the α and $\beta_{CCSD(T)}$ parameters derived by a fit to the atomization energies resulted in a decrease of the overall deviation, as shown in the last two columns of Table 2, with largest errors exhibited by CH_4, CH_3, and chlorine-containing molecules. The deviations appearing in Table 2 constitute an estimate of the intrinsic errors of the IB extrapolation to the complete basis limit. Thus, the uncertainty in thermochemical properties calculated at the CCSD(T)/IB[DT] level of theory cannot be lower than ±8 kJ mol^{-1} for molecules containing H, C, F, Cl, and Br atoms.

Core/Valence Correlation and Scalar-Relativistic Contributions. The calculation of thermochemical properties by theoretical methodologies aiming at achieving a high degree of accuracy must account for the correlation of the inner electrons which is neglected in frozen-core calculations, referred to as the core/valence correlation (CV) correction. In addition, it must account for scalar-relativistic (SR) effects, by computing the corresponding SR corrections. These two effects are almost counteracting[37,45] on the thermochemical properties of small molecules, although their net contribution increases with molecular size.

Correlation-consistent basis sets augmented with core-correlating functions are not available for Br and I atoms, limiting high-quality core/valence correlation calculations to only a subset of the molecules involved in the present work. However, even if these basis sets were available, a reliable treatment of the corresponding CV corrections would demand expensive calculations using large basis sets augmented with tight core functions and the full correlation of all electrons. Therefore, a facilitation of the CV calculation procedure was attempted in this work by inspecting the dependence of the CV effects on the size of the basis set and the presence of core functions. The core/valence correlation corrections on the CH, CH_4, HF, F_2, and CH_3F atomization energies were computed by the difference [CCSD(T,FU) − CCSD(T,FC)] (where FU stands for the correlation of all electrons and FC for the correlation of only the valence electrons) by using the correlation-consistent basis sets augmented with core functions AUG-cc-pCVnZ ($n = D,T,Q$).[75] The difference was also computed by using the conventional correlation-consistent AUG-cc-pVnZ basis sets,

TABLE 2: Zero-Point Exclusive Atomization Energies for the Benchmark Species without Spin−Orbit Corrections[a]

			CCSD (T)/IB[DT]			
molecule	CCSD(T)/ CBS[TQ5]	CCSD(T)/ CBS[DTQ]	E_{HF}, $E_{CCSD(T)}$ fit to CBS[TQ5] data[b]	E_{HF}, $E_{CCSD(T)}$ fit to CBS[DTQ] data[c]	AE_{HF}, $AE_{CCSD(T)}$ fit to CBS[DTQ] data[d]	$AE_{CCSD(T)}$ fit to CBS[DTQ] data (α,β simultaneously)[e]
H_2	457.9	457.9 (0.0)	466.1 (8.2)	464.7 (6.8)	462.2 (4.3)	463.1 (5.2)
F_2	158.9	157.5 (−1.4)	165.4 (6.5)	163.0 (4.1)	159.2 (0.3)	161.3 (2.4)
Cl_2	246.0	244.6 (−1.4)	244.7 (−1.3)	241.9 (−4.1)	237.9 (−8.1)	241.4 (−4.6)
Br_2		225.4	225.1	222.4	217.4	218.2
ClF	257.7	257.3 (−0.4)	257.1 (−0.6)	254.0 (−3.7)	249.6 (−8.1)	254.4 (−3.3)
BrF		266.3	262.7	259.4	254.7	259.2
BrCl		236.4	235.8	233.0	228.5	230.9
HF	592.0	592.4 (0.4)	598.2 (6.2)	595.1 (3.1)	590.3 (−1.7)	593.5 (1.5)
HCl	448.6	449.2 (0.6)	453.6 (5.0)	452.0 (3.4)	448.3 (−0.3)	446.4 (−2.2)
HBr	397.1	398.8 (1.7)	404.3 (7.2)	402.7 (5.6)	398.6 (1.5)	395.7 (−1.4)
CH	350.5	351.0 (0.5)	357.8 (7.3)	356.0 (5.5)	352.4 (1.9)	352.4 (1.9)
CF	551.8	551.4 (−0.4)	555.2 (3.4)	552.3 (0.5)	548.8 (−3.0)	554.7 (2.9)
CCl	405.2	404.5 (−0.7)	402.5 (−2.7)	400.4 (−4.8)	396.6 (−8.6)	397.5 (−7.7)
CBr	346.8	348.3 (1.5)	349.1 (2.3)	346.7 (−0.1)	342.1 (−4.7)	341.6 (−5.2)
CH_2	793.9	794.7 (0.8)	807.2 (13.3)	804.4 (10.5)	798.9 (5.0)	798.7 (4.8)
CHF	886.7	886.4 (−0.3)	897.9 (11.2)	893.6 (6.9)	886.6 (−0.1)	889.8 (3.1)
CHCl	756.0	755.5 (−0.5)	761.8 (5.8)	758.1 (2.1)	750.9 (−5.1)	750.0 (−6.0)
CH_3	1282.4	1283.4 (1.0)	1303.8 (21.4)	1299.4 (17.0)	1290.6 (8.2)	1289.7 (7.3)
CH_2F		1308.4	1325.0	1319.5	1310.1	1313.1
CH_2Cl		1202.9	1215.1	1210.5	1201.3	1200.4
CH_2Br		1158.7	1173.9	1168.9	1158.9	1157.3
CH_4	1752.1	1753.7 (1.6)	1781.1 (29.0)	1775.6 (23.5)	1764.2 (12.1)	1761.2 (9.1)
CH_3F		1764.0	1787.7	1780.9	1768.3	1769.0
CH_3Cl		1651.3	1670.2	1664.4	1652.3	1649.6
CH_3Br		1612.4	1633.6	1627.5	1614.7	1611.3

[a] Deviations from the CCSD(T)/CBS[TQ5] values in parentheses. Containing H, C, F, Cl, Br atoms, calculated at levels of theory employing CCSD(T) and various types of extrapolation to the infinite basis limit: CBS[TQ5], CBS[DTQ], as well as IB[DT], using α and $\beta_{CCSD(T)}$ extrapolation parameters optimized in four different ways (briefly described on top of the corresponding column). [b] $\alpha = 4.50$, $\beta_{CCSD(T)} = 1.85$. [c] $\alpha = 5.30$, $\beta_{CCSD(T)} = 1.97$. [d] $\alpha = 5.02$, $\beta_{CCSD(T)} = 2.41$. [e] $\alpha = 2.63$, $\beta_{CCSD(T)} = 3.02$.

although the validity of using basis sets lacking tight core functions in CV calculations has been seriously questioned.[75] The results showed that the CV correction was smoothly increasing with the size of the AUG-cc-pCVnZ basis sets, asymptotically converging to an upper limit. On the other hand, the dependence on the size of the AUG-cc-pVnZ basis set was erratic, with a well-defined maximum for n = T, while the correction calculated for n = Q was substantially greater than that using the AUG-cc-pCVQZ basis set. Interestingly, the difference between the CV corrections calculated by the AUG-cc-pVDZ and AUG-cc-pCVQZ basis sets was small, on the order of ca. 4 kJ mol^{-1}, and this was tempting to extend these calculations to several chlorine-containing molecules, whose CCSD(T)/AUG-cc-pwCVQZ values have been previously reported.[37,45] Therefore, the CV corrections in the atomization energies of CH, CH_4, HF, F_2, HCl, Cl_2, and CH_3Cl were obtained as the difference [CCSD(T,FU) − CCSD(T,FC)]/cc-pV(n+d)Z for n = D, T, and Q. Although a peak for n = T was also observed, the corrections calculated at the CCSD(T)/cc-pV(D+d)Z level were close to the published values at the CCSD(T)/AUG-cc-p(w)CVQZ level with a maximum deviation of ca. 1 kJ mol^{-1}. This indicated that core/valence correlation effects calculated at the affordable CCSD(T)/cc-pV(D+d)Z level of theory could effectively replace those calculated at the accurate CCSD(T)/AUG-cc-p(w)CVQZ level, and, furthermore, they could be employed to provide rough CV corrections for bromine- and iodine-containing molecules. Thus, the contribution of the residual correlation of the inner electrons to the thermochemical properties of all species was calculated as the difference between the CCSD(T,FU)/(cc)-pV(D+d)Z and CCSD(T,FC)/(cc)-pV(D+d)Z energies, and the corresponding CV corrections to the atomization energies of all molecules involved in this work are presented in Table 3, along with literature values using the AUG-cc-p(w)CVQZ[37,45] and the MTsmall[76] basis sets. A comparison of the CV corrections among the limited set of data available in Table 3 apparently shows that the differences depend on molecular size, and for the largest molecules, they reach values close to 3 kJ mol^{-1}. However, these differences are rather small compared to the uncertainty of the IB method, and their contribution to the overall error in the calculated thermochemical properties is not expected to be significant.

The scalar-relativistic (SR) corrections were initially calculated for a subset of the benchmark data set, employing the modified coupled-pair functional (MCPF) theory[77] with the (cc)-pV(T+d)Z basis set, by including either mass-velocity and Darwin contact term (MVD)[78] or Douglas−Kroll (DK)[79] integrals. In a study of the dependence of the SR correction on the correlation level, the basis set size, and the type of relativistic treatment for the CF, CF_4, and SiF_4 molecules, it was found that the MCPF-DK approach converges rapidly with basis set size, and the difference between MVD and DK diminishes with increasing size of the basis set, concluding that the DK approach should be preferred with basis sets of medium size.[80] However, the SR corrections in the atomization energies of bromine-containing molecules calculated by the DK approach in the present work were all positive and unexpectedly large (ca. 15 kJ mol^{-1}), unlike those calculated by the MVD approach. However, for all other molecules, the SR corrections calculated using either approach were much closer, and the largest differences were obtained for iodine-containing molecules where the DK approach yielded smaller SR corrections (by 2.3, 3.6, and 3.6 kJ mol^{-1} for I_2, CH_2I, and CH_3I, respectively). Furthermore, the enthalpies of formation of bromine-containing molecules were adversely affected by including the CV and the SR corrections calculated by the DK approach, and the deviations from experimental values reached values of almost 20 kJ mol^{-1}. Therefore, the scalar-relativistic corrections to the electronic energy of all species were obtained as the difference

TABLE 3: Core/Valence Correlation Corrections (in kJ mol^{-1}) to the Atomization Energies for the Entire Set of Molecules[a]

molecule	CCSD(T)/ (cc)-pV(D+d)Z	CCSD(T)/ AUG-cc-p(w)CVQZ	CCSD(T)/ MTsmall
H_2	0.0	0.0	
F_2	0.4	−0.4	−0.4
Cl_2	2.0	0.8	0.7
Br_2	1.7		
I_2	1.8		
ClF	1.1	0.8	0.3
BrF	1.4		
BrCl	1.9		
IF	1.8		
ICl	2.6		
HF	0.5	0.8	0.7
HCl	1.9	1.3	0.6
HBr	1.4		
HI	1.5		
CH	0.8	0.8	4.2
CF	1.3		
CCl	2.5		
CBr	2.0		
CH_2	2.0	3.4	3.3
CHF	2.0		
CHCl	3.3		
CH_3	3.1	4.2	4.3
CH_2F	3.2		
CH_2Cl	4.5		
CH_2Br	4.3		
CH_2I	5.2		
CH_4	4.2	5.4	5.0
CH_3F	4.1		
CH_3Cl	5.2	5.0	5.1
CH_3Br	4.9		
CH_3I	5.7		
CF_2	2.4		
CHF_2	3.3		
CH_2F_2	4.2		
CF_3	3.6		
CHF_3	4.5	5.1	
CF_4	4.9		4.2
CCl_2	4.8		
$CHCl_2$	6.0		
CH_2Cl_2	6.6		
CCl_3	7.8		
$CHCl_3$	8.3	6.2	
CCl_4	10.3	6.7	
CHBr	2.8		
CBr_2	3.9		
$CHBr_2$	5.4		
CH_2Br_2	6.0		
CHFCl	4.6		
CH_2FCl	5.3		
CHFBr	4.2		
CH_2FBr	5.0		
CHClBr	5.7		
CH_2ClBr	6.3		
CHFI	5.3		
CH_2FI	5.9		
CHClI	6.8		
CH_2ClI	7.1		
CHBrI	6.5		
CH_2BrI	6.8		
CHI	3.8		
CHI_2	7.6		
CH_2I_2	7.7		
CH_3CH_2	6.6	9.5	
CH_3CH_3	7.5	10.0	
CH_3CH_2F	7.5		
CH_2FCH_2	6.6		
CH_3CHF	6.7		
CH_3CH_2Cl	8.8		
CH_2ClCH_2	7.8		
CH_3CHCl	8.2		
CH_3CH_2Br	8.6		
CH_2BrCH_2	7.6		
CH_3CHBr	7.9		
CH_3CH_2I	9.4		
CH_2ICH_2	8.3		
CH_3CHI	8.9		

[a] Calculated at the CCSD(T)/(cc)-pV(D+d)Z level of theory, including literature values at the CCSD(T)/AUG-cc-p(w)CVQZ (refs 37, 45) and CCSD(T)/MTsmall (ref 76) levels of theory.

between the MCPF-MVD/(cc)-pV(T+d)Z and MCPF-NR/(cc)-pV(T+d)Z energies (NR: nonrelativistic), and the corresponding corrections to the atomization energies for the entire set of molecules are shown in Table 4, along with literature values obtained at the CISD(FC)-MVD/cc-pVTZ,[37,45] MCPF-MVD/MTsmall,[76] and MCPF-DK/cc-pVQZ[80] levels of theory. The individual variations among these four levels of theory are very small, suggesting that the values calculated in this work for molecules containing elements up to Cl are of comparable accuracy. To our knowledge, there are no data for molecules containing Br and I atoms in order to be compared with the presently calculated CV and SR corrections. However, their beneficial effects on the calculated thermochemical properties of all species suggest that they may be considered sufficiently reliable.

Calculation of Thermochemical Properties. The structural parameters and the vibrational frequencies for the benchmark molecules were calculated at the MP2/6-311G(d) level of theory; most of them have been reported elsewhere.[30] The structural parameters and the vibrational frequencies of the additional benchmark molecules (methylidynes and methylenes) considered in the present study are shown in Table 5. The calculated bond lengths and bond angles were found to deviate from experiment by 1.5% and 1.0%, respectively.

The absolute electronic energies of carbon and halogen atoms were corrected for the first-order spin−orbit coupling in their ground states (^3P and ^2P, respectively). The corrections were taken to be the energy difference between the spin−orbit coupled ground state and the weighted J-averaged state, and the energy differences between J states were taken from standard tables of atomic energy levels.[81] Therefore, the electronic energies of the C, F, Cl, Br, and I atoms were lowered by 0.4, 1.6, 3.5, 14.7, and 30.3 kJ mol^{-1}, respectively. Similarly, the spin−orbit coupling in the $^2\Pi$ ground states of the diatomic methylidynes CH (27.95 cm^{-1}), CF (77.12 cm^{-1}), CCl (134.92 cm^{-1}), and CBr (466 cm^{-1})[82] was also taken into account, leading to a lowering of the corresponding electronic energies by 0.2, 0.5, 0.8, and 2.8 kJ mol^{-1}, respectively. All ground states of halomethylenes CHX (X = F, Cl, Br, I) and dihalomethylenes CX_2 (X = F, Cl, Br) were calculated to be singlet in nature at the CCSD(T)/IB[DT] level of theory; the geometry of all singlet and triplet states was also optimized at the MP2/6-311G(d) level. The singlet−triplet splittings were calculated at the CCSD(T)/IB[DT] level of theory to be 63.6, 26.0, 22.7, 14.1, 240.0, 83.5, and 66.4 kJ mol^{-1}, for CHF, CHCl, CHBr, CHI, CF_2, CCl_2, and CBr_2, respectively, in reasonable agreement with experimental data and recent theoretical results.[83−85,24]

The calculated enthalpies of formation at 298.15 K of all benchmark molecules at levels of theory employing CCSD(T) and infinite basis limits extrapolated by CBS[DTQ], CBS[TQ5], and IB[DT] are shown in Table 6, including spin−orbit, CV, and SR corrections, and using the sequence of large basis sets

TABLE 4: Scalar-Relativistic Corrections (in kJ mol^{-1}) to the Atomization Energies for the Entire Set of Molecules[a]

molecule	MCPF-MVD/ (cc)-pV(T+d)Z	CISD(FC)-MVD/ cc-pVTZ	MCPF-DK/ cc-pVQZ	ACPF-MVD/ MTsmall	species	MCPF-MVD/ (cc)-pV(T+d)Z	CISD(FC)-MVD/ cc-pVTZ
H_2	0.0	0.0			$CHCl_2$	−2.3	
F_2	−0.3	−0.4		+0.1	CH_2Cl_2	−2.2	
Cl_2	−0.6	+2.9		−0.6	CCl_3	−2.6	
Br_2	−2.1				$CHCl_3$	−2.4	−2.9
I_2	−4.7				CCl_4	−2.5	−2.6
ClF	−0.7	−0.8		−0.5	CHBr	−7.1	
BrF	−3.3				CBr_2	−12.0	
BrCl	−7.0				$CHBr_2$	−6.7	
IF	−7.9				CH_2Br_2	−5.7	
ICl	−4.4				CHFCl	−2.5	
HF	−1.0	−0.8		−0.8	CH_2FCl	−2.6	
HCl	−0.7	−0.8		−1.1	CHFBr	−4.5	
HBr	−2.6				CH_2FBr	−4.3	
HI	−6.0				CHClBr	−8.5	
CH	−0.2			−0.2	CH_2ClBr	−8.0	
CF	−1.1		−0.7	-	CHFI	−7.4	
CCl	−0.5				CH_2FI	−6.1	
CBr	−2.5				CHClI	−8.4	
CH_2	−0.7			−0.4	CH_2ClI	−6.1	
CHF	−1.4				CHBrI	−10.6	
CHCl	−0.9				CH_2BrI	−8.2	
CH_3	−0.8	0.0		−0.7	CHI	−6.2	
CH_2F	−1.9				CHI_2	−5.9	
CH_2Cl	−1.7				CH_2I_2	−11.0	
CH_2Br	−4.2				CH_3CH_2	−1.7	−1.6
CH_2I	−8.9				CH_3CH_3	−1.8	−1.7
CH_4	−0.9	−0.8		−0.8	CH_3CH_2F	−2.9	
CH_3F	−2.0			−1.6	CH_2FCH_2	−2.7	
CH_3Cl	−1.7	−2.1		−1.8	CH_3CHF	−2.8	
CH_3Br	−3.8				CH_3CH_2Cl	−2.6	
CH_3I	−7.3				CH_2ClCH_2	−2.3	
CF_2	−2.2				CH_3CHCl	−2.6	
CHF_2	−2.9				CH_3CH_2Br	−4.7	
CH_2F_2	−3.0				CH_2BrCH_2	−3.7	
CF_3	−3.9				CH_3CHBr	−5.1	
CHF_3	−4.1	−4.6			CH_3CH_2I	−7.6	
CF_4	−5.3		−3.7	−3.4	CH_2ICH_2	−4.5	
CCl_2	−0.9				CH_3CHI	−9.0	

[a] Calculated at the MCPF-MVD/(cc)-pV(T+d)Z level of theory, including literature values at the CISD(FC)-MVD/cc-pVTZ (refs 37, 45), MCPF-DK/cc-pVQZ (ref 80), and ACPF-MVD/MTsmall (ref 76) levels of theory.

TABLE 5: Structural Parameters and Vibrational Frequencies (Unscaled)[a]

	structural parameters		vibrational frequencies	
molecule	calcd	exptl[b]	calcd	exptl[c]
CH	C−H = 1.118	C−H = 1.120	2947	2859
CF	C−F = 1.274	C−F = 1.272	1345	1308
CCl	C−Cl = 1.657	C−Cl = 1.651	904	
CBr	C−Br = 1.818	C−Br = (1.823)	749	
CH_2	C−H = 1.078 <H−C−H = 132.3	C−H = 1.078 <H−C−H = 130.0	1155, 3201, 3432	963, 3190
CHF	C−H = 1.118 C−F = 1.307 <H−C−F = 102.2		1259, 1502, 2896	1189, 1403, 2643
CHCl	C−H = 1.108 C−Cl = 1.693 <H−C−Cl = 102.9		858, 1288, 2995	812, 1201

[a] Calculated at the MP2/6-311G(d) level of theory for selected small benchmark molecules of the present work (bond lengths in Å, angles in degrees, vibrational frequencies in cm^{-1}). The corresponding experimental values are also shown for comparison. [b] Experimental structural data for the diatomic methylidynes taken from ref 8 (the bond length of CBr is not accurately known), except CCl and CH_2 from ref 5. [c] Experimental vibrational frequencies taken from ref 8.

for iodine. The corresponding values using basis sets augmented with diffuse functions, denoted as IB[aDT], are also shown. The CCSD(T)/CBS[TQ5] and CCSD(T)/CBS[DTQ] values exhibit the closest agreement with experiment, apart from the exceptionally large deviations for CCl and CBr. The error bars for the experimental enthalpies of formation of these two halomethylidynes are large, owing to experimental difficulties in generating and studying these unstable transient species. In addition, their CCSD(T) calculated values may possess contributions from computational errors attributed to the inefficiency of electron-correlation methods based on single-determinant reference wave functions to describe the electronic structure of these species correctly. The examination of the value for the T1 diagnostic[86] of the CCSD method revealed that it exceeds the threshold value of 0.02 for CCl and CBr, indicating the presence of nondynamical correlation effects, and suggesting

TABLE 6: Experimental Enthalpies of Formation (in kJ mol^{-1}) of All Benchmark Molecules at 298.15 K, and Corresponding Deviations of Calculated Values (Including Spin−Orbit, CV, and SR Corrections)

molecule	experimental value[a]	CCSD (T)/CBS [TQ5]	CCSD (T)/CBS [DTQ]	CCSD (T)/IB [DT][b]	CCSD (T)/IB [aDT][c]
H_2	0.0	0.7	0.7	−3.5	−1.6
F_2	0.0	4.8	6.2	4.5	1.3
Cl_2	0.0	2.1	3.6	10.3	7.5
Br_2	30.9 ± 0.1		−3.5	4.4	0.6
I_2	62.4 ± 0.1			14.0	9.0
ClF	−50.3 ± 4.0	−1.1	−0.7	6.9	2.2
BrF	−58.5 ± 4.0		2.1	13.7	4.6
BrCl	14.6 ± 4.0		5.1	12.9	9.5
IF	−94.8 ± 4.0			36.2	24.5
ICl	17.5 ± 4.0			13.8	10.9
HF	−272.5 ± 0.7	0.5	0.1	2.1	1.2
HCl	−92.3 ± 0.1	−0.9	−1.6	−0.6	−0.4
HBr	−36.4 ± 0.2	−3.1	−4.7	−4.5	−5.8
HI	26.4 ± 0.1			−1.0	−2.4
CH	596.4 ± 4.0	1.1	0.7	−0.8	−1.3
CF	255.2 ± 8.0	−5.3	−4.9	−2.3	−4.1
CCl	502.1 ± 20.0	−66.5	−65.7	−57.8	−62.0
CBr	510.4 ± 63.0	−15.0	−16.5	−10.2	−14.7
CH_2	392.5 ± 2.1	2.8	2.0	−2.3	−1.0
CHF	157.0 ± 18.0	−3.5	−3.3	−3.4	−4.6
CHCl	317.0 ± 18.0	6.4	6.9	11.5	8.0
CH_3	145.7 ± 1.0	4.8	3.8	−3.4	0.0
CH_2F	−33.5 ± 8.4		9.6	7.9	7.6
CH_2Cl	121.3 ± 4.2		−1.7	−0.0	−1.4
CH_2Br	167.4 ± 4.2		−0.4	−0.6	−3.1
CH_2I	217.6 ± 6.7			1.1	−2.1
CH_4	−74.9 ± 0.4	6.3	4.8	−5.7	−0.7
CH_3F	−234.3 ± 5.0		3.8	−0.5	0.4
CH_3Cl	−83.7 ± 0.7		4.7	3.6	2.3
CH_3Br	−34.3 ± 0.8		−3.3	−5.7	−9.3
CH_3I	14.3 ± 1.4			−3.0	−7.2

[a] Experimental values taken from ref 7, except CH and CH_2 from ref 5, CHF and CHCl from ref 51, halomethyl radicals from ref 6, CH_3Br from ref 52, and CH_3I from ref 53. [b] $\alpha = 5.02$, $\beta_{CCSD(T)} = 2.41$. [c] $\alpha = 5.02$, $\beta_{CCSD(T)} = 2.77$.

TABLE 7: Deviations from Experimental Values (in kJ mol^{-1}) of Calculated Enthalpies of Formation at 298.15 K for the Iodine-Containing Benchmark Molecules

molecule	CCSD(T)/ IB[DT][a]	CCSD(T)/ IB[aDT][b]	CCSD(T)/ IB[(DT)][a]	CCSD(T)/ IB[(aDT)][b]
I_2	14.0	5.4	−1.7	10.5
IF	36.2	22.8	31.0	26.1
ICl	13.8	8.5	10.5	11.4
HI	−1.0	−4.2	−3.4	−1.4
CH_2I	1.1	−7.4	1.6	2.4
CH_3I	−3.0	−14.0	−4.7	−3.2

[a] $\alpha = 5.02$, $\beta_{CCSD(T)} = 2.41$. [b] $\alpha = 5.02$, $\beta_{CCSD(T)} = 2.77$.

that a multireference treatment of electron correlation would be more suitable. Thus, excluding these two problematic cases, the RMS deviation of the values calculated at the CCSD(T)/CBS[DTQ] and CCSD(T)/CBS[TQ5] levels of theory was reduced to 3.7 and 4.1 kJ mol^{-1}, for 14 and 23 molecules, respectively. By neglecting the CV and SR contributions, the RMS deviation increased by 1.2 and 0.8 kJ mol^{-1}, respectively, which is a additional strong indication that the CV and SR corrections employed in this work are sufficiently accurate for molecules possessing all four halogen atoms. The deviations from experimental values for levels of theory employing infinite basis limits obtained by the IB method (power-law extrapolation of the HF energy, $\alpha = 5.02$, $\beta_{CCSD(T)} = 2.41$) are higher, as expected in light of the inherent deficiencies of the IB method. Besides CCl and CBr, large deviations were also systematically evident for iodine fluoride, IF, which was found to behave similarly in a large number of DFT calculations.[30] The combined results of both studies apparently suggest that the experimentally determined enthalpy of formation for IF[7,8] is probably underestimated by at least 15 kJ mol^{-1}. The overall performance of the IB method with basis sets augmented with diffuse functions, AUG-cc-pV(n+d)Z (n = D,T, denoted as IB[aDT]), was slightly better. However, there was no systematic improvement of the individual deviations on going from IB[DT] to IB[aDT], with a deterioration of the results for most halomethanes and halomethyl radicals. A closer agreement with experimental values could be obtained if the values of the α and $\beta_{CCSD(T)}$ parameters were specifically optimized for the IB extrapolation based on diffuse-functions augmented basis sets. Therefore, by restricting the parameter α to be 5.02, the value of $\beta_{CCSD(T)}$ was adjusted to 2.77 by fitting the calculated enthalpies of formation to the experimental values (excluding CCl, CBr, and IF) at the CCSD(T)/IB[aDT] level, leading to a decrease of the RMS deviation by 1.4 kJ mol^{-1}. The RMS deviations of the values calculated at CCSD(T)/IB[DT] (for $\alpha = 5.02$ and $\beta_{CCSD(T)} = 2.41$) and CCSD(T)/IB[aDT] (for $\alpha = 5.02$ and $\beta_{CCSD(T)} = 2.77$) were 6.8 and 5.1 kJ mol^{-1}, respectively for a set of 28 molecules (excluding CCl, CBr, and IF).

The application of the IB method in iodine-containing molecules was explored in more detail, since the extrapolation was based on a sequence of basis sets lacking the well-defined systematic nature of correlation-consistent ones. Thus, the large double- and triple-ζ basis sets for iodine were replaced with smaller ones, with the additional hope of reducing the computational cost and increasing the applicability of the CCSD(T)/IB[DT] level of theory into a greater range of iodine-containing molecules. A sequence consisting of the smaller double-ζ SV4P[67] and triple-ζ 6-311G(3df)[11] basis sets was thus selected, and the corresponding infinite basis limit will be denoted as IB[(DT)]. A sequence containing their diffuse-function augmented variants SV4PD and 6-311+G(3df) was also considered, and the corresponding limit will be denoted as IB[(aDT)]. This replacement led to enthalpies of formation that were slightly closer to experimental values, with RMS deviations of 5.4 and 7.2 kJ mol^{-1} (compared to 8.9 and 7.2 kJ mol^{-1}) for the CCSD(T)/IB[(DT)] and CCSD(T)/IB[(aDT)] levels, respectively, and a set of 5 iodine-containing molecules (excluding IF). Although the comparison involves a limited amount of data, the result is interesting and may further suggest that thermochemical quantities for larger iodine-containing molecules can be accurately obtained by the IB extrapolation using this sequence of smaller basis sets. An examination of the absolute electronic energies for species containing a single iodine atom shows that although the energies using the large basis sets are lower by ca. 4.6 and 1.1 H for the double- and triple-ζ quality members, respectively, the difference asymptotically reduces to a rather constant value of ca. 0.522 H with a deviation on the order of 0.001 H. This deviation translates to a corresponding difference in thermochemical quantities (derived by absolute energy differences) on the order of a few kilojoules per mole, and provides an explanation for the similar quality of the IB extrapolated results for both sequences. The individual deviations from experimental values for all iodine-containing benchmark molecules using these two sequences of basis sets are shown in Table 7. Excluding IF, the deviations of CCSD(T)/IB[(DT)] are sufficiently small, and could provide a lower limit of ±10 kJ mol^{-1} for the uncertainty in enthalpies of formation calculated by CCSD(T) and the IB extrapolation method, for molecules containing all four halogen atoms.

TABLE 8: Experimental and Calculated Bond Lengths (in Å) and Vibrational Frequencies (Unscaled, in cm^{-1}, in parentheses) for the Diatomic Molecules of the Benchmark Set

molecule	experimental value[a]	CCSD(T)/CBS[TQ5]	CCSD(T)/CBS[DTQ]	CCSD(T)/IB[(DT)]	MP2/6-311G(d)
H_2	0.741 (4401)	0.741 (4461)	0.742 (4464)	0.738 (4449)	0.737 (4458)
F_2	1.412 (917)	1.410 (932)	1.412 (921)	1.410 (967)	1.412 (917)
Cl_2	1.988 (560)	1.990 (559)	1.990 (558)	2.001 (551)	2.028 (538)
Br_2	2.281 (325)		2.272 (335)	2.290 (326)	2.302 (330)
I_2	2.666 (215)			2.665 (238)	2.714 (222)
HF	0.917 (4138)	0.917 (4203)	0.916 (4188)	0.918 (4187)	0.918 (4092)
HCl	1.275 (2991)	1.276 (3003)	1.277 (3010)	1.272 (2984)	1.284 (2951)
HBr	1.414 (2649)	1.409 (2675)	1.410 (2667)	1.408 (2673)	1.429 (2630)
HI	1.609 (2309)			1.615 (2322)	1.639 (2289)
ClF	1.628 (786)	1.628 (793)	1.629 (794)	1.630 (789)	1.673 (734)
BrF	1.759 (671)		1.756 (687)	1.756 (676)	1.802 (644)
BrCl	2.136 (444)		2.133 (451)	2.145 (432)	2.168 (440)
IF	1.910 (610)			1.906 (626)	1.969 (595)
ICl	2.321 (384)			2.323 (422)	2.369 (379)
CH	1.120 (2859)		1.120 (2873)	1.115 (2841)	1.118 (2947)
CF	1.272 (1308)		1.273 (1301)	1.275 (1336)	1.274 (1345)
CCl	1.651 (867)		1.649 (879)	1.653 (883)	1.657 (904)
CBr			1.815 (734)	1.816 (724)	1.818 (748)

[a] Experimental values taken from ref 8, except CCl (ref 5).

The effect of structural parameters accuracy on the quality of thermochemical properties was examined in the case of the diatomic benchmark species. Thus, the CCSD(T)/IB[(DT)] potential energy curves of 18 diatomic molecules were scanned by using a finely controlled variation of the bond lengths until the energy difference between the final successive steps was less than 1 μH. This was accomplished in a significant number of steps, usually higher than 20. The CCSD(T)/CBS[TQ5] and CCSD(T)/CBS[DTQ] potential energy curves for fewer diatomic molecules were also scanned by computing the energies of a small number (6−9) of equidistant points at intervals of 0.005 Å, until the minimum of energy was bracketed by at least 2 points. The lowest part of the potential energy curve was fit to a quadratic expression in order to finely locate the stationary point and calculate the single harmonic vibrational frequency. All bond lengths and vibrational frequencies calculated in this manner, along with the MP2/6-311G(d) ones and the corresponding experimental values, are listed in Table 8. The average deviations from experiment for the bond lengths (Å) and vibrational frequencies (cm^{-1}, in parentheses) were −0.0005 (26), −0.001 (17), 0.001 (16), and 0.023 (−0.7), at the CCSD(T)/CBS[TQ5], CCSD(T)/CBS[DTQ], CCSD(T)/IB[(DT)], and MP2/6-311G(d) levels of theory, respectively. The CCSD(T)/CBS[TQ5] bond lengths were closer to experimental values, although the average deviation in the vibrational frequencies was the highest, with large contributions from the individual errors in H_2 and HF (60 and 65 cm^{-1}, respectively). The deviations from experimental values for the enthalpies of formation at 298.15 K, derived using structures, zero-point energies, and thermal corrections calculated at these high levels of theory, are shown in Table 9. A comparison with the corresponding data in Tables 6 and 7 (derived by using MP2/6-311G(d) geometries and vibrational frequencies) reveals that no significant improvement of the overall agreement was achieved by using structural parameters obtained at higher levels of theory. As seen in Table 8, the MP2/6-311G(d) level overestimates the bond lengths (with a maximum of ca. +0.06 Å for IF), while the maximum absolute deviations for the higher levels of theory are, as expected, much smaller (ca. +0.013 Å for Cl_2 at CCSD(T)/IB[DT] and −0.008 Å for Br_2 at CCSD(T)/CBS[DTQ]). However, an examination of the energy dependence on internuclear distance revealed that for a displacement of 0.05 Å from the optimal value (well above the average error of +0.02 Å in the MP2/6-311G(d) computed bond lengths), the electronic energies at high levels of theory rise by ca. 5 kJ mol^{-1} on the average, with a maximum increase of 10, 8, and 6 kJ mol^{-1} for the stiffest molecules HF, CF, and H_2, respectively, and a slight increase of 2 and 2.5 kJ mol^{-1} for I_2 and Br_2, respectively. Therefore, the bond lengths calculated at the MP2/6-311G(d) level are fortuitously lying close to the center and far from the steep slopes of the high level potential wells, resulting in small differences of a few kilojoules per mole for the calculated thermochemical properties. Errors in vibrational frequencies are also affecting the quality of thermochemical calculations, mostly through zero-point energies. However, the frequencies calculated at the MP2/6-311G(d) level had very small errors (with an RMS deviation of 36 cm^{-1} and a maximum error of +88 cm^{-1} for CH) with a negligible effect amounting to several tenths of kJ mol^{-1} on the quality of thermochemical calculations in diatomic molecules. However, in a low-level optimization of a polyatomic molecule, the individual small errors in each parameter would accumulate, leading to significant

TABLE 9: Deviations from Experimental Values (in kJ mol^{-1}) of the Calculated Enthalpies of Formation for the Diatomic Benchmark Molecules[a]

molecule	CCSD(T)/ CBS[TQ5]// CCSD(T)/ CBS[TQ5]	CCSD(T)/ CBS[DTQ]// CCSD(T)/ CBS[DTQ]	CCSD(T)/ IB[(DT)]// CCSD(T)/ IB[(DT)]
H_2	2.3	0.8	−3.5
F_2	6.2	7.3	5.8
Cl_2	2.1	3.4	10.8
Br_2		−3.0	5.5
I_2			−3.1
ClF	−2.1	−1.8	5.9
BrF		0.9	12.3
BrCl		5.2	13.6
IF			27.9
ICl			10.2
HF	2.7	0.8	2.8
HCl	0.7	−0.9	−0.2
HBr	−1.8	−4.4	−4.3
HI			−3.1
CH		0.7	−0.9
CF		−4.3	−1.5
CCl		−64.9	−56.9
CBr		−15.5	−9.3

[a] With bond lengths, vibrational frequencies, and single-point energies uniquely computed at three high levels of theory (including spin−orbit, CV, and SR corrections).

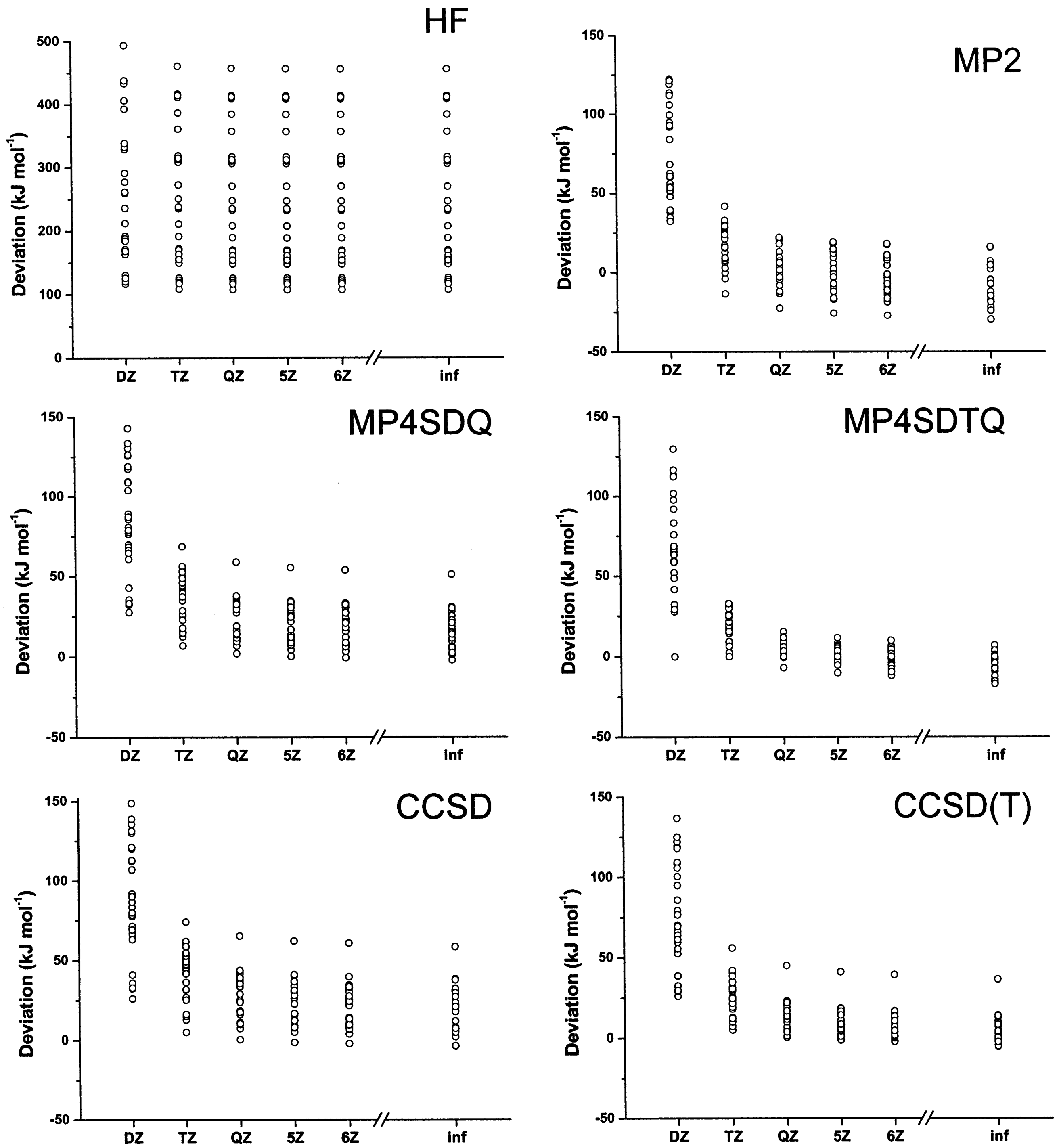

Figure 1. Deviations from experimental values of the calculated enthalpies of formation for the benchmark molecules (in kJ mol^{-1}), as a function of the basis set size for Hartree–Fock and the MP2, MP4SDQ, MP4SDTQ, CCSD, and CCSD(T) methods. Basis sets larger than TZ were extrapolated by the IB method.

deviations for properties computed at an inaccurate stationary point. Indeed, levels of theory including an adequate treatment of electron correlation and even the presence of high angular momentum f-functions in the basis sets have been shown to be necessary in order to obtain accurate structures and vibrational frequencies.[87] However, the geometry optimization of a polyatomic molecule at high levels of theory can be quite impractical due to excessive computational requirements, requiring the recourse to a more affordable level. Considering the size of the molecules employed in the present work and the agreement of the MP2/6-311G(d) calculated structures and vibrational frequencies[30] with experimental and higher quality theoretical data (Tables 5 and 8), this level of theory can be considered adequately reliable for practical purposes.

The examination of the performance for the post-SCF electron correlation treatments in combination with IB extrapolated basis sets would constitute an additional test of the IB method, and furthermore reveal particular features of each treatment. Therefore, the deviations of the calculated enthalpies of formation from experimental values for the benchmark molecules (excluding CCl and CBr) were plotted as a function of the index ζ of the basis set and are shown in Figure 1, for HF, MP2, MP4SDQ, MP4SDTQ, CCSD, and CCSD(T) methods. All values using basis sets with a ζ index greater than 3 were derived by the IB

TABLE 10: Experimental Bond Dissociation Energies (in kJ mol^{-1}) at 298.15 K of All Benchmark Molecules Possessing More than Two Atoms, and Corresponding Deviations of Calculated Values (Including Spin−Orbit, CV, and SR Corrections)

bond	experimental value[a]	CCSD(T)/ CBS[TQ5]	CCSD(T)/ CBS[DTQ]	CCSD(T)/ IB[DT]	CCSD(T)/ IB[(DT)]
CH−H	421.8 ± 4.5	−1.7	−1.3	1.5	1.5
CF−H	316.2 ± 19.7	−1.8	−1.7	1.0	1.0
CCl−H	403.1 ± 26.9	−72.9	−72.6	−69.3	−69.3
CH_2−H	464.8 ± 2.3	−2.0	−1.7	1.2	1.2
CH_3−H	438.6 ± 1.1	−1.6	−1.0	2.2	2.2
CH_2F−H	418.8 ± 9.8		5.8	8.4	8.4
CH_2Cl−H	423.0 ± 4.3		−6.4	−3.7	−3.7
CH_2Br−H	419.7 ± 4.3		3.0	5.1	5.1
CH_2I−H	421.3 ± 6.8			4.1	6.2
CH_3−F	459.4 ± 5.1		−0.0	−3.0	−3.0
CH_3−Cl	350.7 ± 1.2		−0.9	−7.1	−7.1
CH_3−Br	291.8 ± 1.3		7.1	2.2	2.2
CH_3−I	238.1 ± 1.7			−0.5	1.2

[a] Experimental values were computed from the corresponding enthalpies of formation, taken from ref 7, except CH and CH_2 from ref 5, CHF and CHCl from ref 51, halomethyl radicals from ref 6, CH_3Br from ref 52, and CH_3I from ref 53.

extrapolation and a power-law extrapolation of the HF energy. As expected, Hartree−Fock theory largely overestimates the enthalpies of formation, with a negligible dependence on the size of the basis set. The deviations are greatly reduced by using Møller−Plesset second-order perturbation theory (MP2), with a significant dependence on the size of the basis set. As the basis set size increases, the MP2 deviations change sign and become progressively negative, and the best agreement with experimental values is seen for $\zeta = 3$, 4, and 5. The more elaborate MP4SDQ and CCSD methods systematically overestimate the calculated enthalpies of formation, although they both benefit by the increase of the basis set size. The inclusion of triple substitutions in MP4SDTQ has a dramatic increase in accuracy over MP4SDQ, with a dependence on the size of the basis set qualitatively similar to that of MP2. In particular, the RMS deviation at the MP4SDTQ/cc-pV(5+d)Z level of theory was found to be exceptionally low, 4.8 mol^{-1}. The importance of triple substitutions in the efficiency of coupled-cluster theory has been well established (see also ref 28), and it can also be seen clearly in the improvement of the CCSD(T) calculated enthalpies of formation over those of CCSD. The large errors exhibited by iodine fluoride (IF) are discernible across the entire range of ζ for MP4SDQ, CCSD, and CCSD(T) (IF was not included in the MP4SDTQ calculations). The plots in Figure 1 indicate that the gradual increase of the basis set size leads always to a strengthening of chemical bonds.[28] On the other hand, the corresponding effects of Hartree−Fock and post-SCF methods are widely varying from the HF, MP4SDQ, CCSD, and CCSD(T) methods which tend to underbind molecular systems, to MP2 and MP4SDTQ whose behavior varies as a function of basis set size. For the HF, MP4SDQ, and CCSD methods, their tendency cannot be compensated by the size of the basis set, and even at the infinite basis limit, their deviations from experimental values are still large. However, the small underbinding effect of CCSD(T) is gradually compensated by the opposite effect of the basis set, and thus CCSD(T) is only effective at large values of ζ.[28,37,38,45,46] In the case of the MP2 and MP4SDTQ methods, the counteracting errors of basis set convergence and electron correlation recovery are partially canceled out in the range of $\zeta = 3-6$, leading to thermochemical properties in nice agreement with experimental values, although this sense of confidence is obviously false.[28] Since MP4SDTQ is almost as expensive as CCSD(T), MP2 calculations with medium/large basis sets appear to be the best alternative in cases where the computational cost of CCSD(T) is prohibitive. The fortuitous success of levels of theory employing MP2 with medium-sized basis sets is reflected in the reliable structural parameters obtained at the MP2/6-311G(d) level of theory. In addition, it should be stressed that the accuracy of thermochemical properties obtained at levels of theory using CCSD(T) and small/medium basis sets (without any kind of basis set extrapolation or empirical corrections) is very low.

The bond-dissociation energies of all benchmark molecules containing more than two atoms were also calculated at high levels of theory employing CCSD(T) and infinite basis limits attained by the three-point CBS or the two-point IB schemes, and the results are shown in Table 10. By excluding the CCl−H bond, the overall RMS deviations for the CCSD(T)/CBS[TQ5] and CCSD(T)/CBS[DTQ] levels of theory were very low, 1.8 and 3.8 kJ mol^{-1}, for a total of 4 and 10 bonds, respectively. The overall RMS deviations for a total of 12 bonds at the CCSD(T)/IB[DT] and CCSD(T)/IB[(DT)] levels of theory were slightly higher, 4.1 and 4.3 kJ mol^{-1}, respectively. This nice agreement with experimental values suggests that the IB method possesses a comparable efficiency with CBS in calculating bond dissociation energies. The calculated C−H bond strengths by the IB method, of particular importance in tropospheric chemistry, can be very accurate since the errors in extrapolating electronic energies by using a certain set of α and β parameters are almost canceled out between the parent molecule and the corresponding radical.

The effect of the basis set superposition error (BSSE) on the bond dissociation energies calculated by IB was also examined by using the counterpoise method[88] in a set of 31 bond-fission processes for all benchmark molecules. Thus, the electronic energies of all species involved were calculated at the CCSD(T)/(cc)-pV(D+d)Z and CCSD(T)/(cc)-pV(T+d)Z levels of theory, and they were extrapolated to $n = 4$, 5, 6, and ∞. The results showed that BSSE was smoothly decreasing with basis set size, in a similar manner with very large nonextrapolated basis sets.[28] The corresponding average values of BSSE were 12.6, 6.7, 5.5, 5.0, 4.8, and 4.2 kJ mol^{-1}, for n = D, T, Q, 5, 6 and the infinite basis limit IB[(DT)], respectively. However, by correcting the calculated bond dissociation energies for BSSE, the agreement with experimental values deteriorated, and the overall RMS deviation was increased from 6.0 to 8.8 kJ mol^{-1} at the CCSD(T)/[IB(DT)] level of theory, for a set of 26 bonds (excluding the C−Cl, C−Br, CF−H, CCl−H, and I−F bonds). Since the BSSE should theoretically vanish at the infinite basis limit, its small nonzero average value of 4.2 kJ mol^{-1} was attributed to errors of the IB-extrapolated electronic energies, as shown by the higher BSSE for bonds involving bromine and iodine atoms (10.0, 9.7, 8.8, and 8.6 kJ mol^{-1} for I−I, Br−Br, CH_3−I, and CH_3−Br, respectively). Therefore, the

TABLE 11: Enthalpies of Formation at 298.15 K (in kJ mol^{-1}) for the Entire Set of Molecules at the CCSD(T)/IB[(DT)] Level of Theory, along with the Empirically Corrected and Experimental Values (Corresponding Deviations Are Shown in Parentheses)

molecule	experimental value[a]	CCSD(T)/ IB[(DT)]	CCSD(T)/ IB[(DT)] corrected[b]	molecule	experimental value[a]	CCSD(T)/ IB[(DT)]	CCSD(T)/ IB[(DT)] corrected[b]
H_2	0.0	−3.5 (−3.5)	−3.6 (−3.6)	$CHCl_2$	96.2 ± 9.0	106.2 (10.0)	96.7 (0.4)
F_2	0.0	4.5 (4.5)	3.3 (3.3)	$CHCl_2$	96.2 ± 9.0	106.2 (10.0)	96.7 (0.4)
Cl_2	0.0	10.3 (10.3)	4.3 (4.3)	CH_2Cl_2	−95.4 ± 4.2	−82.7 (12.7)	−93.1 (2.3)
Br_2	30.9 ± 0.1	35.3 (4.4)	34.1 (3.2)	CCl_3	79.5 ± 4.2	98.6 (19.1)	77.6 (−1.9)
I_2	62.4 ± 0.1	60.7 (−1.7)	59.5 (−2.9)	$CHCl_3$	−103.2 ± 4.2	−80.6 (22.6)	−102.6 (0.6)
ClF	−50.3 ± 4.0	−43.4 (6.9)	−46.0 (4.2)	CCl_4	−96.0 ± 8.4	−61.5 (34.5)	−99.3 (−3.3)
BrF	−58.5 ± 4.0	−44.8 (13.7)	−46.0 (12.4)	CHBr	373.0 ± 18.0	381.7 (8.7)	380.7 (7.7)
BrCl	14.6 ± 4.0	27.5 (12.9)	24.9 (10.2)	CBr_2	336.6 ± 50.0	357.1 (20.5)	354.6 (18.0)
IF	−94.8 ± 4.0	−63.8 (31.0)	−65.0 (29.8)	$CHBr_2$	188.3 ± 9.0	196.9 (8.7)	194.0 (5.7)
ICl	17.5 ± 4.0	28.0 (10.5)	25.3 (7.8)	CH_2Br_2	−10.9 ± 9.0	2.5 (13.4)	−1.0 (9.9)
HF	−272.5 ± 0.7	−270.4 (2.1)	−270.6 (1.9)	CHFCl	−62.8 ± 8.4	−54.4 (8.4)	−59.7 (3.0)
HCl	−92.3 ± 0.1	−92.9 (−0.6)	−93.3 (−1.0)	CH_2FCl	−261.9 ± 8.4	−256.4 (5.5)	−262.4 (−0.5)
HBr	−36.4 ± 0.2	−41.0 (−4.5)	−41.2 (−4.7)	CHFBr	−4.1	−7.1	
HI	26.4 ± 0.1	23.0 (−3.4)	22.8 (−3.6)	CH_2FBr	−208.6	−212.0	
CH	596.4 ± 4.0	595.6 (−0.8)	595.4 (−0.9)	CHClBr	156.1	150.8	
CF	255.2 ± 8.0	252.9 (−2.3)	252.1 (−3.1)	CH_2ClBr	−20.0 ± 7.0	−35.6 (−15.6)	−41.6 (−21.6)
CCl	502.1 ± 20.0	444.3 (−57.8)	442.7 (−59.4)	CHFI	53.6	50.6	
CBr	510.4 ± 63.0	500.2 (−10.2)	499.5 (−11.0)	CH_2FI	−150.3	−153.8	
CH_2	392.5 ± 2.1	390.2 (−2.3)	390.0 (−2.5)	CHClI	204.6	199.3	
CHF	157.0 ± 18.0	153.6 (−3.4)	152.6 (−4.4)	CH_2ClI	13.0	6.9	
CHCl	317.0 ± 18.0	328.5 (11.5)	326.4 (9.4)	CHBrI	247.9	244.9	
CH_3	145.7 ± 1.0	142.2 (−3.4)	141.8 (−3.9)	CH_2BrI	53.8	50.4	
CH_2F	−33.5 ± 8.4	−25.5 (7.9)	−26.9 (6.6)	CHI	428.0 ± 21.0	433.9 (5.9)	432.9 (4.9)
CH_2Cl	121.3 ± 4.2	121.3 (−0.0)	118.7 (−2.6)	CHI_2	333.9 ± 9.2	287.5 (−46.4)	284.5 (−49.4)
CH_2Br	167.4 ± 4.2	166.8 (−0.6)	165.5 (−1.9)	CH_2I_2	118.0 ± 4.2	102.8 (−15.2)	99.3 (−18.7)
CH_2I	217.6 ± 6.7	219.2 (1.6)	217.8 (0.3)	CH_3CH_2	119.0 ± 2.0	117.8 (−1.2)	116.1 (−2.9)
CH_4	−74.9 ± 0.4	−80.6 (−5.7)	−81.2 (−6.3)	CH_3CH_3	−83.8 ± 0.3	−91.3 (−7.4)	−93.4 (−9.5)
CH_3F	−234.3 ± 5.0	−234.8 (−0.5)	−236.4 (−2.1)	CH_3CH_2F	−263.6 ± 8.4	−273.5 (−9.9)	−277.4 (−13.8)
CH_3Cl	−83.7 ± 0.7	−80.0 (3.6)	−83.1 (0.5)	CH_2FCH_2	−54.6	−58.0	
CH_3Br	−34.3 ± 0.8	−40.0 (−5.7)	−41.6 (−7.3)	CH_3CHF	−71.1 ± 8.4	−70.6 (0.5)	−74.1 (−2.9)
CH_3I	14.3 ± 1.4	9.6 (−4.7)	8.0 (−6.3)	CH_3CH_2Cl	−112.3 ± 0.8	−110.5 (1.8)	−117.0 (−4.7)
CF_2	−194.1 ± 9.2	−183.2 (10.9)	−185.7 (8.4)	CH_2ClCH_2	92.0 ± 8.4	100.3 (8.3)	94.5 (2.5)
CHF_2	−238.9 ± 4.0	−233.6 (5.3)	−236.6 (2.3)	CH_3CHCl	73.6 ± 4.2	84.5 (10.9)	78.7 (5.1)
CH_2F_2	−450.7 ± 4.2	−446.3 (4.4)	−449.7 (1.0)	CH_3CH_2Br	−63.6 ± 8.4	−69.9 (−6.3)	−73.7 (−10.1)
CF_3	−470.3 ± 15.1	−453.8 (16.5)	−459.1 (11.2)	CH_2BrCH_2	133.9 ± 8.4	134.3 (0.4)	130.9 (−3.0)
CHF_3	−697.0 ± 4.2	−688.6 (8.4)	−694.5 (2.5)	CH_3CHBr	125.5 ± 8.4	130.2 (4.7)	126.8 (1.3)
CF_4	−930.0 ± 20.0	−921.2 (8.8)	−930.2 (−0.2)	CH_3CH_2I	−7.2 ± 0.8	−16.6 (−9.4)	−20.4 (−13.2)
CCl_2	238.5 ± 21.0	249.0 (10.5)	240.2 (1.7)	CH_2ICH_2	176.8	173.4	
				CH_3CHI	185.2	181.7	

[a] Experimental values taken from ref 7, except halomethyl radicals, $CHCl_2$, CH_2Cl_2, $CHBr_2$, CH_2Br_2, CHFCl, CH_3CH_2F, and haloethyl radicals from ref 6; CH, CH_2, CF_2, CHF_2, and CHI_2 from ref 5; CHF, CHCl, CHBr, and CHI from ref 51; CH_3Br from ref 52; CH_3I from ref 53; CBr_2 from ref 54; CH_2ClBr from ref 55; CH_2I_2 from ref 56; CH_3CH_2 from ref 57; CH_3CH_3 from ref 58; CH_3CH_2Cl from ref 59; CH_3CH_2Br from ref 60; and CH_3CH_2I from ref 61. [b] The electronic energies at the CCSD(T)/IB[(DT)] level of theory were lowered by $9.37 \times (N_{\mathrm{eff}})^{1.8}$ H, where $N_{\mathrm{eff}} = 1, 4, 7, 17, 7, 7$ for H, C, F, Cl, Br, I, respectively.

results suggest that inclusion of the BSSE correction in CCSD(T)/IB[DT] calculations is inappropriate because of the accumulation of extrapolation errors, and also impractical due to the slowly convergent coupled-cluster calculations in molecular systems containing ghost atoms.

The enthalpies of formation and the bond dissociation energies at 298.15 K for a larger set of molecules, including halomethanes, haloethanes, and the corresponding haloalkyl radicals, were calculated at the CCSD(T)/IB[(DT)] level of theory. The molecules $CH_{(4-k)}F_k$, $CH_{(4-k)}Cl_k$ ($k = 3,4$), CH_2XY (X,Y = F, Cl, Br, I), and CH_3CH_2X (X = H, F, Cl, Br, I) were selected, for most of which experimental enthalpies of formation are available.[5−9,54−61] Their structural parameters and vibrational frequencies were also calculated at the MP2/6-311G(d) level of theory, and they were verified to correspond to true potential energy minima by the absence of imaginary frequencies. The calculated frequencies were also scaled down by the factor 0.9872. The calculated enthalpies of formation and bond dissociation energies (corrected for spin−orbit splitting, CV, and SR contributions) at 298.15 K, along with the corresponding experimental values available, are shown in Tables 11 and 12, respectively.

For the set of 61 molecules (after exclusion of CCl, CBr, and IF), the overall RMS deviation of the calculated enthalpies of formation at the CCSD(T)/IB[(DT)] level of theory from experimental values was found to be 11.5 kJ mol^{-1}, with a mean absolute deviation of 8.3 kJ mol^{-1} and an average deviation of +3.2 kJ mol^{-1}, with several particularly large deviations for CF_3, CCl_3, $CHCl_3$, CCl_4, CH_2ClBr, CBr_2, CHI_2, and CH_2I_2, as shown in Table 11. Omission of the CV and SR corrections led to an increase of all three deviations by 1 kJ mol^{-1}, supporting the validity of the applied corrections and suggesting that the source of the large errors lies in the IB extrapolation method. Indeed, a closer look revealed that the enthalpies of formation for all species possessing more than one chlorine atom (Cl_2, CH_2Cl_2, $CHCl_2$, CCl_2, $CHCl_3$, CCl_3, and CCl_4) are consistently overestimated, and the deviations systematically increase with the number of chlorine atoms. It should be interesting to note that the IB extrapolation based on the sequence of the original cc-pVnZ (n = D,T) basis sets[48] for

TABLE 12: Bond Dissociation Energies at 298.15 K (in kJ mol^{-1}) for the Molecules of the Entire Set Possessing More than Two Atoms at the CCSD(T)/IB[(DT)] Level of Theory, along with the Empirically Corrected and Experimental Values (Corresponding Deviations Are Shown in Parentheses)

bond	experimental value[a]	CCSD(T)/ IB[(DT)]	CCSD(T)/IB[(DT)] corrected[b]	bond	experimental value	CCSD(T)/ IB[(DT)]	CCSD(T)/IB[(DT)] corrected[b]
$CH-H$	421.8 ± 4.5	423.3 (1.5)	423.5 (1.6)	CH_2Br-Br	290.1 ± 9.9	276.2 (−13.9)	278.3 (−11.8)
$CF-H$	316.2 ± 19.7	317.3 (1.0)	317.5 (1.3)	$CHFCl-H$	417.2 ± 11.9	420.0 (2.8)	420.6 (3.5)
$CCl-H$	403.1 ± 26.9	333.8 (−69.3)	334.3 (−68.8)	CH_2F-Cl	349.8 ± 11.9	352.1 (2.4)	356.8 (7.1)
CH_2-H	464.8 ± 2.3	466.0 (1.2)	466.2 (1.3)	CH_2Cl-F	462.6 ± 9.4	457.1 (−5.6)	460.5 (−2.1)
CH_3-H	438.6 ± 1.1	440.8 (2.2)	441.0 (2.4)	$CHFBr-H$		422.5	422.9
CH_2F-H	418.8 ± 9.8	427.2 (8.4)	427.5 (8.7)	CH_2F-Br		294.9	297.0
CH_2Cl-H	423.0 ± 4.3	419.3 (−3.7)	419.9 (−3.1)	CH_2Br-F		454.8	456.9
CH_2Br-H	419.7 ± 4.3	424.8 (5.1)	425.1 (5.5)	$CHClBr-H$		409.7	410.4
CH_2I-H	421.3 ± 6.8	427.5 (6.2)	427.8 (6.6)	CH_2Cl-Br	253.2 ± 8.2	268.7 (15.5)	272.2 (19.0)
CH_3-F	459.4 ± 5.1	456.4 (−3.0)	457.6 (−1.8)	CH_2Br-Cl	308.7 ± 8.2	323.7 (15.0)	328.4 (19.7)
CH_3-Cl	350.7 ± 1.2	343.6 (−7.1)	346.2 (−4.4)	$CHFI-H$		421.9	422.4
CH_3-Br	291.8 ± 1.3	294.1 (2.2)	295.3 (3.4)	CH_2F-I		231.5	233.6
CH_3-I	238.1 ± 1.7	239.4 (1.2)	240.6 (2.4)	CH_2I-F		448.9	451.0
$CHF-H$	408.5 ± 19.9	397.2 (−11.3)	397.5 (−11.0)	$CHClI-H$		409.7	410.3
$CHCl-H$	413.7 ± 18.5	425.2 (11.5)	425.7 (12.0)	CH_2Cl-I		215.1	218.6
$CHBr-H$	423.6 ± 18.5	432.9 (9.2)	433.2 (9.6)	CH_2I-Cl		327.5	332.2
$CHI-H$	428.4 ± 22.0	432.7 (4.3)	433.0 (4.6)	$CHBrI-H$		412.0	412.5
CH_2-F	505.4 ± 8.7	495.2 (−10.2)	496.2 (−9.1)	CH_2Br-I		219.7	221.8
CH_2-Cl	392.5 ± 4.7	390.2 (−2.2)	392.5 (0.1)	CH_2I-Br		277.2	279.3
CH_2-Br	337.0 ± 4.7	335.3 (−1.7)	336.3 (−0.7)	$CH-I$	275.1 ± 21.4	268.4 (−6.7)	269.3 (−5.8)
CH_2-I	281.7 ± 7.0	277.8 (−3.9)	278.9 (−2.8)	$CHI-I$	200.9 ± 22.9	253.2 (52.3)	255.1 (54.3)
$CF-F$	528.7 ± 12.2	515.5 (−13.2)	517.3 (−11.4)	CHI_2-H	433.9 ± 10.1	402.7 (−31.2)	403.2 (−30.7)
CF_2-H	262.8 ± 10.0	268.4 (5.6)	268.8 (6.0)	CH_2I-I	206.3 ± 7.9	223.2 (16.8)	225.3 (18.9)
$CHF-F$	475.3 ± 18.4	466.6 (−8.7)	468.6 (−6.7)	CH_3CH_2-H	420.8 ± 2.0	427.1 (6.2)	427.4 (6.6)
CHF_2-H	429.8 ± 5.8	430.7 (0.9)	431.1 (1.4)	CH_3-CH_3	375.2 ± 1.4	375.7 (0.5)	376.9 (1.7)
CH_2F-F	496.6 ± 9.4	500.1 (3.5)	502.2 (5.6)	CH_3CHF-H	410.5 ± 11.9	420.9 (10.4)	421.3 (10.9)
CF_2-F	355.6 ± 17.7	350.0 (−5.6)	352.8 (−2.8)	CH_2FCH_2-H		437.0	437.4
CF_3-H	444.8 ± 15.7	452.8 (8.1)	453.4 (8.6)	CH_3-CH_2F	375.8 ± 11.9	390.2 (14.4)	392.3 (16.5)
CHF_2-F	537.5 ± 5.8	534.4 (−3.1)	537.3 (−0.2)	CH_2F-CH_2		419.2	421.1
CF_3-F	539.1 ± 25.1	546.8 (7.7)	550.5 (11.4)	CH_3-CHF	373.8 ± 19.9	366.5 (−7.3)	368.5 (−5.4)
$CCl-Cl$	384.9 ± 20.0	316.6 (−68.3)	323.8 (−61.1)	$CH_3CHCl-H$	403.9 ± 4.3	413.1 (9.1)	413.7 (9.8)
CCl_2-H	360.3 ± 9.0	360.8 (0.5)	361.6 (1.3)	CH_2ClCH_2-H	422.3 ± 8.4	428.9 (6.5)	429.5 (7.2)
$CHCl-Cl$	342.1 ± 20.1	343.6 (1.5)	351.1 (9.0)	CH_3-CH_2Cl	379.3 ± 4.4	374.1 (−5.3)	377.5 (−1.8)
$CHCl_2-H$	409.6 ± 9.9	407.0 (−2.7)	407.8 (−1.9)	CH_2Cl-CH_2	421.8 ± 9.6	411.2 (−10.6)	414.2 (−7.6)
CH_2Cl-Cl	338.0 ± 5.9	325.3 (−12.7)	333.2 (−4.9)	CH_3-CHCl	389.0 ± 18.5	386.2 (−2.8)	389.5 (0.5)
CCl_2-Cl	280.3 ± 4.2	271.7 (−8.6)	283.9 (3.6)	$CH_3CHBr-H$	407.1 ± 11.9	418.1 (10.9)	418.5 (11.4)
CCl_3-H	400.7 ± 5.9	397.2 (−3.5)	398.3 (−2.4)	CH_2BrCH_2-H	415.5 ± 11.9	422.2 (6.7)	422.6 (7.1)
$CHCl_2-Cl$	320.7 ± 9.9	308.1 (−12.6)	320.6 (−0.1)	CH_3-CH_2Br	376.6 ± 9.4	378.9 (2.3)	381.0 (4.4)
CCl_3-Cl	296.8 ± 9.4	281.4 (−15.4)	298.2 (1.4)	CH_2Br-CH_2	426.0 ± 9.6	422.7 (−3.3)	424.5 (−1.4)
$CBr-H$	355.4 ± 65.5	336.5 (−18.9)	336.8 (−18.6)	CH_3-CHBr	393.2 ± 19.9	393.7 (0.6)	395.7 (2.5)
$CH-Br$	335.2 ± 18.4	325.7 (−9.5)	326.6 (−8.6)	CH_3CHI-H		419.7	420.2
$CBr-Br$	285.7 ± 80.4	254.9 (−30.8)	256.7 (−29.0)	CH_2ICH_2-H		411.4	411.8
CBr_2-H	366.3 ± 50.8	378.2 (11.9)	378.6 (12.3)	CH_3-CH_2I	370.5 ± 6.8	378.0 (7.5)	380.1 (9.6)
$CHBr-Br$	296.6 ± 20.1	296.6 (0.0)	298.6 (2.0)	CH_2I-CH_2		432.6	434.4
$CHBr_2-H$	417.2 ± 12.7	412.5 (−4.7)	412.9 (−4.2)	CH_3-CHI		391.0	392.9

[a] Experimental values were computed from the corresponding enthalpies of formation taken from ref 7, except halomethyl radicals, $CHCl_2$, CH_2Cl_2, $CHBr_2$, CH_2Br_2, CHFCl, CH_3CH_2F, and haloethyl radicals from ref 6; CH, CH_2, CF_2, CHF_2, and CHI_2 from ref 5; CHF, CHCl, CHBr, and CHI from ref 51; CH_3Br from ref 52; CH_3I from ref 53; CBr_2 from ref 54; CH_2ClBr from ref 55; CH_2I_2 from ref 56; CH_3CH_2 from ref 57; CH_3CH_3 from ref 58; CH_3CH_2Cl from ref 59; CH_3CH_2Br from ref 60; and CH_3CH_2I from ref 61. [b] The electronic energies at the CCSD(T)/IB[(DT)] level of theory were lowered by $9.37 \times (N_{\mathrm{eff}})^{1.8}$ H, where $N_{\mathrm{eff}} = 1, 4, 7, 17, 7, 7$ for H, C, F, Cl, Br, I, respectively.

chlorine (using the initial values of $\alpha = 3.39$ and $\beta_{\mathrm{CCSD(T)}} = 2.02^{43b}$) was even worse, with a maximum deviation of 50 kJ mol^{-1} for CCl_4. Thus, the improved convergence properties of the cc-pV(n+d)Z basis sets[50] could also be reflected in the improved performance of the IB-extrapolated values. However, particularly large deviations for halogenated molecules were also obtained in earlier studies employing the compound methods G2, G2(MP2), CBS-4 and, CBS-Q.[15,17] In fact, these deviations systematically increased with the number of halogen atoms, allowing the application of bond additivity corrections (BAC) which improved the agreement with experiment.[15] Moreover, the behavior of the Gaussian compound methods (G2, G3, and their variants[89,90]) was found to be markedly different from the family of CBS methods (CBS-4, CBS-Q[35,91]) and CCSD(T) complete basis set extrapolation schemes,[20,22] with respect to their ability to calculate reliable enthalpies of formation for highly fluorinated and chlorinated species.[13,15,17,20,22,27,29,32] In general, complete basis set methods were shown to be capable of computing reliable thermochemical properties for fluorinated species, while they potentially and systematically failed in the case of the chlorinated ones.[15,17] The enthalpies of formation for all chloromethanes and chloromethyl radicals have also been calculated at the MP4SDTQ/6-311G(2df,p) level of theory, succeeding in a remarkable agreement within ca. 4 kJ mol^{-1} with experimental values,[14] apparently due to a fortuitous cancellation of errors, as was previously discussed. However, recent (R/U)CCSD(T)/CBS[aDTQ] calculations in a set of large molecules led to much lower deviations of ca. 6 kJ mol^{-1} for the atomization energies of $CHCl_3$ and CCl_4, by employing the combined Gaussian/exponential CBS extrapolation formula and the sequence of AUG-cc-pV(n+d)Z (n = D, T, Q) basis sets.[37] Therefore, apart from the presence of diffuse functions whose effect would be a rather slight improvement of the results (as was previously shown), the addition of a third point (for n = Q) in the extrapolation scheme induces a dramatic increase in accuracy over the two-point IB extrapolation.

The case of CH_2ClBr deserves some attention, since its CCSD(T)/IB[DT] calculated enthalpy of formation is lower by 15.6 kJ mol^{-1} from the most recent experimental value,[7,55] in contrast with the overall tendency of the CCSD(T)/IB[(DT)] level for all other molecules containing more than one halogen atom. The enthalpies of formation of CH_2ClBr as well as of the CHClBr radical were previously determined at various levels of theory including G2 and the concepts of hydrogenation and isodesmic reactions.[23] The G2 results were close to earlier experimental values,[92,93] suggesting the values of −46.9 and +146.0 kJ mol^{-1} for CH_2ClBr and CHClBr, respectively. Our CCSD(T)/IB[DT] values are closer to those calculated by G2 theory, with an average difference of +10 kJ mol^{-1}. Therefore, both G2 and CCSD(T)/IB[DT] results probably indicate that the recently reported value of -20.0 ± 7.0 kJ mol^{-1} [7,55] for the enthalpy of formation of CH_2ClBr is overestimated by as much as 25 kJ mol^{-1}. The disagreement observed for CH_2I_2 and CHI_2 could be attributed to computational errors as well as to erroneous experimental enthalpies of formation, especially for CHI_2.

The contribution of the molecular second-order spin−orbit effects to computational accuracy was also considered, since omission of these effects could adversely affect the calculated properties for the heavy bromine- and iodine-containing molecules. Previous calculations using an adequate treatment of electron correlation and relativistic effective-core potentials have provided the magnitude of these effects which lead to an increase of molecular binding.[94,95] The corresponding corrections to the enthalpies of formation were inferred from the published data, and were found to be −0.4 kJ mol^{-1} for HBr and Br_2,[94] and −5.0 and −5.7 kJ mol^{-1} for HI and CH_3I, respectively.[95] While the second-order spin−orbit corrections are indeed negligible for bromine-containing molecules, they become comparable (and of opposite sign) with the corresponding SR corrections for HI and CH_3I. However, their magnitude is smaller than the uncertainty assumed for the IB procedure in iodine-containing molecules (±10 kJ mol^{-1}), and, thus, they were ignored.

The individual contribution of the Hartree−Fock extrapolation error was examined in a subset of molecules, including several large ones. Thus, the HF/CBS[TQ5] electronic energies were first computed by the combined Gaussian/exponential function for the molecules HX, X_2 (X = F,Cl,Br), $CH_{(4-k)}F_k$, $CH_{(4-k)}Cl_k$ ($k = 2-4$), CH_2Br_2, CH_3CH_2X (X = H, F, Cl, Br), and various halomethylenes and halomethyl radicals. Subsequently, the deviations of the zero-point exclusive HF/IB[DT] atomization energies from those calculated at the HF/CBS[TQ5] level were computed for both forms of the HF energy extrapolation (power-law and exponential), and the results are shown in Table 13. The data for this wider set of molecules strongly suggest that the IB method is virtually insensitive to the form of HF energy extrapolation, provided that appropriately optimized α parameters are employed. It is also evident that the deviations from the HF/CBS[TQ5] atomization energies are very small for molecules possessing chlorine atoms, and the largest deviations from the HF/CBS[TQ5] atomization energies are surprisingly exhibited by fluorine-containing molecules, with a maximum of 8.2 kJ mol^{-1} for CF_4. The overall RMS deviation was very small, 2.2 kJ mol^{-1}, with could be further lowered to 1.6 kJ mol^{-1} by a re-optimization of the α parameter to a value of 5.84 or 2.37, for the power-law or exponential form, respectively. Therefore, the errors in the HF energy extrapolation constitute a minor component of the large systematic deviations presented by the IB method. The use of α = 5.84 resulted in an increase of the RMS deviation for the entire set of molecules by 0.5 kJ mol^{-1}, which suggested that a re-optimization of the $\beta_{CCSD(T)}$ parameter was also required by a procedure which should use the reliable experimental values as reference. Therefore, by varying $\beta_{CCSD(T)}$, a minimization of the RMS deviation between the calculated enthalpies of formation (including spin−orbit, CV, and SR corrections) and the experimental ones was performed for all molecules, excluding CCl, CBr, IF, CH_2ClBr, CBr_2, CHI_2, and CH_2I_2. The RMS deviation was lowered from 10.4 to 9.2 kJ mol^{-1} for $\beta_{CCSD(T)} = 2.22$, although large deviations were still persisting for most chlorine-containing molecules (30.9 kJ mol^{-1} for CCl_4). A simultaneous optimization of parameters α and $\beta_{CCSD(T)}$ could lower the RMS deviation even further to 8.2 kJ mol^{-1} for α = 3.17 and $\beta_{CCSD(T)} = 2.50$, with a negligible decrease of the individual large deviations by 1 kJ mol^{-1}.

TABLE 13: Deviations (in kJ mol^{-1}) of the Zero-Point Exclusive HF/IB[DT] Atomization Energies from Those Calculated at the HF/CBS[TQ5] Level of Theory

molecule	HF/IB[DT] (power-law extrapolation)[a]	HF/IB[DT] (exponential extrapolation)[b]
HF	−2.1	−2.1
F_2	3.3	3.3
Cl_2	0.6	0.6
HCl	−0.4	−0.4
Br_2	0.5	0.5
HBr	−0.3	−0.3
CH_2F	−0.2	−0.2
CH_3F	0.2	0.2
CH_2Cl	0.2	0.2
CH_3Cl	0.7	0.7
CH_2Br	2.1	2.1
CH_3Br	1.8	1.8
CF_2	2.6	2.6
CHF_2	1.3	1.3
CH_2F_2	2.2	2.2
CF_3	3.9	3.9
CHF_3	5.2	5.2
CF_4	8.2	8.1
CCl_2	−1.3	−1.3
$CHCl_2$	−0.6	−0.6
CH_2Cl_2	0.4	0.4
CCl_3	−0.8	−0.8
$CHCl_3$	0.4	0.4
CCl_4	−0.0	−0.1
CBr_2	0.1	0.1
$CHBr_2$	1.3	1.3
CH_2Br_2	1.6	1.5
CH_3CH_2	0.2	0.2
CH_3CH_3	0.8	0.8
CH_3CH_2F	1.0	1.0
CH_3CH_2Cl	0.5	0.5
CH_3CH_2Br	1.3	1.2

[a] α = 5.02. [b] α = 2.04.

Calculations of the dependence of the electron correlation on the size of cc-pVnZ basis sets for first-row atoms have shown that there is a significant loss of correlation recovery for $n = 2$, which gradually increases across the row and is maximized for the rightmost elements.[28] Since IB is heavily relying on electronic energies calculated for $n = 2$, this could provide an additional explanation of its systematic errors, which can be clearly attributed to the inadequacy of the (D,T)-extrapolation of correlation energy. Furthermore, the loss of correlation recovery for the rightmost elements suggests that the present application of IB in halogen-containing molecules represents its most difficult case, expecting a better performance for molecular systems containing other (excluding noble gases) main-group elements. The systematic nature of the errors and the inability to provide corrections by a refinement of the IB extrapolation parameters suggested that a drastic improvement could be possibly achieved by empirical adjustments, which should take into account the dependence of the error on the number of halogen atoms present, and mostly chlorine atoms. Thus, the variable N_{eff}, corresponding to an effective number of electrons for each species, was introduced, taken to be the sum of an effective number of electrons arbitrarily defined for each constituent atom, which for elements excluding chlorine was the number of their valence electrons (1, 4, 7, 7, and 7 for H, C, F, Br, and I, respectively), while for Cl it was taken to be 17, its total number of electrons. The systematic overestimation of the molecular enthalpies of formation could be corrected by lowering the total energy, E_{tot}, of all species by the expression:

$$E_{\mathrm{tot}} = E_{\mathrm{tot}} - Q(N_{\mathrm{eff}})^{\gamma}$$

where Q and γ are adjustable parameters. These two parameters were simultaneously adjusted by minimizing the overall RMS deviation of the calculated enthalpies of formation from the experimental ones (including spin−orbit, scalar-relativistic, and core/valence correlation corrections), for both forms of the Hartree−Fock energy extrapolation, excluding CCl, CBr, IF, CH_2ClBr, CBr_2, CHI_2, and CH_2I_2. By using either form of the Hartree−Fock energy extrapolation (with $\alpha = 5.02$ or 2.04, for the power-law or exponential form, respectively, and $\beta_{\mathrm{CCSD(T)}} = 2.41$), the total RMS deviation for a set of 57 molecules was lowered from 9.4 to 5.7 kJ mol^{-1} for $Q = 9.37 \times 10^{-6}$ and $\gamma = 1.80$. The corresponding RMS deviation for a set of 76 bond dissociation energies (excluding also those containing the molecules above) could be lowered from 7.1 to 6.3 kJ mol^{-1}. The corrected CCSD(T)/IB[(DT)] enthalpies of formation and bond dissociation energies are also listed in the second column of Tables 11 and 12, respectively. The empirically corrected thermochemical properties calculated for halogen-containing molecules at the CCSD(T)/IB[(DT)] levels of theory can be considered sufficiently accurate, with an error bar on the order of ±10 kJ mol^{-1}.

Conclusions

The infinite basis extrapolation method (IB), based on the double- and triple-ζ correlation-consistent basis sets, IB[DT], has been applied to a series of halogenated molecules, containing all four halogen atoms, including spin−orbit, core/valence-correlation, and scalar-relativistic corrections. The sequence of the new correlation-consistent basis sets cc-pV(n+d)Z for chlorine was employed, and the values of the IB extrapolation parameters were re-optimized by using the zero-point exclusive atomization energies calculated by a three-point CBS extrapolation as reference. No significant differences in the calculated properties were found by using either a power-law or an exponential extrapolation of the Hartree−Fock energy. The use of the relatively small SV4P and 6-311G(3df) basis sets for iodine was very successful in approximating the convergence properties of the first two members of correlation-consistent basis sets. The MP2/6-311G(d) level of theory was shown to be sufficiently accurate for geometry optimization purposes, especially for halogenated diatomic molecules. The core/valence and scalar-relativistic corrections to the calculated thermochemical properties were computed at the CCSD(T,FU/FC)/(cc)-pV(D+d)Z and MCPF-MVD/(cc)-pV(T+d)Z levels of theory, and they led to a better agreement with experimental values.

The systematic errors in the extrapolation of the correlation energy by the IB method were empirically corrected by lowering the CCSD(T)/IB[(DT)] energies by the quantity $Q(N_{\mathrm{eff}})^{\gamma}$ where N_{eff} is the sum of the effective number of electrons for all constituent atoms (defined as 1, 4, 7, 17, 7, and 7 for H, C, F, Cl, Br, and I, respectively). A fit to reliable experimental data yielded the values 9.37×10^{-6} and 1.80 for the parameters Q and γ, respectively. The empirically corrected CCSD(T)/IB-[(DT)] values for a set of 57 enthalpies of formation presented an RMS deviation of 5.7 kJ mol^{-1}, while the corresponding deviation for a set of 76 bond dissociation energies was 6.3 kJ mol^{-1}. Therefore, empirically corrected CCSD(T) energies extrapolated by the IB method can reach the accuracy of a CBS-[DTQ] extrapolation which is an order of magnitude more expensive, and constitute a computationally affordable level of theory for the calculation of the thermochemical properties for halogen-containing molecules with an estimated uncertainty of ±10 kJ mol^{-1}.

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