

## Computationally Efficient Methodology to Calculate C–H and C–X (X = F, Cl, and Br) Bond Dissociation Energies in Haloalkanes

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A computationally efficient method for calculating C–H and C–X (X = F, Cl, and Br) bond dissociation energies in haloalkanes has been developed by determining correction factors to MP2/cc-pVtz energies. Corrections for basis set effects were determined by the difference in bond dissociation energies calculated at the MP2/cc-pVtz and MP2/cc-pV5z levels, and correlation effects were corrected by calculating the difference in energies at the MP2/cc-pVtz and CCSD(T)/cc-pVtz levels. Subsequent corrections for the spin–orbit energy of the atomic fragment and zero-point energy were applied to give a final bond dissociation energy. The correction factors were determined using CH<sub>4</sub>, CH<sub>3</sub>F, CH<sub>3</sub>Cl, and CH<sub>3</sub>Br and are found to yield bond dissociation energies in excellent agreement with experimental results. This correction may also be broadly applied to multihalogen compounds, as shown in calculations of the C–H and C–X bond dissociation energies of CH<sub>2</sub>X<sub>2</sub> and CHX<sub>3</sub> (X = F, Cl, and Br) compounds, which accurately reproduce experimental values.

### I. Introduction

The study of small haloalkanes has broad-reaching implications in the understanding of atmospheric chemistry.<sup>1</sup> Gas-phase hydrogen abstraction reactions involving these systems have received renewed attention, mainly as a result of environmental concern associated with emission of atmospheric pollutants. Hydrogen abstraction by either hydroxyl radicals<sup>2,3</sup> or reactive chlorine atoms in the troposphere and, in particular, in the marine boundary layer<sup>4–6</sup> is a reaction pathway by which the oxidation of atmospheric pollutants is initiated in the atmosphere. Hydrogen abstraction reactions of simple alkanes and their halogenated derivatives are of particular interest because of the natural abundance of such species in the atmosphere. Methane, CH<sub>4</sub>, is abundant at midstratospheric levels,<sup>7</sup> while CH<sub>3</sub>Cl is one of the most abundant halogenated methanes in nature.<sup>8</sup> In addition to oceanic sources, the anthropogenic emission of CH<sub>3</sub>Br as a soil fumigant is important.<sup>9</sup> Multihalogen compounds, such as CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, and CHBr<sub>2</sub>Cl, are primarily released into the atmosphere by biogenic sources as a result of photosynthetic processes<sup>10</sup> and have long atmospheric lifetimes (> 14 days) and moderate (parts per trillion, volume) concentrations in the troposphere.<sup>11</sup> Understanding the reactivity of these species with OH and Cl is essential to estimating their atmospheric lifetime, which determines the efficiency of transport of haloalkanes to the stratosphere.

The reactivity trends for hydrogen abstraction from halogenated alkanes has been found to be strongly correlated to the C–H bond dissociation energies of these species.<sup>12,13</sup> Pickard and Rodgers<sup>14</sup> have reported C–H bond energies for the full series of fluoromethanes, and C–H bond energies for chloro-

romethanes have been reported by Weissman and Benson.<sup>15</sup> Until recently, however, the C–H bond energies for the bromomethanes had not been reported in the literature. Several studies have recently been performed to determine the relevant thermodynamic quantities, both theoretically and experimentally, for bromomethanes and to examine their atmospheric impact.<sup>16–20</sup> There are numerous kinetic studies of hydrogen abstraction reactions by Cl atoms with CH<sub>3</sub>F,<sup>21–23</sup> with CH<sub>3</sub>Cl,<sup>12,21,24</sup> and with CH<sub>3</sub>Br.<sup>13,25</sup> The kinetics of hydrogen abstraction by OH radicals for the same series of halogenated methanes are also well documented.<sup>1,21</sup> The reactions of Cl and OH with CH<sub>2</sub>BrCl, CHBrCl<sub>2</sub>, CF<sub>3</sub>CHBrCl, and CBr<sub>2</sub>Cl<sub>2</sub> have also been recently studied.<sup>26</sup> Although a computational determination of the energies and structures of the transition states for abstraction reactions could provide an avenue for obtaining direct rate information for modeling studies, such calculations are time-consuming and impractical given the large number of relevant chemical species. The previously observed correlation between hydrogen abstraction rates and C–H bond energies suggests that trends in reactivity and relative rate constants can be estimated from accurate ab initio calculations of bond strengths.

The relative strengths of carbon–halogen bonds also have other important atmospheric consequences. Many multihalogen compounds have reaction rates with hydroxyl radicals in the troposphere that exceed rates of removal by solar photolysis. However, the higher solar flux at shorter wavelengths in the stratosphere results in the rapid photodissociation of halogenated compounds that are transported to the stratosphere. Understanding the ultraviolet photolysis of these compounds and the fate of the resulting free radicals provides important insights into the complex chemistry of chlorine and bromine in the stratosphere. The determination of bond dissociation energies also provides information on the energetics of haloalkyl radicals,

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allowing their overall reactivity to be estimated. In addition, the ultraviolet absorption spectra of haloalkanes, which reflect the propensity of such compounds to undergo solar photolysis, are influenced by the strength of the C–X bond. A weakening of the C–X bond produces a red shift in the  $n \rightarrow \sigma^*$  absorption transition. Photodissociation experiments that examine the detailed photochemistry of these molecules often require an accurate knowledge of bond dissociation energies in order to confirm photochemical quantum yields, assess energy partitioning, and correctly distinguish between possible dissociation mechanisms.

Despite the importance of such fundamental thermochemical and photochemical information, bond energies are notoriously difficult to determine experimentally. The primary method for the experimental determination of bond dissociation energies is bomb calorimetry, but accurate measurements using this method require the precise knowledge of numerous experimental parameters that are difficult to determine. Calculations should provide an alternative avenue for the determination of these bond energies. However, conventional computational methods yielding bond energies in haloalkanes at sufficient accuracy are at present exceedingly expensive and often prohibitive, especially when more than one halogen atom is present in the molecule. Calculations are commonly performed using a set of isodesmic reactions in order to approximately cancel basis set superposition errors (BSSE). However, the accuracy of isodesmic reaction calculations depends not only on the level of theory itself but also on the accuracy of the experimental data utilized. In this study, we present a computational method of moderate expense for the calculation of the carbon–halogen and carbon–hydrogen bond energies of haloalkanes. This method not only rivals coupled cluster methods in its accuracy but also uses basis sets that yield very small BSSE. The procedure has been developed by calculating bond dissociation energies for  $\text{CH}_4$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CH}_3\text{Br}$  with a large number of basis sets and different levels of correlation. It was found that the results of second-order Moller–Plesset (MP2) calculations using correlation consistent polarized valence (cc-pV $xz$ ) basis sets may successfully be corrected for basis set effects (infinite basis set approximation) and electron correlation followed by corrections for spin–orbit energy and zero-point energies to give a final bond energy.<sup>27,28</sup> We show that these correction factors may be broadly applied to multihalogen compounds,  $\text{CH}_2\text{X}_2$  and  $\text{CHX}_3$  (X = F, Cl, and Br) in this paper, where the use of highly correlated methods and large basis sets is prohibitive. We also illustrate that the correlation consistent basis sets (only recently developed for bromine by Dunning and co-workers<sup>29</sup>) are more suitable for the accurate calculation of bond energies than the widely used 6-31 $x$ G basis sets, even when a large number of polarization and diffuse functions are included.

## II. Calculations

The accurate but computationally efficient calculation of bond-breaking energies is a difficult task, especially for bonds involving elements from the second and third rows of the periodic table. Calculations with large basis sets at high levels of electron correlation for many haloalkanes are beyond present computational capabilities even on supercomputers; therefore, we have adopted and tested the following strategy. (1) We have performed second-order Moller–Plesset (MP2) and coupled-cluster with single and double excitations using perturbative triple excitations (CCSD(T)) calculations with a large number of different Pople-style (6-31 $x$ G) and correlation-consistent polarized valence (cc-pV $xz$ )<sup>29–31</sup> basis sets for  $\text{CH}_3\text{X}$  (X = H,

**TABLE 1: Correlation and Basis Set Effects on the Calculated Equilibrium Geometry of  $\text{CH}_3\text{Br}$  (Distances in Angstroms and Angles in Degrees)**

method and basis set	$r(\text{C}-\text{H})$	$r(\text{C}-\text{Br})$	$\alpha(\text{Br}-\text{C}-\text{H})$
MP2/cc-pVdz	1.098	1.938	108.3
MP2/cc-pVtz	1.083	1.905	109.0
MP2/6-311+G*	1.087	1.940	108.3
MP2/6-311++G(2df,2p)	1.082	1.932	108.1
MP2/6-311++G(3df,3pd)	1.083	1.929	108.1
CCSD(T)/6-311++G(2df,2p)	1.084	1.946	107.9
CCSD(T)/cc-pVdz	1.101	1.953	108.1
CCSD(T)/6-311++G(3df,3pd)	1.085	1.944	107.9
experiment <sup>a</sup>	1.095	1.939	107.2

<sup>a</sup> Ref 42.

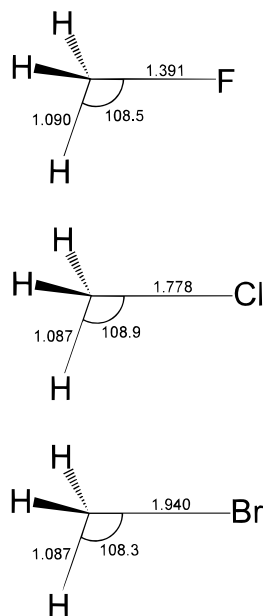
F, Cl, and Br) and evaluated the C–H and C–X bond dissociation energies at all levels. (2) We have developed correction factors for basis set effects (approximating the infinite basis set limit) and correlation effects (calculating the difference between the MP2 and CCSD(T) levels). (3) We have applied correction factors for the zero-point energies and, for C–X bond breaking, the spin–orbit energy of the atomic fragment. (4) We have tested the applicability of the correction factors to molecules containing more than one halogen atom.

Full geometry optimizations were performed and vibrational frequencies were evaluated at several different levels. All calculations were performed using Gaussian 94<sup>32</sup> or Gaussian 98.<sup>33</sup> MP2 and CCSD(T) calculations were performed by correlating only the valence electrons (frozen core approximation) unless noted otherwise. For the bond dissociation energy calculations, zero-point corrections and frequencies were determined at the MP2/6-311+G\* level. Other frequency calculations are identified specifically in the text. Vibrational frequencies were left unscaled. Basis set superposition errors (BSSE) were calculated using the counterpoise method.<sup>34</sup>

## III. Results and Discussion

**Geometries and Frequencies.** Full geometry optimizations were performed for all species at the MP2 and CCSD(T) levels using a number of different basis sets. As an illustrative example, Table 1 shows the dependence of the characteristic distances and angles for  $\text{CH}_3\text{Br}$  at different levels of theory. In general, all calculated geometries were consistent with available experimental geometries.<sup>35–42</sup> Basis set effects are important in the calculated geometries, resulting in relatively large changes between calculations performed using double- and triple- $\zeta$  basis sets. The cc-pV $xz$  basis sets performed consistently worse for the C–H bond lengths than the 6-31 $x$  basis sets in reproducing the experimental values, typically yielding  $>0.01$  Å larger C–H bond lengths. The level of correlation, however, had a substantially smaller effect on the calculated geometry. Bond lengths typically differed by  $<0.005$  Å and angles by  $\sim 0.2^\circ$  when optimizing at the MP2 and CCSD(T) levels. In general, however, the bond dissociation energy is relatively insensitive to the geometry used. CCSD(T)/cc-pVdz level bond dissociation energies change only 0.03 kcal/mol when calculated at the CCSD(T)/cc-pVdz geometry instead of the MP2/6-311+G\* geometry, despite the more than 0.01 Å change in the C–H internuclear distances. Therefore, we have selected the MP2/6-311+G\* level for further geometry optimizations as a good compromise between accuracy and computational cost. Figure 1 illustrates the optimized structures at this level of theory for  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ , and  $\text{CH}_3\text{Br}$ .

Harmonic vibrational frequencies were calculated at several levels of theory with numerous basis sets. Representative results



**Figure 1.** MP2/6-311+G\* optimized structures of CH<sub>3</sub>X (X = F, Cl, and Br).

are provided in Table 2 for the CH<sub>2</sub>X (X = H, F, Cl, and Br) radicals calculated at the MP2/6-311++G(2df,2p) and CCSD(T)/6-311++G(2df,2p) levels of theory. For these species, there are a total of six fundamental vibrational frequencies. All six frequencies for CH<sub>3</sub>, CH<sub>2</sub>F, CH<sub>2</sub>Cl, and CH<sub>2</sub>Br species are positive, indicating that minima on the potential energy surfaces were found in each case. The calculated frequencies show only a modest dependence on the computational method. The MP2 frequency calculations agree well with the CCSD(T) calculations, differing by less than 75 cm<sup>-1</sup> for every mode. With the exception of the  $\nu_4$  umbrella-type motion, the calculated values also show good agreement with the experimental values, though the C–H stretching frequency in CH<sub>3</sub> is overestimated by 144 cm<sup>-1</sup> for the MP2/6-311++G(2df,2p) calculation. For both calculations, the  $\nu_4$  umbrella mode is significantly underestimated, deviating from experimental results for CH<sub>2</sub>Br by over 300 cm<sup>-1</sup> at the MP2/6-311++G(2df,2p) level and over 200 cm<sup>-1</sup> at the CCSD(T)/6-311++G(2df,2p) level. In general, such a large error in a vibrational frequency would be expected to introduce error into the zero-point correction. However, the difference is in a low-frequency mode that contributes little to the total zero-point energy. We find that the MP2/6-311+G\* and CCSD(T)/6-311++G(2df,2p) zero-point energy corrections agree to within 0.2 kcal/mol and do not consider this error to be significant for the carbon–halogen bond energies.

**CH<sub>3</sub>–X Bond Dissociation Energies.** Our goal is the development of a method for the direct calculation of bond dissociation energies in halogenated hydrocarbons that may be applied to molecules with multiple halogen atoms. The direct calculation of bond dissociation energies for multihalogen molecules is presently beyond the reach of most highly accurate theoretical methods, which include a high level of electron correlation and large basis sets. In light of this difficulty, we have developed a methodology for the calculation of C–X bond energies with only moderate computational expense. In the first step, we determine C–X bond dissociation energies in the simplest halogenated hydrocarbons (CH<sub>3</sub>X, X = H, F, Cl, and Br) at different levels of theory and with several different basis sets. Representative results, after zero-point correction, are shown for the C–Cl bond dissociation energy of CH<sub>3</sub>Cl in Figure 2.

It can be seen in the figure that both basis set effects and correlation effects play an important role in the calculated values of the bond dissociation energies. A change from a double- $\zeta$  to a triple- $\zeta$  level basis set (namely, from 6-31G\* to 6-311++G-(3df, 3pd) or from cc-pVdz to cc-pVtz) changes the bond dissociation energy by approximately 6 kcal/mol. In this region, the traditional Gaussian-type 6-31xG basis sets and the correlation consistent sets are of comparable accuracy. However, when one applies higher level correlation consistent basis sets (namely, cc-pVqz or cc-pV5z), there is an additional 4 kcal/mol change in the value of the bond dissociation energy, as shown in Figure 2. The addition of any number of polarization and diffuse functions to traditional 6-31xG basis sets cannot account for this 4 kcal/mol change in energy. Since there is only a very modest improvement over the cc-pVqz result when the cc-pV5z basis set is used, we conclude that the cc-pV5z results represent a fair approximation to the infinite basis set limit. There are two other observations illustrating the same point. First, the effect of using the augmented correlation consistent sets (aug-cc-pVxz versus cc-pVxz) is almost completely diminished at the 5z level. Second, the BSSE calculated by the counterpoise method decreases for the C–Cl bond in CH<sub>3</sub>Cl from 3.4 kcal/mol using the cc-pVdz basis set to 0.7 kcal/mol using the cc-pVqz basis set. Though the counterpoise correction does not necessarily provide an upper limit to the BSSE, it can provide a reasonable approximation.<sup>43</sup> Since the BSSE at the cc-pVqz level is less than 1 kcal/mol, it is reasonable to assume that the BSSE may safely be neglected at the 5z level. It is also interesting to point out that the BSSE is still 2.7 kcal/mol for the C–Cl bond of CH<sub>3</sub>Cl when using the largest available traditional Gaussian-type set, 6-311++G(3df,3pd).

To fully examine the assumption that the cc-pV5z basis set represents a good approximation to the infinite basis set limit, we have considered the infinite basis (IB) method developed by Truhlar and co-workers.<sup>44,45</sup> In this method, total energies calculated using correlation consistent basis sets are extrapolated as a function of the highest angular momentum component of the basis set used. Parameters for the extrapolation are determined by optimizing the total energies of atoms and molecules in a test suite to minimize the root mean square of the deviation from the known complete basis set energy. We have applied the IB method to the total energies of all of the CH<sub>3</sub>X (X = F, Cl, Br) species and to all products of the C–X bond dissociation reactions. Each calculation was performed at both the Hartree–Fock (HF) and CCSD(T) levels using cc-pVdz and cc-pVtz basis sets at the MP2/6-311+G\* geometries, and the IB method was applied using the parameters of ref 44. MP2/6-311+G\* zero-point and atomic spin–orbit corrections (vide infra) were added to the IB-corrected total energies, which were then used to calculate the C–X bond dissociation energies. Table 3 shows the results of these calculations along with the experimental bond dissociation energies. Both methods reproduce the experimental bond energies to within 2 kcal/mol except for the IB calculation of the C–Cl bond in CH<sub>3</sub>Cl, which underestimates the experimental bond dissociation energy by 3.2 kcal/mol. The results of the present methodology and the IB method show good agreement, differing by less than 1 kcal/mol for CH<sub>3</sub>Cl and CH<sub>3</sub>Br and by 1.4 kcal/mol for CH<sub>3</sub>F. Since the IB method has been shown to accurately reproduce the complete basis limit for a large number of compounds,<sup>45</sup> we believe that the cc-pV5z basis set is a good approximation to the infinite basis set limit.

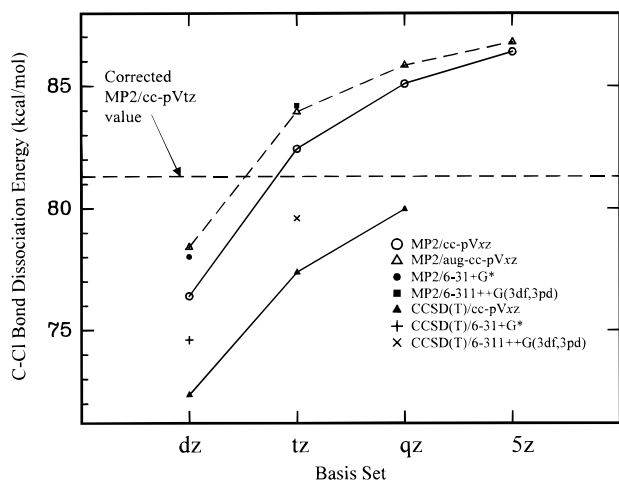
The effect of electron correlation on the bond dissociation energy was studied by comparing MP2 and CCSD(T) results



TABLE 2: Vibrational Frequencies for CH<sub>2</sub>X, Where X = H, F, Cl, and Br at Two Levels of Theory

species	mode symmetry	mode number	mode description	MP2/6-311++G(2df,2p) <sup>a</sup>	CCSD(T)/6-311++G(2df,2p) <sup>b</sup>	expt <sup>c</sup>
CH <sub>3</sub>	a <sub>1</sub> '	1	CH sym stretch	3188	3126	3044
	a <sub>2</sub> ''	2	HCH deformation	506	514	606
	e'	3	CH stretch	3379	3307	3161
		4	HCH deformation	1440	1422	1396
CH <sub>2</sub> F	a'	1	CH sym stretch	3212	3158	
		2	CH <sub>2</sub> scissor	1502	1482	
		3	CF stretch	1200	1195	
	a'	4	CH <sub>2</sub> F umbrella	617	569	
		5	CH asym stretch	3376	3314	
		6	CH <sub>2</sub> rock	1199	1184	
CH <sub>2</sub> Cl	a'	1	CH sym stretch	3246	3191	
		2	CH <sub>2</sub> scissor	1451	1428	
		3	CCl stretch	871	878	
	a''	4	CH <sub>2</sub> Cl umbrella	90	137	
		5	CH asym stretch	3402	3341	
		6	CH <sub>2</sub> rock	1021	1002	
CH <sub>2</sub> Br	a'	1	CH sym stretch	3244	3194	
		2	CH <sub>2</sub> scissor	1420	1396	1356
		3	CBr stretch	738	713	693
	a''	4	CH <sub>2</sub> Br umbrella	50	124	368
		5	CH asym stretch	3402	3346	
		6	CH <sub>2</sub> rock	950	928	953

<sup>a</sup> Geometry calculated at the MP2/6-311++G(2df,2p) level. <sup>b</sup> Geometry calculated at the CCSD(T)/6-311++G(2df,2p). <sup>c</sup> Refs 35 and 42.



**Figure 2.** Zero-point and spin-orbit corrected bond dissociation energies for CH<sub>3</sub>Cl as a function of basis set size at different levels of correlation. The symbols represent bond dissociation energies at the following levels: open circles, MP2/cc-pVxz ( $x = d, t, q,$  and  $5$ ); open triangles, MP2/aug-cc-pVxz; filled circle, MP2/6-31+G\*; filled square, MP2/6-311++G(3df,3pd); filled triangles, CCSD(T)/cc-pVxz; plus, CCSD(T)/6-31+G\*; cross, CCSD(T)/6-311++G(3df,3pd).

**TABLE 3: Comparison of Present Methodology to Infinite Basis (IB) Method and Experiment**

species	bond dissociation energy (kcal/mol)		
	this work	IB method	expt
H <sub>3</sub> C-F	108.0	108.1	109.2
H <sub>3</sub> C-Cl	81.4	80.0	83.2
H <sub>3</sub> C-Br	69.7	69.1	70.9 ± 0.4

calculated with identical basis sets. It can be seen in Figure 2 that higher levels of correlation decrease the bond dissociation energy and, within the range of the basis sets studied, the difference between the CCSD(T) energy and the corresponding MP2 energy is approximately constant. The correlation effect is approximately 4.0 kcal/mol for the C-Cl bond in CH<sub>3</sub>Cl. For the breaking of a bond containing a heavy atom, a full treatment of the electronic wave function must include relativistic effects to account for the large velocities of the electrons

in the core and interactions between the electron spin and the electronic angular momentum. However, recent studies of the bond dissociation energies of HX and X<sub>2</sub> (X = F, Cl, Br, and I)<sup>46,47</sup> have shown that the spin-orbit energy of the atomic halogen fragment represents the major difference between the relativistic and nonrelativistic treatments. Therefore, we have chosen to apply an atomic spin-orbit correction defined as  $1/3$  of the known spin-orbit energy for each halogen atom. This correction represents the statistical weighted average of the relative energies of the 4-fold-degenerate  $^2P_{3/2}$  and the higher-energy doubly degenerate  $^2P_{1/2}$  electronic states. The correction decreases the calculated nonrelativistic bond energy to correctly model the dissociation on the ground-state potential energy surface to give CH<sub>3</sub> + X( $^2P_{3/2}$ ) products (X = F, Cl, and Br). The presence of spin contamination in the calculated open-shell wave functions, which can introduce significant error into the calculated bond dissociation energy, was also considered. However, since  $\langle S^2 \rangle$  is less than 0.775 before annihilation for all open-shell species studied, the effects of spin contamination on the calculated bond dissociation energy are small.

The above observations allowed the development of the following method for the direct calculation of bond dissociation energies in halocarbons. First, geometries are optimized at the MP2/6-311+G\* level, and single-point energies are evaluated at the MP2/cc-pVtz level. Second, basis set effects (approximating the infinite basis set limit) are taken into account by calculating the difference between the MP2/cc-pV5z and MP2/cc-pVtz results. Third, a correlation correction factor is determined by calculating the difference between CCSD(T)/cc-pVtz and MP2/cc-pVtz results. In the case of C-X bond dissociation, an atomic spin-orbit energy correction factor is then applied. In the end, the bond dissociation energy is directly calculated by adding a single correction factor to the results of a zero-point-corrected MP2/cc-pVtz bond energy calculation.

Table 4 summarizes the correction factors and bond dissociation energies for CH<sub>3</sub>X (X = F, Cl, Br) as calculated with our method. Table 5 shows the corrected MP2/cc-pVtz energy, as well as the energy calculated directly at the CCSD(T)/6-311++G(3df,3pd) level and the experimental data. MP2/6-311+G\* zero-point energy and atomic spin-orbit energy

**TABLE 4: Correction Factors for C–X (X = F, Cl, and Br) Bond Dissociation Energies (kcal/mol)**

species	raw MP2/cc-pVtz energy	basis set correction	correlation correction	atomic spin-orbit correction	total correction factor	zero-point correction	corrected bond dissociation energy
CH <sub>3</sub> –F	117.6	4.0	–6.9	–0.4	–3.3	–6.3	108.0
CH <sub>3</sub> –Cl	88.6	4.0	–5.0	–0.8	–1.8	–5.4	81.4
CH <sub>3</sub> –Br	79.1	3.5	–4.5	–3.5	–4.5	–4.9	69.7

**TABLE 5: Effectiveness of the Corrected MP2/cc-pVtz C–X Bond Dissociation Energies**

	CCSD(T)/6-311 ++G(3df,3pd) energy (kcal/mol) <sup>a</sup>	corrected MP2/cc-pVtz energy (kcal/mol)	expt (kcal/mol)	ref
CH <sub>3</sub> –F	107.1	108.0	109.2	49 <sup>b</sup>
CH <sub>3</sub> –Cl	79.6	81.4	83.2	49 <sup>b</sup>
CH <sub>3</sub> –Br	65.8	69.7	70.9 ± 0.3	16

<sup>a</sup> Geometries calculated at the CCSD(T)/6-311++G(3df,3pd) level. Energies corrected for zero-point energy and atomic spin-orbit energy.

<sup>b</sup> Derived from standard enthalpies of formation. Reference 49 did not report error bars for the enthalpies, so no error bars are given for the bond dissociation energies.

**TABLE 6: Basis Set Dependence of C–Br Bond Dissociation Energies and Correction Factors for CH<sub>3</sub>Br (kcal/mol)**

	cc-pVdz	cc-pVtz	cc-pVqz
MP2 <sup>a</sup>	72.8	79.1	81.8
basis set correction <sup>b</sup>	+9.8	+3.5	+0.8
CCSD(T) <sup>a</sup>	69.2	74.6	77.1
correlation correction	–3.6	–4.5	–4.7
atomic spin-orbit energy correction	–3.5	–3.5	–3.5
total correction factor	+2.7	–4.5	–7.4
zero-point correction	–4.9	–4.9	–4.9
corrected bond dissociation energy <sup>c</sup>	70.6	69.7	69.5

<sup>a</sup> All-electron calculations. <sup>b</sup> The cc-pV5z basis set is assumed to represent the infinite basis set limit. <sup>c</sup> Sum of the MP2/cc-pVxz bond dissociation energy, total correction factor, and zero-point correction.

corrections have been added to the CCSD(T) energies. When direct measurements of bond dissociation energies were not available, the experimental values were derived from available standard enthalpies of formation at 298 K and were corrected to provide a bond dissociation energy at 0 K. Thermodynamic values were typically taken from the most recent review of thermodynamic data available.<sup>48,49</sup> No error bars were associated with enthalpies of formation taken from ref 49, so no error bars are given for experimental BDE's that were calculated from these enthalpies. However, we estimate that the error is about 1–2 kcal/mol, based on previously published values.<sup>18,19</sup> The calculated values agree remarkably well with experimental values, differing by less than 2 kcal/mol for all C–X (X = F, Cl, and Br) bond dissociation energies. For the C–Br bond in CH<sub>3</sub>Br, the basis set effects at the triple- $\zeta$  level are found to exactly cancel the spin-orbit energy correction. Calculations of C–Br bond dissociation energies performed using Pople-style basis sets at the triple- $\zeta$  level are found to reproduce experimental values well. However, these energies may be a result of a fortuitous cancellation of the basis set error and the

atomic spin-orbit energy of the atomic fragment, which would reproduce the experimental values poorly if a more flexible basis set was used.

To examine the basis set dependence of the corrected bond dissociation energies, correction factors were determined using cc-pVdz, cc-pVtz, and cc-pVqz basis sets and are shown in Table 6, assuming that the cc-pV5z basis set represents the infinite basis set limit. The uncorrected MP2 energies differ by ~9 kcal/mol, yielding a similarly large difference in the basis set corrections. However, the corrected MP2 values are constant to within ~1 kcal/mol, demonstrating the robustness of the method. The effect of using the frozen core approximation was also examined by determining correction factors using MP2 and CCSD(T) methods where all electrons were correlated. The all-electron methods were found to yield correlation corrections that differ from the frozen core results by <0.1 kcal/mol. This difference is insufficient to justify the additional cost of computing bond dissociation energies without the frozen core assumption.

**CH<sub>2</sub>X–H Bond Energies.** Correction factors for C–H bond energies of the CH<sub>3</sub>X derivatives were determined using a method similar to that used for the C–X bond energies. Basis set effects are estimated by calculating the difference in bond dissociation energies of MP2/cc-pVtz and MP2/cc-pV5z calculations. As in the case of the C–X bond energies, the BSSE was less than 1 kcal/mol at the cc-pVqz level, and the cc-pV5z basis set was assumed to represent the infinite basis set limit. The IB method was also applied to the C–H bond dissociation energies. The present methodology underestimates the results of the IB method by only 0.5–0.7 kcal/mol for the C–H bond energy in all of the CH<sub>3</sub>X (X = H, F, Cl, Br) compounds. Similar to the C–X (X = F, Cl, Br) bond dissociation energies (cf. Figure 2), the effects of using aug-cc-pVxz basis sets is almost completely diminished at the 5z level. As a result, the assumption that the cc-pV5z basis represents the infinite basis set limit appears to be valid for C–H bond energies. Correlation effects were determined by calculating the difference between MP2/cc-pVtz and CCSD(T)/cc-pVtz bond dissociation energies. Similar to the C–X bond dissociation energies shown in Table 6, the correlation correction appears to be approximately independent of the basis set above the cc-pVdz level. We note that the C–H correlation correction factors are generally much smaller and of opposite sign than for the corresponding C–X bond dissociation energy. The correction factors and zero-point-corrected bond dissociation energies for the CH<sub>3</sub>X species are shown in Table 7. Table 8 compares the corrected MP2/cc-pVtz bond dissociation energies to energies calculated directly at the CCSD(T)/6-311++G(3df,3pd) level and experimentally

**TABLE 7: Correction Factors for C–H Bond Dissociation Energies (kcal/mol)**

species	raw MP2/cc-pVtz energy	basis set correction	correlation correction	total correction factor	zero-point correction	corrected bond dissociation energy
CH <sub>3</sub> –H	110.6	1.2	0.7	+1.9	–9.7	102.8
CH <sub>2</sub> F–H	106.5	1.7	0.7	+2.4	–9.2	99.7
CH <sub>2</sub> Cl–H	105.9	1.2	0.2	+1.4	–9.6	97.7
CH <sub>2</sub> Br–H	107.1	1.4	–0.1	+1.3	–9.5	98.9

**TABLE 8: Effectiveness of Corrected MP2/cc-pVtz C–H Bond Dissociation Energies**

species	CCSD(T)/6-311++G(3df,3pd) energy (kcal/mol) <sup>a</sup>	corrected MP2/cc-pVtz energy (kcal/mol)	expt (kcal/mol)	ref
CH <sub>3</sub> –H	103.8	102.8	105.1	49 <sup>b</sup>
CH <sub>2</sub> F–H	98.5	99.7	101.3 ± 1	14
CH <sub>2</sub> Cl–H	96.6	97.7	99.5 ± 0.6	51
CH <sub>2</sub> Br–H	97.6	98.9	101.6 ± 1	16

<sup>a</sup> Geometries calculated at the CCSD(T)/6-311++G(3df,3pd) level.

<sup>b</sup> Derived from standard enthalpies of formation and corrected to give bond dissociation energies at 0 K. Reference 49 did not report error bars for the enthalpies, so no error bars are given for the bond dissociation energies.

determined values. For all species, the corrected MP2/cc-pVtz energy agrees with experimental values to within ~3 kcal/mol. The relatively large differences between the calculated and experimental values may be partially attributed to errors in the zero-point correction. The zero-point corrections for C–H bonds are large because of the loss of high-frequency C–H stretching modes in the dissociation. Therefore, errors in the C–H stretch frequencies, as shown in Table 2, can introduce significant error into the zero-point correction.<sup>50</sup> Although the error could be reduced by using scaled MP2 frequencies, the determination of a proper scaling factor for these systems would require extensive benchmarking on a large number of haloalkane systems and is beyond the scope of the current study. The calculations reproduce the experimental decrease in C–H bond energy from CH<sub>3</sub>F to CH<sub>3</sub>Cl and the slight increase from CH<sub>3</sub>Cl to CH<sub>3</sub>Br. Recent studies have shown a strong correlation between the C–H bond dissociation energy and the rate of hydrogen abstraction reactions.<sup>12,13</sup> The reported values for the normalized activation energy ( $E_a/R$ ) are 1500 ± 300, 1400 ± 250, and 1470 ± 150 for hydrogen abstraction by OH from CH<sub>3</sub>F, CH<sub>3</sub>Cl, and CH<sub>3</sub>Br, respectively.<sup>1</sup> Although the reported error bars are large, the calculated bond dissociation energies are consistent with the reported average values of the activation energy.

**Multihalogenated Compounds.** To assess the applicability of this methodology to more highly substituted systems, C–X and C–H bond dissociation energies were calculated for CH<sub>2</sub>X<sub>2</sub> and CHX<sub>3</sub> (X = F, Cl, and Br) systems at the MP2/cc-pVtz//MP2/6-311+G\* level. In each case, the previously determined correction factors for the C–X (X = H, F, Cl, and Br) bond determined from the CH<sub>3</sub>X model calculations were applied to the results to yield a final bond dissociation energy. Table 9 shows the calculated and experimental bond dissociation energies of the multihalogenated species. The calculated bond

dissociation energies reproduce the experimental values well, differing by less than 3 kcal/mol for all of the compounds studied with the exception of the C–H bond energy in CH<sub>2</sub>Br<sub>2</sub>, which differs by 3.4 kcal/mol. We note that, in general, the calculated C–H bond dissociation energies are not reproduced as accurately as C–X bonds. However, most of the experimental values have large reported error bars. Tschuikow-Roux and Paddison have described some of the difficulties in finding accurate experimental values for C–H and C–X bond dissociation energies of halocarbons for comparison to calculated values.<sup>16</sup> As an example, the three C–H bond dissociation energies for CH<sub>2</sub>Br<sub>2</sub> reported in ref 16 are 103.7 ± 2, 109.1 ± 2.3, and 99.8 ± 1.8 kcal/mol. Although this energy shows the largest deviation from our calculated results, it is difficult to assess the accuracy of the calculations because the energies do not overlap within the stated error bars of each. We have chosen the value with the lowest stated error for comparison, though we estimate the error to be substantially larger. We believe that reproducing the experimental bond dissociation energies to within 3 kcal/mol for the series of methane derivatives is strong evidence for the broad applicability of the method but highlights the need for more accurate experimental determinations of bond energies. This methodology will allow the efficient calculation of the entire series of multihalogen compounds that have atmospheric relevance and whose thermochemistry is important to atmospheric chemistry models.

#### IV. Summary

The bond dissociation energies for the breakage of C–H and C–X bonds in halomethanes have been determined using both correlation consistent (cc-pVxz) and Pople-style basis sets (6-311xG) at the MP2 and CCSD(T) levels. A general methodology has been developed to correct MP2/cc-pVtz calculations for basis set and electron correlation effects in halogenated alkanes. The fully corrected energies reproduce the experimental values extremely well in all cases and are found to give superior results to CCSD(T) calculations performed with large Pople-style basis sets, especially when applied to C–X bonds. Furthermore, by determining C–H and C–X bond dissociation energies for species of the forms CH<sub>2</sub>X<sub>2</sub> and CHX<sub>3</sub> (X = F, Cl, Br), we have shown that this methodology may be broadly applied to multihalogen compounds, which are presently too large to perform high-level coupled cluster studies. In the future, we plan to further test the methodology on larger halocarbon molecules with greater numbers of halogen atoms in order to define the scope of the methodology. We are currently extending this methodology to calculate bond energies of secondary free

**TABLE 9: Comparison of the Corrected MP2/cc-pVtz Bond Dissociation Energy of Multihalogenated Compounds to Experimental Results (kcal/mol)**

reaction	MP2/cc-pVtz	correction factor	ZPC	corrected energy	expt	ref
CH <sub>2</sub> F <sub>2</sub> → CH <sub>2</sub> F + F	127.7	–3.3	–5.1	119.3	118.8	48, 49 <sup>a</sup>
CH <sub>2</sub> F <sub>2</sub> → CHF <sub>2</sub> + H	106.4	+2.4	–8.8	100.0	101.3 ± 1	14
CH <sub>2</sub> Cl <sub>2</sub> → CH <sub>2</sub> Cl + Cl	84.7	–1.8	–4.4	78.5	80.9 ± 1	16
CH <sub>2</sub> Cl <sub>2</sub> → CHCl <sub>2</sub> + H	101.1	+1.4	–8.7	93.8	95.6 ± 0.6	51
CH <sub>2</sub> Br <sub>2</sub> → CH <sub>2</sub> Br + Br	75.2	–4.5	–3.7	67.0	69.8 ± 2	16
CH <sub>2</sub> Br <sub>2</sub> → CHBr <sub>2</sub> + H	103.5	+1.3	–8.5	96.3	99.7 ± 1.8	16
CHF <sub>3</sub> → CF <sub>2</sub> H + F	135.0	–3.3	–3.9	127.8	127.0	48, 49 <sup>a</sup>
CHF <sub>3</sub> → CF <sub>3</sub> + H	111.2	+2.4	–8.5	105.1	106.7 ± 0.7	16
CHCl <sub>3</sub> → CHCl <sub>2</sub> + Cl	80.1	–1.8	–2.7	75.6	77.8	48, 49 <sup>a</sup>
CHCl <sub>3</sub> → CCl <sub>3</sub> + H	100.0	+1.4	–8.2	93.2	95.8 ± 1	16
CHBr <sub>3</sub> → CHBr <sub>2</sub> + Br	70.4	–4.5	–2.1	63.8	66 ± 4	52
CHBr <sub>3</sub> → CBr <sub>3</sub> + H	99.9	+1.3	–8.0	93.2	96 ± 1.6	16

<sup>a</sup> Derived from standard enthalpies of formation and corrected to give bond dissociation energies at 0 K. Reference 49 did not report error bars for the enthalpies, so no error bars are given for the calculated bond dissociation energies.



radical products derived from the photodissociation of multi-halogenated compounds.

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