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Investigation of Thermodynamic Properties of Halomethanes Using High-Level Ab Initio Computations: Evaluation of Enthalpy of Formation and Carbon-Halogen Bond Dissociation Energies

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Abstract: Thermodynamic properties of halomethane compounds were investigated using high-level ab initio computations. HF, MP2 and B3LYP at different basis sets and composite methods CBS-QB3, G3MP2 and G4 were evaluated for their ability to predict enthalpy of formations and carbon-halogen bond dissociation energies of halomethanes containing F, Cl or Br. G3MP2 and G4 have shown excellent agreement with the available experimental data. The results were compared with benchmark G4 values. Moreover, bond dissociation enthalpies (EBD) were calculated using the direct and isogyric methods. The two methods gave similar linear square fit R2 related to the G4 method.

Keywords: Halomethanes, Ab Initio Computations, Thermodynamic Properties, Enthalpy of Formation, Bond Dissociation Energies.

1. Introduction

Halomethanes, a group of compounds characterized by the substitution of one or more hydrogen atoms in methane with halogen atoms (fluorine, chlorine, bromine, or iodine), play a significant role in environmental chemistry. They are major contributors to stratospheric ozone depletion due to the release of halogen atoms under ultraviolet light exposure, which leads to catalytic destruction of ozone molecules [1–3]. Despite their reduced use in industrialized nations, halomethanes continue to persist in the atmosphere because of their long atmospheric lifetimes, maintaining their impact on the ozone layer.

Historically, halomethanes were extensively used in various commercial applications, most notably as refrigerants in cooling systems and propellants in aerosol sprays. These compounds were also widely employed as solvents in laboratory settings due to their effectiveness in dissolving various substances [4]. Even though humans manufacture the majority of halomethanes, they are also naturally occurring, with significant concentrations found in marine environments. For example, many aquatic organisms biosynthesize halomethanes [5–7] mostly contain bromine (the oceans are predicted to produce between one to two million tons of bromomethane annually) [8, 9].

The biosynthesize of halomethanes is catalyzed by chloroperoxidase or bromoperoxidase enzymes. The typical equation is shown below:

$$CH_4+X^-+½\,O_2 \rightarrow CH_3X+OH^- \text{ (X is Cl or Br)} \qquad (1)$$

The significant role of halogenated compounds, especially those that contain chlorine or bromine atoms in stratospheric ozone reduction, has been known since the late 1970s [10, 11]. Halomethanes are the primary natural source in the troposphere and stratosphere among the halogenated compounds. [12].

With the action of ultraviolet light (UV), the Cl and Br atoms are liberated from the halomethanes as soon as they reach the stratosphere. For example, chlorofluorocarbons stay very stable in the atmosphere until they reach the stratosphere. The UV radiation causes hemolytic cleavage to produce the chlorine radicals:

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$CFCl_3$ + ultraviolet light → $Cl^{\bullet}$+$CFCl_2^{\bullet}$ (2)

After that, the ozone molecule (O_3) reacts with the chlorine atom to yield chlorine monoxide (ClO) and oxygen molecules.

$Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$ (3)

The chlorine monoxide can react with another ozone molecule to produce chlorine atoms and two oxygen molecules.

$ClO^{\bullet} + O_3 \rightarrow Cl^{\bullet} + 2O_2$ (4)

According to the U.S. Environmental Protection Agency, each chlorine atom can destroy 100,000 ozone molecules [13]. About 90 percent of chlorofluorocarbons (CFCs) in the atmosphere were released by industrialized countries, such as North America and Europe. These countries were banned by 1996 in the Kyoto Protocol [14]. Although the use of halomethanes in developed countries has gradually decreased since 1996, the concentrations of halomethanes are still rising because of the long atmospheric lifetime [15].

The accurate experimental determination of thermodynamic properties for halomethanes remains a challenging task. Reliable experimental data are particularly scarce for species containing bromine and iodine. Existing databases, including NIST, Pedley, and JPL, often exhibit significant error margins or inconsistencies [16–19]. Additionally, the number of experimental studies is limited, and the available data are often inaccurate [20–23]. Thermodynamic data of halomethanes is usually obtained by calorimetry and equilibrium studies. The challenge comes from accomplishing complete combustion when halogen is absorbed in solution, and because the total energy issue may be huge compared with the heat of combustion. There needs to be more consistency in the literature. [24]. For example, the heat of formation (ΔH^0_f) of tetrabromomethane (CBr_4) compound in the gas phase has an extensive range of 50–120 kJ/mol of experimental data (Table 1).

Table 1. All isodesmic reactions that have been used to compute enthalpies of formation ΔH_f^0, summary of available experimental data ΔH_f^0 kJ/mol at 298.15K (gaseous state), and calculated G4 method with their deviation errors from literature data (calc. - expr.) in kJ/mol

Species	**Isodesmic Rxn.**	**Expr. ΔH_f^0**	**References**	**Calc.G4^a**
a. Monohalomethanes				
CH3F	CH4 + CH2F2 → 2CH3F	-234.3	[25]	-236(-1)
		-247	[26]	
CH3Cl	CH4 + CH2Cl2 → 2CH3Cl	-81.9 ± 1.5	[27]	-83(-1)
		-83.68	[25]	
		-81.96 ± 0.67	[28]	
		-85.90 ± 0.59	[29]	
CH3Br	CH4 + CH2Br2 → 2CH3Br	-34.3 ± 0.8,	[30]	-32(2)
		-38.0 ± 1.3	[31]	
		-37.5 ± 1.5	[32]	
b. Dihalomethanes				
CH2F2	2CH3F → CH2F2 + CH4	-450.66	[25]	-448(3)
		-452.21 ± 0.92	[33]	
CH2Cl2	2CH3Cl → CH2Cl2 + CH4	-95.1 ± 2.5	[27]	-94(1)
		-95.52	[25]	
		-95.7 ± 1.3	[34]	
CH2Br2	2CH3Br → CH2Br2 + CH4	10 ± 15	[35]	6(-4)
CH2BrF	CH3F + CH3Br → CH2BrF + CH4			-207
CH2ClF	CH3F + CH3Cl → CH2ClF + CH4	-261.92	[25]	-262(0)
CH2ClBr	CH3Cl + CH3Br → CH2ClBr + CH4	-50.2	[36]	-43(7)
		-20. ± 7	[37]	
c. Trihalomethanes				

CHF3	CH3F + CH2F2 → CHF3 + CH4	-697.05	[25]	-694(3)
		-690.8	[38]	
		-695.4 ± 2.7	[39]	
CHCl3	CH3Cl + CH2Cl2 → CHCl3 + CH4	-102.9 ± 2.5	[27]	-104(-1)
		-103.18	[25]	
CHBr3	CH3Br + CH2Br2 → CHBr3 + CH4	55.4 ± 3.3	[40]	55(0)
CHClF2	CH3Cl + CH2F2 → CHClF2 + CH4	-481.58	[25]	-481(0)
		-483. ± 3	[41]	
CHBrF2	CH3Br + CH2F2 → CHBrF2 + CH4	-425.3 ± 0.9	[42]	-422(3)
CHBr2F	CH3F + CH2Br2 → CHBr2F + CH4			-168
CHFCl2	CH3F + CH2Cl2 → CHFCl2 + CH4	-283.26	[25]	-284(0)
CHBrClF	CH3F + CH2ClBr → CHBrClF + CH4			-233
CHBr2Cl	CH3Cl + CH2Br2 → CHBr2Cl + CH4			5
CHBrCl2	CH3Br + CH2Cl2 → CHBrCl2 + CH4			-52
d. Tetrahalomethanes				
CF4	CH3F + CHF3 → CF4 + CH4	-933.20 ± 0.75	[35]	-932(1)
CBr4	CH3Br + CHBr3 → CBr4 + CH4	115.8 ± 3.9	[40]	110(-6)
		50.21	[25]	
		83.9 ± 3.4	[43]	
		120 ± 15	[35]	
CCl4	CH3Cl + CHCl3 → CCl4 + CH4	-95.60 ± 1	[35]	-101(-6)
CF3Br	CH3Br + CHF3 → CF3Br + CH4	-648.94	[25]	-650(-1)
		-647.3 ± 2.9	[44]	
		-649.4 ± 3.2	[45]	
CF3Cl	CH3Cl + CHF3 → CF3Cl + CH4	-707.8 ± 2.8	[35]	-710(-2)
CF2Br2	CH3Br + CHBrF2 → CF2Br2 + CH4			-382
CF2Cl2	CH3F + CHFCl2 → CF2Cl2 + CH4	-491.62	[25]	-492(0)
		-477.6 ± 5.6	[46]	
		-477. ± 13	[44]	
		-469. ± 8	[45]	
CBrClF2	CH3Cl + CHBrF2 → CBrClF2 + CH4			-439
CBr2ClF	CH3F + CHBr2Cl → CBr2ClF + CH4			-175
CBrCl2F	CH3Br + CHFCl2 → CBrCl2F + CH4			-235
CFCl3	CH3F + CHCl3 → CFCl3 + CH4	-288.7	[25]	-290(-1)
		-268.3 ± 8.4	[47]	
		-290. ± 20	[47]	
		-278. ± 8.8	[48]	
CBr3F	CH3F + CHBr3 → CBr3F + CH4			-121
CBrCl3	CH3Br + CHCl3 → CBrCl3 + CH4	-42 ± 1	[49]	-49(-7)
CBr2Cl2	CH3Cl + CHBr2Cl → CBr2Cl2 + CH4			8
CBr3Cl	CH3Cl + CHBr3 → CBr3Cl + CH4			59

a. the number in parenthesis refers to the deviation of G4 from experimental data (Calc.-Expr.)

Accurate thermodynamic properties of halocarbons are important in atmospheric chemistry to help understand their radical properties. [50, 51] And their concentrations in the stratosphere. Moreover, in the field of molecular biology, the thermodynamic properties of halogens are very important in the molecular recognition process. [52, 53].

In addition, some studies have been done on designing supermolecular materials by taking advantage of halogen thermodynamics to control the crystallization of these compounds. Accurate thermodynamic data is required in kinetic modelling and mechanistic deduction. [54–59]. As a result, halogens have significant interest in organic, inorganic and biological chemistry.

To address these challenges, quantum chemical calculations offer a reliable alternative. Advancements in quantum mechanical calculations allow for predictions of standard molar enthalpies of formation ($\Delta H_f°$), bond dissociation energies, and heat capacities with accuracies up to ±1 kJ mol⁻¹ for small molecules, making highly accurate data more achievable than ever before [60–63]. These predictions are crucial for designing compounds with desired functionalities since properties like enthalpy, heat capacity, standard entropy, and Gibbs free energy dictate the stability and reactivity of molecules [64–67].

This study aims to provide a comprehensive analysis of the thermodynamic properties of halomethanes using high-level computational methods. In this research, estimation of enthalpy of formation (ΔH^0_f) at 298.15K of mono, di, and tetra CH_nX_{4-n} (X = F, Cl, Br; n = 1,2,3) halomethane compounds have been investigated with ab initio and density functional methods. The work has been extended by calculating the bond dissociation energies of halogen bonds (C-X, where X=F, Cl, or Br). The purposes of the present study are to afford computed thermodynamic properties for these compounds and to compare the accuracy of each method based on the available experimental values. The mean absolute deviations (MAD) were also computed, which was traditionally used to evaluate the reliability of calculated methods.

2. Computational Method

For this study, all calculations were carried out using Gaussian 09 software.[68]. The optimization of the geometries and the frequencies of compounds were performed at different levels of theory HF, B3LYP, and MP2 using a variety of basis sets including 6-31G, 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p). Additionally, three high-level composite methods CBS-QB3 (Complete Basis Set-Quartet Basis Set 3), G3MP2 (Gaussian-3 Method using second-order Møller-Plesset perturbation theory) and G4 (Gaussian-4) were employed to ensure accuracy in the prediction of thermodynamic properties. Two different isodesmic reactions were used to compute the enthalpies of formation ΔH_f° at 298.15K of halomethanes (Table 1). In isodesmic reactions, the number and types of bonds are conserved on both sides.

In the case of monohalomethanes (CH_3X, where X= F, Cl, or Br), the following general equation has been used:

$$CH_2X_{2(g)} + CH_{4(g)} \rightarrow 2CH_3X_{(g)} \quad (5)$$

where X= F, Cl, or Br

The enthalpy of formation ΔH_f° for monohalomethanes can be estimated as shown in Equation (6),

$$\Delta H_f^\circ(CH_3X)=½[\Delta H_{rxn}^\circ+\Delta H_f^\circ(CH_2X_2)+\Delta H_f^\circ(CH_4)] \quad (6)$$

where $\Delta H_f^\circ(CH_2X_2)$ and $\Delta H_f^\circ(CH_4)$ are the experimental enthalpies of the formation of CH_2X_2 and CH_4 in a gaseous state at 298.15K, respectively (Table 1).

However, in the case of di, tri and tetrahalomethanes CH_nX_{4-n} (X = F, Cl, Br; n = 1,2,3), the general equation for the isodesmic reaction is:

$$CH_3X_{(g)} + CH_nX_{4-n(g)} \rightarrow CX_{4(g)} + CH_{4(g)} \quad (7)$$

where the enthalpy of formation is calculated as follows:

$$\Delta H_f^\circ(CX_4)=\Delta H_{rxn}^\circ-\Delta H_f^\circ(CH_4)+\Delta H_f^\circ(CH_3X)+\Delta H_f^\circ(CHX_3) \quad (8)$$

Table 1 summarizes all available experimental values used to calculate the enthalpies of formation in a gaseous state at 298.15 K for all the considered species in this work. However, because the enthalpy of the formation of the $CHClBr_2$ compound is not available in the literature, the computed G4 (5 kJ/mol) has been used to calculate enthalpies of formation for CCl_2Br_2 and $CFClBr_2$.

Bond dissociation energies E_{BD} of C-X (where X = F, Cl, or Br) of halomethanes at 298.15K were calculated. The calculations were completed by using two methods. The first was by direct hemolytic dissociation reaction as below:

$$CX_{4(g)} \rightarrow CX_3^\bullet{}_{(g)} + X^\bullet{}_{(g)} \quad (9)$$

where (X = H, F, Cl, or Br)

In this case, E_{BD}(C-X) has been calculated by using the following equation:

$$E_{BD}(C\text{-}X)=\Delta H^0(CX_3^\bullet)+\Delta H^0(X^\bullet)-\Delta H^0(CX_4) \quad (10)$$

The second method calculates the bond dissociation energies EBD of the C-X isogyric reaction. In an isogyric reaction, the number of paired electrons is conserved on both reaction sides. To achieve this purpose, isogyric equation has been used as below:

$$CX_{4(g)} + CH_3{}^\bullet{}_{(g)} \rightarrow CX_3{}^\bullet{}_{(g)} + CH_3X_{(g)} \quad (11)$$

where (X = H, F, Cl, or Br).

The enthalpy of formation can be calculated as below:

$$\Delta H^0(rxn) = \Delta H^0(CX_3^\bullet) + \Delta H^0(CH_3X) - \Delta H^0(CX_4) - \Delta H^0(CH_3^\bullet) \quad (12)$$

Reaction (11) can also be expressed as following steps:

$$CX_{4(g)} \rightarrow CX_3{}^\bullet{}_{(g)} + X^\bullet{}_{(g)},\ E_{BD}(C\text{-}X) \quad (13)$$

$$X^\bullet{}_{(g)} + CH_3{}^\bullet{}_{(g)} \rightarrow CH_3X_{(g)},\ -E_{BD}(CH_3X) \quad (14)$$

Because the experimental bond dissociation energies of CH_3X compounds are known at 298.15K in a gaseous state (Table 2), E_{BD}(C-X) has been computed as below:

$$E_{BD}(C\text{-}X) = \Delta H^0(rxn) + E_{BD}(CH_3X) \quad (15)$$

3. Results and discussion

In the comparison of results with experimental data, we present a summary to highlight the excellent agreement between the computational methods and the experimental values. A summary of the available experimental data for enthalpies of formation (ΔH_f°) and bond dissociation energies (EBD) is provided in Tables 1 and 2, respectively. The calculated results from G4, CBS-QB3, and G3MP2 methods show outstanding agreement with experimental data, with mean absolute deviations (MADs) of 4, 2, and 2 kJ/mol, respectively.

Table 2. All isogyric reactions that have been used to compute bond dissociation energy E_{BD}, and summary of available experimental data in gaseous state (kJ/mol) at 298.15K

Species	**Isogyric Rxn.**	**EBD (kJ/mol) at 298.15K (gaseous state)** [a]	
CH3-F		459.6	[69]
CH2F-F	CH2F2 + CH3 → CH2F + CH3F	496.2 ± 8.8	[70]
CH2Cl-F	CH2ClF + CH3 → CH2Cl + CH3F	465.3 ± 9.6	[70]
CH2Br-F	CH2BrF + CH3 → CH2Br + CH3F		
CHF2-F	CHF3 + CH3 → CHF2 + CH3F	533.9 ± 5.9	[70]
CHFCl-F	CHClF2 + CH3 → CHFCl + CH3F	465.3	[71]
		462.3 ± 10.0	[70]
CHFBr-F	CHBrF2 + CH3 → CHFBr + CH3F		
CHCl2-F	CHFCl2 + CH3 → CHCl2 + CH3F		
CHClBr-F	CHBrClF + CH3 → CHClBr + CH3F		
CHBr2-F	CHBr2F + CH3 → CHBr2 + CH3F		
CF3-F	CF4 + CH3 → CF3 + CH3F	546.8 ± 2.1	[70]
CCl3-F	CFCl3 + CH3 → CCl3 + CH3F	439.3 ± 4	[70]
CBr3-F	CBr3F + CH3 → CBr3 + CH3F		
CF2Cl-F	CF3Cl + CH3 → CF2Cl + CH3F	511.7	[70]
		490	[71]
CF2Br-F	CF3Br + CH3 → CF2Br + CH3F		
CFCl2-F	CF2Cl2 + CH3 → CFCl2 + CH3F	482.0 ± 10.5	[70]
		462.3	[71]
CFBr2-F	CF2Br2 + CH3 → CFBr2 + CH3F		
CFClBr-F	CBrClF2 + CH3 → CFClBr + CH3F		
CCl2Br-F	CBrCl2F + CH3 → CCl2Br + CH3F		
CClBr2-F	CBr2ClF + CH3 → CClBr2 + CH3F		
CH3-Cl		347.2	[69]
CH2F-Cl	CH2ClF + CH3 → CH2F + CH3Cl	354.4 ± 11.7	[70]

CH2Cl-Cl	CH2Cl2 + CH3 → CH2Cl + CH3Cl	338.0 ± 3.3	[70]
		350.2 ± 0.8	[71]
CH2Br-Cl	CH2ClBr + CH3 → CH2Br + CH3Cl	332.8 ± 4.6	[70]
CHF2-Cl	CHClF2 + CH3 → CHF2 + CH3Cl	364 ± 8	[70]
CHFCl-Cl	CHFCl2 + CH3 → CHFCl + CH3Cl	346.0 ± 13.4	[70]
		354.4	[71]
CHFBr-Cl	CHBrClF + CH3 → CHFBr + CH3Cl		
CHCl2-Cl	CHCl3 + CH3 → CHCl2 + CH3Cl	311.1 ± 2.0	[70]
		338.5	[71]
CHClBr-Cl	CHBrCl2 + CH3 → CHClBr + CH3Cl		
CHBr2-Cl	CHBr2Cl + CH3 → CHBr2 + CH3Cl		
CF3-Cl	CF3Cl + CH3 → CF3 + CH3Cl	360.2	[71]
		365.3 ± 3.8	[69]
CCl3-Cl	CCl4 + CH3 → CCl3 + CH3Cl	296.6	[70]
		305.9 ± 7.5	[71]
CBr3-Cl	CBr3Cl + CH3 → CBr3 + CH3Cl		
CF2Cl-Cl	CF2Cl2 + CH3 → CF2Cl + CH3Cl	333.9 ± 10.5	[70]
		346	[71]
CF2Br-Cl	CBrClF2 + CH3 → CF2Br + CH3Cl		
CFCl2-Cl	CFCl3 + CH3 → CFCl2 + CH3Cl	320.9 ± 8.4	[70]
		305	[71]
CFBr2-Cl	CBr2ClF + CH3 → CFBr2 + CH3Cl		
CFClBr-Cl	CBrCl2F + CH3 → CFClBr + CH3Cl		
CCl2Br-Cl	CBrCl3 + CH3 → CCl2Br + CH3Cl	287 ± 10.5	[70]
CClBr2-Cl	CBr2Cl2 + CH3 → CClBr2 + CH3Cl		
CH3-Br		291.5	[69]
CH2F-Br	CH2BrF + CH3 → CH2F + CH3Br		
CH2Cl-Br	CH2ClBr + CH3 → CH2Cl + CH3Br	277.3 ± 3.6	[70]
CH2Br-Br	CH2Br2 + CH3 → CH2Br + CH3Br	276.1 ± 5.3	[70]
		296.7	[71]
CHF2-Br	CHBrF2 + CH3 → CHF2 + CH3Br	288.7 ± 8.4	[70]
		289	[71]
CHFCl-Br	CHBrClF + CH3 → CHFCl + CH3Br		
CHFBr-Br	CHBr2F + CH3 → CHFBr + CH3Br		
CHCl2-Br	CHBrCl2 + CH3 → CHCl2 + CH3Br		
CHClBr-Br	CHBr2Cl + CH3 → CHClBr + CH3Br		
CHBr2-Br	CHBr3 + CH3 → CHBr2 + CH3Br	274.9 ± 13.0	[70]
		292	[71]
CF3-Br	CF3Br + CH3 → CF3 + CH3Br	296.2 ± 1.3	[70]
CCl3-Br	CBrCl3 + CH3 → CCl3 + CH3Br	231.4 ± 4.2	[70]
		231.1	[71]
CBr3-Br	CBr4 + CH3 → CBr3 + CH3Br	235.1	[71]
		242.3 ± 8.4	[70]
CF2Cl-Br	CBrClF2 + CH3 → CF2Cl + CH3Br	269.9 ± 6.3	[70]
CF2Br-Br	CF2Br2 + CH3 → CF2Br + CH3Br		
CFCl2-Br	CBrCl2F + CH3 → CFCl2 + CH3Br		
CFBr2-Br	CBr3F + CH3 → CFBr2 + CH3Br		
CFClBr-Br	CBr2ClF + CH3 → CFClBr + CH3Br		
CCl2Br-Br	CBr2Cl2 + CH3 → CCl2Br + CH3Br		
CClBr2-Br	CBr3Cl + CH3 → CClBr2 + CH3Br		

[a]the number in brackets refer to the reference number

Enthalpies of formation ΔH_f°

The results were computed using isodesmic reactions, equations (5) for mono- and (7) for di, tri and tetrahalomethanes (Table 1). Mean absolute deviation (MAD) was computed for enthalpies of formation with the experimental data at different theory levels and basis sets given in Table S1. The estimated enthalpies are shown in Tables S2 to S5.

The calculated G4 results are in excellent agreement with available experimental data, with linear square fit R2 = 0.9999 (Figure 1) and no more than 7 kJ/mol fluctuation (Figure 2).

Because there is a wide range of experimental data for the same species, the experimental value close to the computed G4 has been carefully chosen (the first value in Table 1 for each species). All composite methods CBS-QB3, G3MP2 and G4 agreed well with the available experimental data, with MAD = 4, 2, and 2 kJ/mol, respectively (Figure S1.b) (Table S1).

Using the HF level of theory for computing the enthalpy of formation of monohalomethanes showed an excellent agreement with the experimental data MAD = 5 to 7 kJ/mol for all basis sets except for 6-31G (the MAD is 11 kJ/mol). On the other hand, the HF level of theory for di, tri and tetrahalomethanes with (d) function for heavy atoms basis sets 6-31G(d), 6-31+G(d), 6-31G(d,p) and 6-31+G(d,p) performed a good agreement with experimental data, MAD = 12 to 19 kJ/mol. Higher basis sets made the results worse, with MAD 14 to 26 kJ/mol (Table S1).

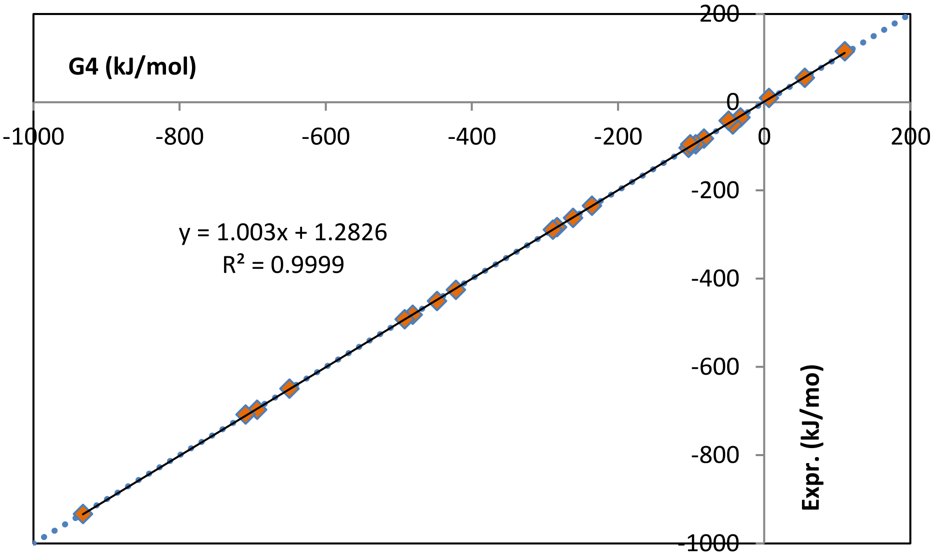


Figure 1. Comparison of the G4 method and the available experimental heat of enthalpies ΔH_f^0 (kJ/mol) at 298.15K in halomethanes compounds. (22 compared compounds).

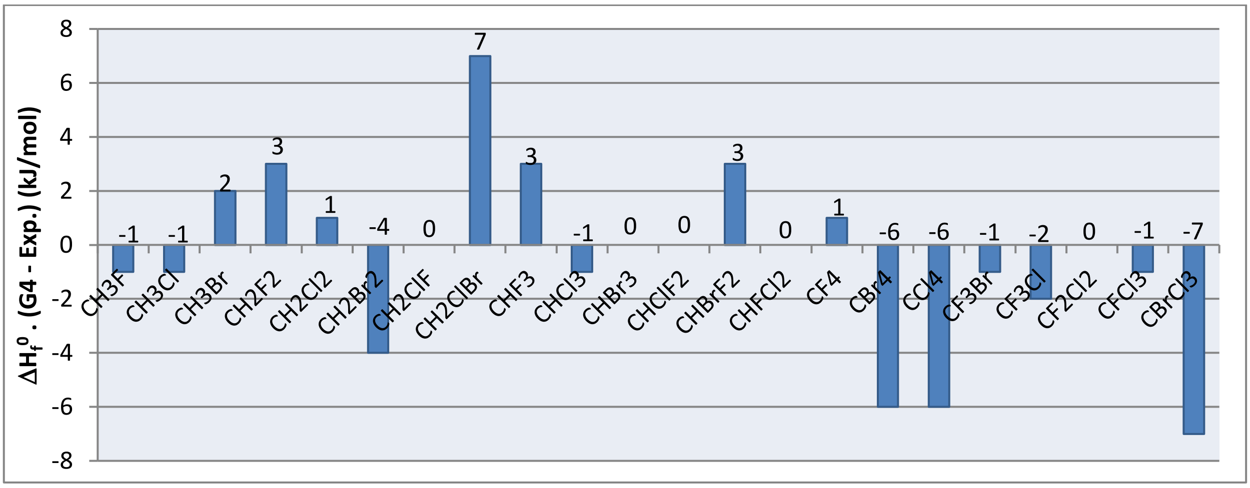


Figure 2. Deviation of G4 method and available experimental heat of enthalpies ΔH_f^0 (kJ/mol) at 298.15K in halomethanes compounds. (22 compared compounds).

Table 3. The linear fit coefficients between the calculated HF, B3LYP and MP2 levels of theory and the computed G4 method for enthalpy of formation ΔH_f^0 (kJ/mol).
Calc(fitted)=a * Calc(unfitted) + b

	HF			B3LYP			MP2		
Basis set	a	b	R^2	a	b	R^2	a	b	R^2
6-31G	0.9965	31.6690	0.996	1.0056	13.5585	0.999	0.9956	10.9739	0.999
6-31G(d)	1.0363	22.4451	0.998	1.0284	6.0056	0.999	1.0206	-0.4129	0.999
6-31+G(d)	1.0044	15.4806	0.999	0.9871	-0.5488	0.999	0.9773	-9.9520	0.999
6-31G(d,p)	1.0359	22.8887	0.998	1.0283	6.3341	0.999	1.0200	-0.9163	0.999
6-31+G(d,p)	1.0045	15.8820	0.999	0.9877	-0.4316	0.999	0.9785	-10.6964	0.999
6-311G(d,p)	1.0306	29.2072	0.997	1.0228	12.3500	0.999	1.0162	4.1618	1.000
6-311+G(d,p)	1.0223	27.7379	0.997	1.0066	11.3606	0.999	1.0019	-0.0958	1.000
6-311++G(d,p)	1.0222	27.9615	0.997	1.0065	11.5449	0.999	1.0021	0.5280	1.000

Table 4. Summary of mean absolute deviation (MAD) bond dissociation energy E_{BD} with the experimental data (kJ/mol) at 298.15K by direct method

	6-31G	6-31G(d)	6-31+G(d)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	6-311++G(d,p)
HF	203	149	151	150	151	159	159	159
B3LYP	49	17	23	18	23	28	30	30
MP2	77	14	14	14	14	9	7	7
CBS-QB3					13			
G3MP2					5			
G4					5			

Table 5. Summary of mean absolute deviation (MAD) bond dissociation energy E_{BD} with the experimental data (kJ/mol) at 298.15K by using isogyric reaction

	6-31G	6-31G(d)	6-31+G(d)	6-31G(d,p)	6-31+G(d,p)	6-311G(d,p)	6-311+G(d,p)	6-311++G(d,p)
HF	13	14	8	14	8	14	11	11
B3LYP	15	15	14	15	13	17	17	17
MP2	11	10	11	9	11	7	7	7
CBS-QB3					7			
G3MP2					5			
G4					6			

B3LYP level of theory achieved excellent work for all basis sets, with MAD 6 to 14 kJ/mol. On the other hand, MP2 did an excellent work, especially with MP2/6-311G(d,p), MP2/6-311+G(d,p), and MP2/6-311G++(d,p) basis sets (MAD = 4, 3 and 3 kJ/mol respectively)

HF, B3LYP, and MP2 levels of theory and the composite methods CBS-QB3 and G3MP2 agreed with the computed G4 method, the linear square fit R^2 close to 1.000 (Figures S2 and S3). As a result, the errors are systematic, which means that the linear fitting coefficients can be used to better agree with the experimental data (Table 3).

Bond dissociation energy E_{BD}

The calculations of bond dissociation energies E_{BD} of C-X (where X = F, Cl, or Br) of halomethanes at 298.15K were achieved by using two methods by direct hemolytic dissociation equation (9) and by using isogyric reaction equation (11). The MADs with the experimental data are in Tables 4 and 5. The results of bond dissociation energies are shown in Tables S6 to S14.

By using both methods - direct and isogyric - to calculate G4 values, the computed values show an excellent agreement with the available experimental data with MAD around 5 kJ/mol (Figure S4.b and Figure S5.b) and a linear square fit

R2 = 0.9941 (Figure 3), with no more than 11 kJ/mol deviation (excluding CHFCl-F, and CHBr2-Br) (Figure 4).

Direct Method

The composite method G3MP2 agreed with the experimental data with MAD = 5 kJ/mol (Figure S4.b). However, CBS-QB3 gave a very good MAD = 13 kJ/mol (Figure S4.b).

G3MP2 and CBS-QB3 were compared with the G4 method, giving a linear square fit R2 0.9997 and 0.9970, respectively (Figure S6). As shown in Figure S6.b, the computed CBS-QB3 results are too large compared with G4 values with MAD= 17 kJ/mol. Moreover, the CBS-QB3 method did not work very well to compute C-Br bond dissociations, where C-Br bond dissociation energies are mostly between 225 to 290 kJ/mol; that is because of the possibility of Gaussian software using none standard basis sets for the third row in CBS-QB3 method.

HF level of theory provided a very poor MAD with experimental data (Figure S4.a). The MAD was more than 200 kJ/mol for the HF/6-31G basis set and around 150 kJ/mol for all other HF basis sets. In B3LYP/6-31G and MP2/6-31G, the MADs are poor compared with the literature data (MAD = 49 and 77 kJ/mol, respectively). In contrast, the MADs for B3LYP and MP2 are better using other basis sets (MADs between 17 to 30 kJ/mol for B3LYP and between 7 to 14 kJ/mol for MP2) (Figure S4.a) (Table 4).

MAD is significantly improved for all theories after adding the (d) function for heavy atoms. The smallest MADs are observed with MP2 using higher basis sets (Figure S4.a) (Table 4).

The calculated bond dissociation energy of HF, B3LYP and MP2 was compared with the G4 method (Figure S7). HF, B3LYP and MP2 with 6-31G basis sets have poor linear square fit compared with other sets with polarized functions (Figure S7). The most excellent linear square fit is observed with MP2 level of theory using higher basis sets 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p), R^2=0.9967, 0.9976 and 0.9976 respectively. Conversely, HF/6-31G has the lowest linear square fit, 0.9033, and about 0.96, compared to other basis sets (Figure S7) (Table S15).

For further analysis, all Carbon-halogen bond dissociated species were classified into three groups: Carbon- (a) Fluorine, (b) Chlorine and (c) Bromine bond dissociations. Each group was compared with the G4 method (Figure 5).

By comparing MP2/6-31+G(d) and MP2/6-31+G(d,p) with the G4 method, an inferior linear square fit was obtained, close to 0.82 and 0.55 with Carbon-Chlorine and Carbon-Bromine bond dissociation respectively (Figure 5). Because of this, the effect of geometry has been investigated. The bond dissociation energies of MP2 theory were computed at different basis sets using a fixed optimized geometry. The geometry optimized by G4 of B3LYP/6-31G(2df,p) has been used. Unfortunately, MP2/6-31+G(d) and MP2/6-31+G(d,p) using a fixed optimized geometry B3LYP/6-31G(2df,p) still give poor linear square fit with G4 (Figure S8).

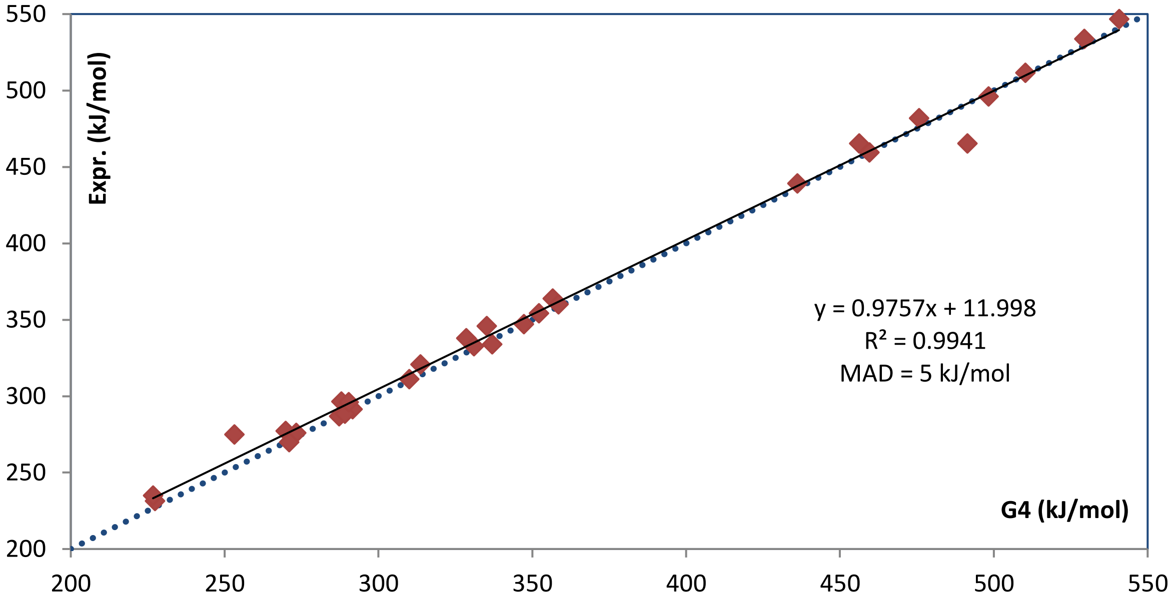


Figure 3. Comparison of the G4 method and the available experimental direct Carbon-halogen (F, Cl and Br) bond dissociation energies E_{BD} (kJ/mol) at 298.15K in halomethanes compounds. (30 compared).

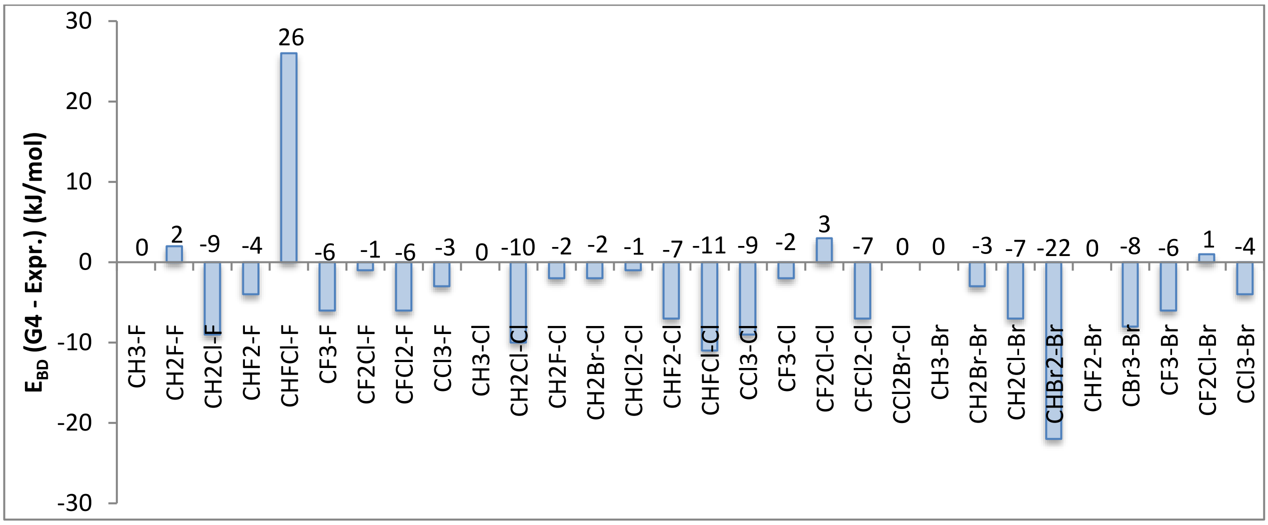
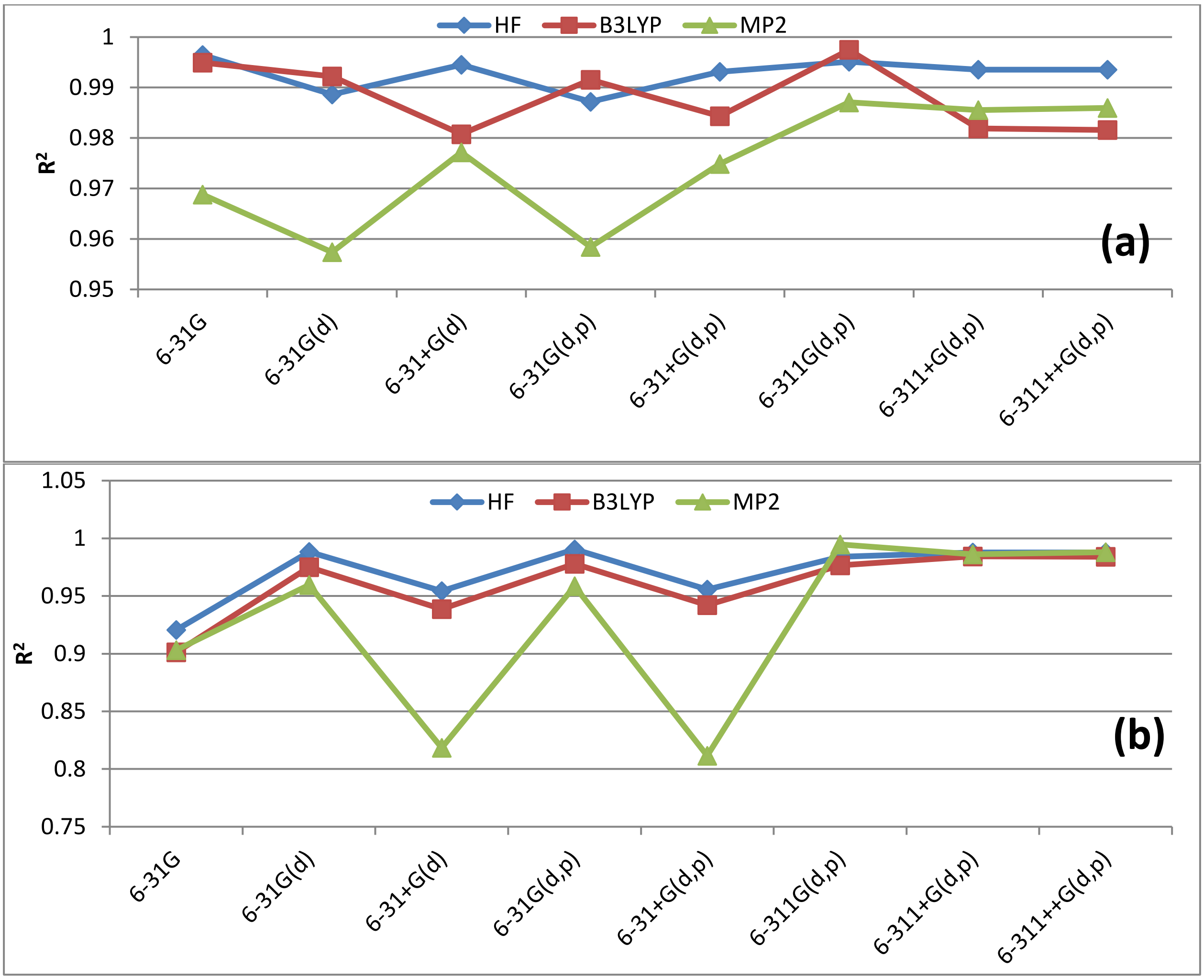


Figure 4. Deviation of G4 method and available experimental direct Carbon-halogen (F, Cl and Br) bond dissociation energies E_{BD} (kJ/mol) at 298.15K in halomethanes compounds. (30 compared).



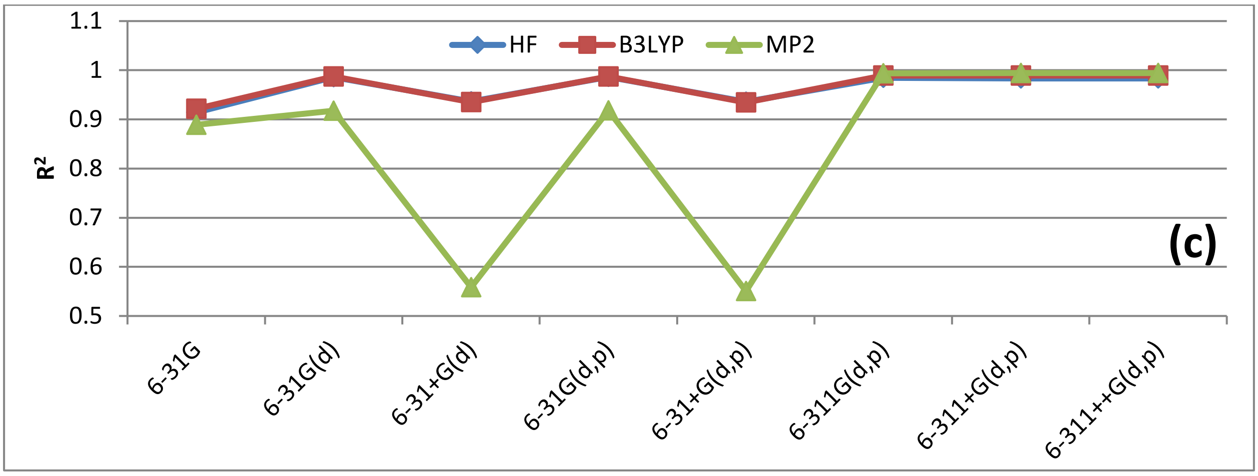


Figure 5. Summary of the square of the Pearson product-moment correlations coefficient (R^2) direct Carbon- (a) Fluorine (b) Chlorine and (c) Bromine bond dissociation energies E_{BD} (kJ/mol) at 298.15K for HF, B3LYP and MP2 methods and the computed G4 method in halomethanes compounds. (20 compared for each)

Isogyric Method

The computation of isogyric reaction bond dissociation energies, where the number of electron pairs is conserved on both sides of the reaction, is much favoured due to the cancellation of electron correlation errors.

A significant enhancement of computed bond dissociation energies using HF level of theory, MAD about 15 kJ/mol with literature data (Figure S5.a). Similarly, the B3LYP level of the theory worked very well, with fluctuated MAD around 8 kJ/mol by using 6-31+G(d) and 6-31+G(d,p) and about 12 kJ/mol using 6-31G(d), 6-31G(d,p) and 6-311G(d,p) basis sets. On the other hand, the MP2 level of theory with all studied basis sets provided an excellent MAD of 8 to 10 kJ/mol (Figure S5.a). Noticeably, there is no vital effect for adding the (d) function of the heavy atoms basis set.

The G3MP2 method continues to produce excellent results, with MAD = 5 kJ/mol, along with the experimental data (Figure S5.b). G3MP2 gave an accurate thermochemical property as G4 theory with less time-consuming.

Complete Basis Set CBS-QB3 offers better MAD = 7 kJ/mol using isogyric reaction, compared with the direct method, MAD = 13 kJ/mol (Figure S5.b).

The calculated bond dissociation energy of HF, B3LYP and MP2 gave a perfect linear square fit with the G4 method, R^2 between 0.9844 and 0.9989. (Figure S9) (Table S16). Remarkably, there is no essential effect for the polarized function of heavy atoms. On the other hand, the coefficients of determination with G4 are almost the same as those of the direct method (systematic error).

For additional analysis, each of the Carbon- (a) Fluorine, (b) Chlorine, and (c) Bromine bond dissociations were compared with the G4 method (Figure S11). MP2/6-31+G(d) and MP2/6-31+G(d,p) with the G4 method gave poor linear square fit, close to 0.82 and 0.55 with Carbon-Chlorine and Carbon- Bromine bond dissociation, respectively (Figure S11).

The bond dissociation energies of the MP2 level of theory were calculated at different basis sets using a fixed optimized geometry B3LYP/6-31G(2df,p). A poor linear square fit with G4 resulted (Figure S12). This means that the geometry does not play an essential role in determining bond dissociation energies for at least MP2/6-31+G(d) and MP2/6-31+G(d,p).

Further investigation is needed for MP2/6-31+G(d) and MP2/6-31+G(d,p). Adding diffuse functions to heavy atoms has a significant effect. For example, comparing the linear square fit for MP2/6-31G(d) and MP2/6-31+G(d) with the G4 method in Carbon-Bromine bond cleavage gives 0.8962 and 0.5120, respectively. A comparison of MP2/6-31G(d,p) and MP2/6-31+G(d,p) with G4 gives a linear square fit of 0.8951 and 0.5222, respectively.

4. Conclusions

HF, MP2 and B3LYP levels of theory at 6-31G, 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-311+G(d,p) and 6-311++G(d,p) basis sets along with the composite methods CBS-QB3, G3MP2 and G4 were investigated to measure thermodynamic properties including enthalpies of formation as well as carbon-halogen bond dissociation energies of halomethanes which contain (F, Cl or Br).

G4 and G3MP2 agreed with the experimental data to compute the enthalpies of formation (MAD = 2 kJ/mol for each). As well as they gave excellent results in computing the carbon-halogen bond dissociation energies (MAD = 5 kJ/mol for each with experimental data). Diffused and polarized functions for heavy atom basis sets play a vital role in many cases, especially in computing bond dissociation energies.

The results obtained were compared with those obtained using the G4 method. Moreover, bond dissociation enthalpies (EBD) were calculated using direct and isogyric methods. The two methods gave similar linear square fit compared with G4, which means the correlation energy effect could be reduced using linear fit coefficients (systematic error).

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