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Theoretical calculation of heats of formation, bond dissociation energies, and gas-phase acidities of fluoromethanes, chloromethanes, and eight other monoderivatives of methane

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ABSTRACT

The heats of formation (HOFs), bond dissociation energies (BDEs) and gas-phase acidities (GPAs) of small methane halogenated (F, Cl) and monoderivatives of methane molecules were theoretically calculated, and the results were compared with the available experimental values in order to examine the accuracy of the six high levels of ab initio calculations CBS-Q, CBS-QB3, G2, G3, G3B3 and G4 in thermochemical studies. The HOFs were derived from ab initio calculations and thermodynamic cycles, using experimentally measured reactions and formation enthalpies. The HOFs of all the radicals of ·CH$_3$, ·CH$_2$X and ·X (X = F, Cl, C, O, N) were calculated by atomization reactions. The bond dissociation energies of homolytic cleavage of C–H and C–X (X = F, Cl, C, O, N) bond at 298.15 K were calculated. The gas-phase acidities were measured for the H-contained molecules, and the values were combined with the previously reported gas-phase deprotonation enthalpies. Regarding the calculated HOFs, BDEs and GPAs of the set of molecules, G4 theory was found to be the most accurate, with an RMS deviation of 1.62, 5.39, 3.61 kJ mol^{-1} respectively.

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1. Introduction

In the last several decades, numerous computational studies have been reported regarding halogenated hydrocarbons [1–5] due to their environmental impacts, including global warming and stratospheric ozone depletion [6–8]. Halogenated hydrocarbons are constantly released into the environment by natural, as well as anthropogenic, emissions, leading to serious environmental problems [1,9]. These compounds have been extensively investigated in solution [3] or in the atmosphere [3–5], and their fate in ozone depletion has been well-documented [10–14]. The atmospheric lifetime of halogen species is determined by their homogeneous and heterogeneous reactions toward OH, O(^{1}D) radicals, and Cl atoms in the marine environment, which have modest global warming potentials [1,3,6]. Photolysis by sunlight gives rise to free halogen atoms, and is the initial step of their degradation at stratospheric levels. These free halogens catalytically contribute to the destruction of stratospheric ozone [1,3]. In most cases, halogenated

hydrocarbons react with atmospheric oxidants (OH, NO$_3$, Cl) via the metathesis of a hydrogen atom [1,3,6].

$$OH + CH_3Cl \rightarrow H_2O + CH_2Cl$$
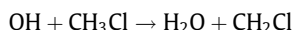
As a simple rule in the crude assessment of their atmospheric instability, the replacement ratios of hydrogen atoms are correlated with their C–H bond strengths [1,3]. Furthermore, the strength of the C–X bonds in halogenated compounds is directly related to their photodissociation ability and the energetically accessible pathways available for their primary photolysis [1,3,15]. Halogenated compounds, particularly fluoro- and chlorocarbons, are of considerable significance [5,9,10,16]. Fluorinated molecules have been regarded as alternative ozone-friendly refrigerants and fire-suppressing agents [1], while chlorinated molecules are very important compounds in illustrating and quantifying the ozone depletion potential of halogenated hydrocarbons molecules [17]. In particular, the mechanism and dynamics of ultraviolet photodissociation have remained heatedly debatable over the years, as different experiments appear to support different models [18]. The properties of C–X bonds in halogenated compounds have also been studied in the field of molecular biology, and evidence has shown the importance of these interactions in molecular recognition processes [19]. Resnati et al. capitalized on the advantages of these halogen bonds and used them to control the crystallization of or-

ganic compounds in designing new supramolecular materials [19–21]. Thus, C–X bonds have created considerable interest in organic, inorganic, and biological chemistry, and their study contributes to the understanding of the mechanisms of chemical reactivity reactions [19].

Determination of accurate thermodynamic data for small, halogenated hydrocarbons is essential to their further study. The HOFs of these simple model compounds are necessary in isodesmic reaction schemes to treat larger molecules in other quantum chemistry calculations [22]. Since measuring the BDEs of C–H and C–X bonds is difficult, and there is very little experimental thermochemical information on the anions, electron affinities, and GPAs of these halogenated hydrocarbons, high-level theoretical calculations are required to obtain accurate values. Present-day theoretical studies of computational chemistry methods can now correctly provide reliable predictions of HOFs and BDEs to within 4 kJ mol^{-1} for most molecules not included in many Refs. [1,22,23].

In the current study, theoretical calculations were performed in an attempt to reproduce the experimentally known HOFs, BDEs, and GPAs of eight small halomethanes CH_3X (X = F, Cl) and eight simple monoderivatives of methane at 298.15 K, giving particular emphasis on the accuracy and efficiency of such computational results. The HOFs, BDEs, and GPAs of the molecules were calculated using six high-level accuracy calculations: CBS-Q, CBS-QB3, G2, G3, G3B3, and G4. Bozzelli et al. determined some accurate HOFs for aldehydes through a series of thermodynamic cycles that used computational chemistry, experimental reactions, and HOFs from the literatures, and gained positive results [24]. In the present work, HOFs were determined using existing thermochemical data with experimental reactions [23,24], ab initio calculations utilizing isogyric [5,25] and isodesmic reactions [26], and atomization methods [23,24]. The use of atomization methods provided the most accurate results. BDEs were computed from the HOFs of the molecules and their corresponding radicals using the methods presented above, and the results were compared with the experimental data available. GPAs, or gas-phase deprotonation enthalpies, were also calculated with the above methods, and were derived from the equation [27]:

$$\Delta H^\circ acid(HAB) = BDE(H - AB) + IP(H) - EA(AB)$$

Since the scarcity of experimental data is severe for many molecules, theoretical studies may be used to derive accurate values.

2. Computational method

All theoretical calculations were carried out using the Gaussian 09 suite of programs [28]. CBS-Q [29], CBS-QB3 [30], G2 [31], G3 [32], G3B3 [33], and G4 [34] were employed to calculate HOFs, BDEs, and GPAs.

The G4 theory [34] is a new method of the Gaussian-*n* series that contains several new features not included in the G3 theory, leading to improved performance. In the G4 method, geometry optimization and zero point energy are both carried out at the B3LYP/6-31G(2df,p) level. The B3LYP/6-31G(2df,p) vibrational frequencies are scaled at 0.9854, giving the zero-point energy E (ZPE) used to obtain E_0. Next, the Hartree–Fock energy limit E (HF/limit) is calculated, a step not included in previous methods. Correlation level calculations are performed using the Moller–Plesset perturbation theory up to the fourth order and the coupled cluster theory, with parameters as follows: E[MP4/6-31G(d)], a correction for diffuse functions $\Delta E(+)$, a correction for higher polarization functions $\Delta E(2df,p)$, a coupled cluster correction $\Delta E(CC)$, a correction for larger basis set effects $\Delta E(G3LargeXP)$, a correction for the HF limit $\Delta E(HF)$, and a spin–orbit correction $\Delta E(SO)$. In addition, a higher-level correction (HLC) is applied in the calculation to take into account remaining deficiencies in the energy calculations E(HLC). Finally, the total energy at 0 K is obtained by the following formula:

$$E_0(G4) = E[MP4/6 - 31G(d)] + \Delta E(+) + \Delta E(2df, p) + \Delta E(CC) \\ + \Delta E(G3LargeXP) + \Delta E(HF) + \Delta E(SO) + E(HLC) + E(ZPE)$$

Three approaches were employed to determine the HOFs. First, reaction enthalpies were computed for some reactions involving methane derivatives; in these reactions, the HOFs for all other reaction species were accurately known. However, the HOFs of only seven derivatives were achieved via this method because determining proper gas-phase reactions for other derivatives proved difficult. Second, the HOFs were calculated using isogyric and isodesmic reactions. Isogyric reactions, in which the total number of unpaired electron spins is preserved [5,25]. The isogyric reactions used in the present study all correspond to the general formula

$$C_xH_yX_z + zH_2 \rightarrow C_xH_{y+z} + zHX$$
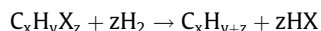
The concept of isogyric reactions can be taken a step further using isodesmic reactions such that the number of electron pairs and the number of bonds of each formal type are preserved [25]. Here, systematic computational errors are canceled out in the computed reaction enthalpy. The isodesmic reactions in the present work are as follows:

$$C_xH_yX_z + zCH_4 \rightarrow C_xH_{y+z} + zCH_3X$$

$$C_xH_yX_z + zCH_3CH_3 \rightarrow C_xH_{y+z} + zCH_3CH_2X$$
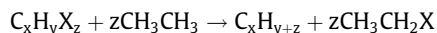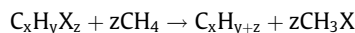
The last approach utilized atomization enthalpies. The HOFs used accurately known experimental enthalpies of C (711.20 kJ mol^{-1}), H (216.02 kJ mol^{-1}), O (246.81 kJ mol^{-1}), N (470.83 kJ mol^{-1}), F (77.28 kJ mol^{-1}), and Cl (119.62 kJ mol^{-1}) [35], and atomization corresponded with the following reaction:

$$C_xH_yX_z \rightarrow xC + yH + zX$$
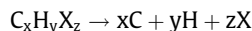
Only homolytic C–H and C–X BDEs were calculated from 298.15 K enthalpies. The HOFs of each of the radicals corresponding to C–H and C–X bond cleavage [36] also used the six ab initio methods above.

$$AB \rightarrow A + B$$
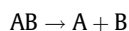
Table 1
Reactions involving CH_3Cl, CH_2Cl_2, $CHCl_3$, CH_3CH_3, CH_3CHO, CH_3NH_2, their experimental $\Delta_{rxn}H^\circ_{298.15}$ values and average absolute error (kJ mol^{-1}).

	Reaction	CBS-Q	CBS-QB3	G2	G3	G3B3	G4	$\Delta_{rxn}H^\circ_{298.15}$	AVE
1	$CH_3Cl + H_2 \rightarrow CH_4 + HCl$	−78.83	−79.31	−81.51	−84.16	−83.76	−82.27	−80.8 ± 0.4 [38]	1.76
2	$CH_2Cl_2 + 2H_2 \rightarrow CH_4 + 2HCl$	−150.99	−153.41	−158.38	−161.97	−161.93	−159.88	−163.4 ± 1.3 [39]	5.85
3	$2CHCl_2F \rightarrow CHCl_3 + CHClF_2$	−18.31	−15.51	−14.08	−14.96	−15.34	−16.43	−14.2 ± 2.0 [40]	1.43
4	$H_2 + CH_2CH_2 \rightarrow CH_3CH_3$	−133.34	−133.13	−134.96	−134.99	−133.77	−134.1	−136.3 ± 0.3 [41]	2.25
5	$2H_2 + CHCH \rightarrow CH_3CH_3$	−307.06	−306.94	−310.46	−311.10	−307.92	−309.14	−312.0 ± 0.63 [42]	3.23
6	$H_2 + CH_3CHO \rightarrow CH_3CH_2OH$	−63.57	−64.33	−63.46	−66.90	−66.46	−66.38	−69.08 ± 0.42 [43]	3.90
7	$2CH_3NH_2 \rightarrow (CH_3)_2NH + NH_3$	−19.82	−19.76	−18.82	−19.55	−19.53	−19.17	−19.7 [44]	0.32

Table 2
Experimental and computed HOFs for the species involved in thermodynamic cycle and isodesmic, isogyric reactions at 298.15 K (kJ mol^{-1}).

	$\Delta_f H^\circ_{298.15}$(exp)[c]	CBS-Q	CBS-QB3	G2	G3	G3B3	G4
H_2	0.0	−4.75	−4.74	−4.50	−1.92	−1.73	−1.41
CH_4	−74.6	−74.04	−74.48	−77.77	−75.95	−74.84	−74.77
HCl	−92.3	−96.22	−97.18	−93.91	−91.69	−90.61	−90.48
$CHCl_2F$	−283.26	−301.82	−301.42	−295.93	−286.72	−282.54	−283.01
$CHClF_2$	−482.6	−496.34	−497.14	−498.16	−485.3	−481.92	−481.45
CH_2CH_2	52.4	56.37	55.17	53.29	51.61	51.49	51.93
CHCH	227.4	234.84	233.75	233.29	229.63	227.37	228.38
CH_3CH_2OH	−234.8	−234.68	−237.04	−239.45	−235.44	−235.62	−234.34
$(CH_3)_2NH$	−18.8	−12.28	−15.74	−19.69	−14.67	−15.23	−15.97
NH_3	−45.9	−41.81	−43.88	−45.17	−42.51	−43.03	−42.54
CH_3CH_2Cl	−112.1	−115.80	−116.30	−115.47	−111.90	−109.64	−110.48
HF	−273.3	−276.61	−276.47	−276.87	−273.48	−272.97	−273.63
CH_3OH	−201.0	−202.30	−204.51	−206.79	−201.35	−201.82	−201.21
HCOOH	−378.7	−383.44	−384.76	−387.18	−379	−380.67	−378.99
HCN	135.1	134.60	132.57	130.36	131.08	128.07	128.15
HCHO	−108.6	−112.75	−114.35	−117.11	−111.23	−112.49	−112.12
H_2O	−241.8	−242.46	−243.52	−243.02	−240.45	−241.00	−240.07
CH_3Cl	−81.9 ± 1.5[b]	−86.68	−87.61	−85.66	−81.55	−79.97	−81.57
CH_3F	−234.3[a]	−239.01	−240.98	−244.15	−237.88	−236.95	−236.06
CH_3CH_3	−84 ± 0.4[b]	−81.72	−82.70	−86.18	−85.29	−84.01	−83.59

[a] From Ref. [3].
[b] From Ref. [46].
[c] From Ref. [47].

Table 3
HOFs for CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, CH$_3$CH$_3$, CH$_3$CHO, CH$_3$NH$_2$ from thermodynamic cycle (kJ mol^{-1}).

	$\Delta_f H^\circ_{298.15}$ (this study)	$\Delta_f H^\circ_{298.15}$(exp)
CH_3Cl	−86.1	−81.9 ± 1.5[b]
CH_2Cl_2	−95.8	−95.4[c]
$CHCl_3$	−98.12	−102.7[c]
CH_3CH_3 (reaction 5)	−83.9	−84 ± 0.4[b]
CH_3CH_3 (reaction 6)	−84.6	−84 ± 0.4[b]
CH_3CHO	−165.72	−166.2[c]
CH_3NH_2	−22.5	−22.5[c]

[a] From Ref. [3].
[b] From Ref. [46].
[c] From Ref. [47].

$$D(A - B) = E(A) + E(B) - E(AB)$$

The ΔH_{acid} is defined by the reaction HA → A$^-$ + H$^+$ [27]. GPAs were calculated according to the equation:

$$\Delta H^\circ_{acid}(HAB) = BDE(H - AB) + IP(H) - E(AB)$$

The published enthalpy value of 1312.102 kJ mol^{-1} was applied as the IP(H) [37].

The accuracy of each method was assessed by the root-mean-square (RMS) of the differences between the calculated and experimentally available values for the entire set of thermodynamic data. The mean absolute deviation (MAD), the average deviation (AVD), and the maximum negative and positive deviations (MND and MPD) were also computed. MAD is traditionally used to assess the reliability of calculated methods [1], while the three latter valuations indicate the degree of balancing of errors for all the data, revealing systematic trends toward over- or underestimation of the calculation proper.

3. Results and discussion

3.1. Heats of formation

A substantial uncertainty was found for a number of the small compounds. For example, the HOF of CH$_3$Cl reported in the National Institute of Standards and Technology NIST Chemistry Web-Book database yields three different values, while information from other literature shows that CH$_3$Cl has six experimental enthalpies. Accurately determining the HOF of CH$_3$Cl is crucial as it is used in many isodesmic reactions to treat larger molecules. The HOF of a molecule can be calculated indirectly from the existing experimental enthalpy of a reaction involving that molecule and the HOFs of all other species in the reaction. This thermodynamic cycle can provide more accurate HOFs, as experimentally measured enthalpies can have uncertainties of 0.4 kJ mol^{-1} or lower [24]. In the present work, the thermodynamic cycle method was first evaluated in terms of the accuracy of experimental enthalpy values using computational techniques. Such techniques are capable of calculating reaction enthalpies to around 4 kJ mol^{-1} [23]. Known enthalpies for reactions involving the small molecule, along with the measured HOFs of other species appearing in the reaction, were used. In this manner, experimental HOFs were derived.

A series of reactions involving CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, CH$_3$CH$_3$, CH$_3$CHO, and CH$_3$NH$_2$ with reaction enthalpies from the literatures are presented in Table 1. No simple reactions were found for other small molecules. Table 1 further shows the reaction enthalpies calculated with the CBS-Q, CBS-QB3, G2, G3, G3B3, and G4 methods, along with the absolute difference between the average computational and experimental values. The average values were all small enough for us to consider these experimental values to be correct. Thus, only these reactions will be used in the thermodynamic analysis.

The required HOFs for species in the reactions are provided in Table 2, the values of which were compared with the six computational values. The enthalpy calculations are expected to be accurate, and can therefore be used to select the most accurate experimental enthalpies. Using the reaction and HOFs recommended in Tables 1 and 2, the HOFs of CH$_3$Cl, CH$_2$Cl$_2$, CH$_3$Cl CH$_3$CH$_3$, CH$_3$CHO, and CH$_3$NH$_2$ were calculated and are provided in Table 3 in comparison with previous experimental measurements. Except for CH$_3$Cl and CHCl$_3$, the HOFs of the other molecules were below 1 kJ mol^{-1}, proving that the thermodynamic cycle method is a good method for calculations as long as accurate experimental values are obtained.

The computation of isogyric and isodesmic reaction energies, where the number of bond types in the former and only the number of electron pairs in the latter are conserved on both sides of the reaction, is much less demanding with respect to the resolution of

Table 4
Isodesmic and isogyric reaction schemes and computed and experimental HOFs for the molecules at 298.15 K (kJ mol^{-1}).

	CBS-Q	CBS-QB3	G2	G3	G3B3	G4	Exp
9 $CH_3Cl + H_2 \rightarrow CH_4 + HCl$	−88.07	−87.59	−85.39	−82.74	−83.14	−84.63	−81.9 ± 1.5[b]
10 $CH3Cl + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2Cl$	−81.25	−82.25	−81.30	−81.71	−82.21	−82.60	−81.9 ± 1.5[b]
11 $CH_2Cl_2 + 2H_2 \rightarrow CH_4 + 2HCl$	−108.21	−105.79	−100.82	−97.23	−97.27	−99.32	−95.4[c]
12 $CH_2Cl_2 + 2CH_3CH_3 \rightarrow CH_4 + 2CH_3CH_2Cl$	−94.55	−95.11	−92.65	−95.18	−95.41	−95.27	−95.4[c]
13 $CH_2Cl_2 + 2CH_4 \rightarrow CH_4 + 2CH_3Cl$	−95.86	−94.42	−93.84	−95.55	−94.78	−93.85	−95.4[c]
14 $CHCl_3 + 3H_2 \rightarrow CH_4 + 3HCl$	−128.66	−120.91	−113.28	−109.35	−108.50	−110.53	−102.7[c]
15 $CHCl_3 + 3CH_3CH_3 \rightarrow CH_4 + 3CH_3CH_2Cl$	−108.18	−104.89	−101.02	−106.27	−105.70	−104.45	−102.7[c]
16 $CHCl_3 + 3CH_4 \rightarrow CH_4 + 3CH_3Cl$	−110.13	−103.85	−102.81	−106.83	−104.77	−102.33	−102.7[c]
17 $CCl_4 + 4H_2 \rightarrow CH_4 + 4HCl$	−141.91	−125.74	−116.30	−111.96	−110.15	−111.62	−95.7[c]
18 $CCl_4 + 4CH_3CH_3 \rightarrow CH_4 + 4CH_3CH_2Cl$	−114.60	−104.39	−99.95	−107.85	−106.43	−103.52	−95.7[c]
19 $CCl_4 + 4CH_4 \rightarrow CH_4 + 4CH_3Cl$	−117.21	−103.00	−102.34	−108.60	−105.18	−100.69	−95.7[c]
20 $CH_3F + H_2 \rightarrow CH_4 + HF$	−241.01	−242.66	−241.91	−238.26	−238.76	−236.98	−234.30[b]
21 $CH_2F_2 + 2H_2 \rightarrow CH_4 + 2HF$	−461.45	−463.60	−462.42	−455.56	−456.27	−453.23	−452.21 ± 0.92[b]
22 $CH_2F_2 + 2CH_4 \rightarrow CH_4 + 2CH_3F$	−448.03	−446.88	−447.20	−447.64	−447.35	−447.87	−452.21 ± 0.92[b]
23 $CHF_3 + 3H_2 \rightarrow CH_4 + 3HF$	−712.10	−713.56	−713.69	−703.21	−703.30	−699.48	−697.89[a]
24 $CHF_3 + 3CH_4 \rightarrow CH_4 + 3CH_3F$	−691.98	−688.48	−690.87	−691.33	−689.93	−691.45	−697.89[a]
25 $CF_4 + 4H_2 \rightarrow CH_4 + 4HF$	−954.76	−954.98	−957.10	−942.47	−941.45	−937.43	−933.6[c]
26 $CF_4 + 4CH_4 \rightarrow CH_4 + 4CH_3F$	−927.94	−921.54	−926.67	−926.63	−923.62	−926.71	−933.6[c]
27 $CH_3CH_3 + H_2 \rightarrow 2CH_4$	−87.59	−87.67	−84.35	−84.52	−85.26	−84.66	−84 ± 0.4[b]
28 $CH_3OCH_3 + 2H_2 \rightarrow 2CH_4 + H_2O$	−196.14	−197.87	−194.12	−188.41	−190.00	−189.46	−184.1 ± 0.5[b]
29 $CH_3OCH_3 + CH_4 \rightarrow CH_3CH_3 + CH_3OH$	−186.60	−187.54	−187.86	−185.61	−185.63	−185.62	−184.1 ± 0.5[c]
30 $CH_3COOH + H_2 \rightarrow CH_4 + HCOOH$	−435.70	−435.24	−432.03	−432.51	−432.67	−431.50	−432.2[c]
31 $CH_3COOH + CH_4 \rightarrow CH_3CH_3 + HCOOH$	−432.11	−431.56	−431.69	−432.00	−431.41	−430.84	−432.2[c]
32 $CH_3CN + H_2 \rightarrow CH_4 + HCN$	73.33	74.42	78.84	77.87	77.47	78.29	74.04 ± 0.37[b]
33 $CH_3CN + CH_4 \rightarrow CH_3CH_3 + HCN$	76.92	78.09	79.19	78.39	78.72	78.95	74.04 ± 0.37[b]
34 $CH_3CHO + H_2 \rightarrow CH_4 + HCHO$	−167.52	−167.07	−164.32	−164.57	−165.03	−164.28	−166.2[c]
35 $CH_3CHO + CH_4 \rightarrow CH_3CH_3 + HCHO$	−163.93	−163.40	−163.97	−164.05	−163.76	−163.62	−166.2[c]
36 $CH_3OH + H_2 \rightarrow CH_4 + H_2O$	−206.95	−207.66	−206.91	−203.28	−204.11	−204.18	−201[c]
37 $CH_3OH + CH_4 \rightarrow CH_3CH_3 + H_2O$	−203.36	−203.99	−206.57	−202.76	−202.85	−203.52	−201[c]
38 $CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$	−26.53	−26.81	−25.09	−22.78	−23.72	−24.27	−22.5[c]
39 $CH_3NH_2 + CH_4 \rightarrow CH_3CH_3 + NH_3$	−22.94	−23.13	−24.74	−22.26	−22.47	−23.61	−22.5[c]

[a] From Ref. [3].
[b] From Ref. [46].
[c] From Ref. [47].

electron correlation due to the cancellation of errors that occur, and can result in considerable improvements in HOFs calculated by ab initio techniques. However, the success of such an approach depends crucially on the availability of the types of molecules in the reactions and the accuracy of their thermochemical data. In the current work, isogyric and isodesmic reactions were used extensively to obtain the most precise HOFs for the species of interest, as well as to verify the consistency of the various methods used. HOFs at 298.15 K may be attained from atomization energies at 0 K (ΣD_0), as proposed by Curtiss et al. The experimental HOFs of the elements at 0 K combine with ΣD_0 to yield the corresponding HOF of the molecule at 0 K. The calculation of HOFs at 0 K is then enabled by adding the appropriate enthalpy differences ($H_{298.15} - H_0$) to the $\Delta_f H_0^0$ of the molecule of interest, for which accurate elemental experimental values are available, and readily calculated from their rotational constants and vibrational frequencies [45]. Table 4 lists the isogyric and isodesmic work reactions, as well as calculated values for all the molecules. The reference HOFs of the reactions are displayed in Table 2. Isodesmic reaction data are better than their isogyric analogues, with the G4 method performing the best. For instance, the HOFs of $CHCl_3$ were found to be −110.53 (IG), −104.45 (ID), −102.33 (ID), and −102.7 kJ mol^{-1} (exp). Differences of 8 and 2 kJ mol^{-1} were respectively observed from the isogyric and isodesmic work reactions. Isodesmic reaction energies, in which the number of bond types is preserved, were much more accurate with respect to the electron correlation conserved. Therefore, reasonably accurate predictions of HOFs are possible by utilizing isodesmic reactions, even at relatively low levels of theory. Table 5 shows the HOFs obtained at 298.15 K from atomization enthalpies including radicals. The various data yielded very consistent results both in the isodesmic and the atomization enthalpies. Table 8 shows the accuracy of each method, including

their RMS, MAD, AVD, MND, and MPD. The atomization enthalpies obtained from the G4 method performed the best. From Table 8, G3, G3B3, G4 methods led to better results with the RMS deviations 1.88, 1.71, 1.62 kJ mol^{-1}, and MAD 2.76, 2.34, 2.05 kJ mol^{-1}. The success of isodesmic reactions appeared to crucially depend on the availability of accurate thermochemical data for molecules used in the reaction. The G4 theory in atomization energies performed so well that major improvements in the HOFs by isodesmic reaction energy calculations are not expected. What we do expect, however, is a higher level of consistency among the six methods used, from which the most accurate method could be selected.

3.2. Bond dissociation energies

Knowledge of halomethane BDEs is important in understanding their reaction chemistry in stratospheric ozone depletion and molecular biology recognition processes. We calculated the BDEs corresponding to homolytic C–H and C–Cl bond cleavage from 298.15 K HOFs. BDEs for each of the molecules are shown in Table 6, along with the available literature values. In Table 6, good agreement between our calculated BDEs and the experimental BDEs can be observed. HOFs for each of the radicals corresponding to C–H and C–X bond cleavage were also calculated, and are shown in Table 5. Furthermore, the accuracy of each method was evaluated, and the results are presented in Table 8. The G3, G3B3 and G4 methods distinctly proved to be better for predicting BDEs with the RMS deviations of 5.79, 5.88, 5.39 kJ mol^{-1}. The $CHCl_x$ ($x = 1-4$) BDEs of C–Cl bond cleavage (G4) are 347.21, 328.42, 309.97, and 287.82 kJ mol^{-1}, respectively. As the number of chlorine atoms increased, the BDEs of C–Cl bond cleavage decreased. The reverse was detected in fluoromethane. Hence, if the number

Table 5
HOFs of the molecules and radicals from atomization energy calculations and experimental at 298.15 K (kJ mol^{-1}).

	CBS-Q	CBS-QB3	G2	G3	G3B3	G4	Exp
CH_3Cl	−86.68	−87.61	−85.66	−81.55	−79.97	−81.57	−81.9 ± 1.5[b]
CH_2Cl_2	−105.99	−105.95	−98.20	−93.52	−90.67	−93.02	−95.4[c]
$CHCl_3$	−125.61	−121.20	−107.77	−103.10	−98.48	−101.00	−102.7[c]
CCl_4	−138.02	−126.17	−107.89	−103.18	−96.72	−98.86	−95.7[c]
CHF_3	−239.01	−240.98	−244.15	−237.88	−236.95	−236.06	−234.30[b]
CH_2F_2	−458.01	−460.35	−463.72	−453.44	−452.39	−451.22	−452.21 ± 0.92[b]
CHF_3	−707.23	−708.74	−714.06	−699.35	−697.37	−696.39	−697.89[a]
CF_4	−948.45	−948.60	−956.53	−936.88	−933.46	−933.24	−933.6[c]
CH_3CH_3	−81.72	−82.70	−86.18	−85.29	−84.01	−83.59	−84 ± 0.4[b]
CH_3OCH_3	−186.18	−189.88	−192.66	−185.91	−186.22	−185.24	−184.1 ± 0.5[b]
CH_3COOH	−435.13	−436.43	−439.18	−432.24	−433.16	−430.55	−432.2[c]
CH_3CN	78.14	76.75	75.44	74.42	71.93	72.59	74[c]
CH_3CHO	−166.36	−167.96	−171.49	−166.63	−167.42	−166.55	−166.2[c]
CH_3OH	−202.30	−204.52	−206.79	−201.35	−201.82	−201.21	−201[c]
CH_3NO_2	−80.94	−83.92	−85.68	−74.51	−77.53	−78.06	−80.8[c]
CH_3NH_2	−17.14	−19.93	−23.02	−18.81	−19.36	−19.67	−22.5[c]
·H	217.99	217.99	217.99	217.99	217.99	217.99	217.99[a]
·Cl	121.21	121.22	121.21	121.22	121.22	121.21	120.92[a]
·CH3	147.54	148.44	146.89	142.21	143.49	144.43	145.687 ± 0.8[b]
·CHCl$_2$	79.26	79.56	91.49	90.43	93.46	87.76	87.1 ± 1.6[c]
·CH$_2$Cl	113.50	112.54	118.32	116.02	117.08	114.18	117.2 ± 2.9[c]
·CCl$_3$	50.29	53.30	71.27	70.54	75.42	67.74	71.1 ± 2.5[c]
·F	79.08	79.08	79.08	79.08	79.08	79.08	79.39 ± 0.30[b]
·CH$_2$F	−31.29	−32.80	−32.27	−32.17	−32.02	−32.06	−31.8 ± 4.2[c]
·CHF$_2$	−249.18	−249.82	−250.36	−245.36	−244.31	−246.06	−242.67[a]
·CF$_3$	−477.44	−477.22	−479.92	−469.61	−467.17	−471.65	−470.28 ± 4.2[b]
·OCH$_3$	21.55	17.8572	19.90	20.46	18.50	17.43	21.0 ± 2.1[c]
·CN	447.81	445.825	448.86	446.52	438.96	442.31	439.3 ± 2.9[c]
·CHO	39.70	40.3441	38.81	40.60	39.50	38.81	42.5 ± 0.5[c]
·OH	37.56	36.89	37.93	35.21	35.01	36.15	37.36 ± 0.13[c]
·NH$_2$	190.12	188.43	188.29	186.26	185.21	186.03	186.2 ± 1.0[c]
·CH$_2$CH$_3$	125.797	124.79	125.15	119.96	120.53	119.67	118.8 ± 1.3[c]
·CH$_2$OCH$_3$	0.69741	−1.92	−1.82	−0.62	−0.96	−2.67	0 ± 4.2[c]
·CH$_2$CN	261.591	261.48	267.03	258.57	256.62	257.47	252.6 ± 4[c]
·CH$_2$CHO	17.143	12.59	16.46	14.56	12.80	12.48	13.0 ± 2[c]
·CH$_2$OH	−15.723	−17.20	−16.06	−16.45	−17.05	−17.68	−17.0 ± 0.7[c]
·CH$_2$NH$_2$	152.77	152.93	154.63	152.56	152.02	150.13	151.9 ± 8.4[c]

[a] From Ref. [3].
[b] From Ref. [46].
[c] From Ref. [47].

of Cl atoms for a compound is small, the strong release of Cl atoms may be observed. The opposite is true for F-containing compounds.

For the monoderivatives of methane compounds, the BDEs of C–C bonds were lower than their corresponding C–H bond counterparts, except CH_3CN; this is expected and in line with their charge distributions. The order of BDEs of C–H bond cleavage is BDE(H–CH$_2$NH$_2$) < BDE(H–CH$_2$CHO) < BDE(H–CH$_2$COOH) < BDE(H–CH$_2$OH) < BDE(H–CH$_2$OCH$_3$) < BDE(H–CH$_2$CN) < BDE(H–CH$_2$NO$_2$) < BDE(CH$_3$CH$_2$–H). For the C–C bond, the order is BDE(CH$_3$–NO$_2$) < BDE(CH$_3$–OCH$_3$) < BDE(CH$_3$–CHO) < BDE(CH$_3$–NH$_2$) < BDE(CH$_3$–CH$_3$) < BDE(CH$_3$–COOH) < BDE(CH$_3$–OH) < BDE(CH$_3$–CN). The orders appear to be controlled by the electronegativity of the substituents X and the hybridization of the bond from X.

3.3. Gas-phase acidities

The GPAs of most H-containing molecules are difficult to measure. In the current study, the GPAs of 14 H-containing compounds were calculated using the six high-level theories. Table 7 lists the calculated values with the available experimental data from the NIST database. Averages for most of the experimental data were calculated and included in the last column of the table as the accuracy standard due to the absence of available data. From the data, only six compounds (CH_3Cl, CHF_3, CH_3CH_3, CH_3CN, CH_3CHO, and CH_3NO_2) were used in calculating the RMS, among others. The calculated and experimental differences of the other compounds were too large to use; thus, it is likely that more accurate measurements

of the experimental data are necessary. The G4 method yielded the best results, as evidenced by the fact that it yielded a weighted RMS deviation value of only 3.61 kJ mol^{-1} (Table 8). No experimental data was available for CH_3OH; hence, the G4 value 1731.98 kJ mol^{-1} was used as its GPA.

4. Conclusion

The energies for 16 small molecules and their radicals were calculated using the CBS-Q, CBS-QB3, G2, G3, G3B3, and G4 theoretical models. Comparisons made between the available experimental HOFs, BDEs, and GPAs consistently gave RMS, MAD, AVD, MND, and MPD errors giving particular emphasis on the computational accuracy and efficiency. The HOFs for the 16 molecules were determined from thermodynamic cycles with existing enthalpies of reactions and ab initio calculations. In this study, the close agreement between six theoretical approaches and 16 experimental HOFs confirm the accuracy of the latter. BDEs and GPAs for all C–H and C–X were achieved via the six theoretical methods and produced good results. The best of the six methods chosen in this work has a maximum positive deviation of 4.87 kJ/mol and a maximum negative deviation of −3.69 kJ/mol. Overall, compared with the six methods for a set of small molecules and their radicals, the G4 method provided the most reliable HOFs (1.62 kJ mol^{-1} RMS error), BDEs (5.39 kJ mol^{-1} RMS error), and GPAs (3.61 kJ mol^{-1} RMS error).

Table 6
Computed and experimental BDEs for C–H and C–X bonds in the molecules at 298.15 K (kJ mol^{-1}).

	CBS-Q	CBS-QB3	G2	G3	G3B3	G4	Exp[c]
CH$_3$–Cl	355.44	357.26	353.77	344.98	344.68	347.21	350.2
H–CH$_2$Cl	418.17	418.14	421.98	415.57	415.05	413.74	419
CH$_2$Cl–Cl	340.70	339.70	337.74	330.75	328.98	328.42	338
H–CHCl$_2$	403.25	403.50	407.68	401.94	402.13	398.77	400.6
CHCl$_2$–Cl	326.08	321.98	320.47	314.75	313.16	309.97	311.1
H–CCl$_3$	393.89	392.49	397.03	391.64	391.89	386.73	392.5
CCl$_3$–Cl	309.53	300.69	300.38	294.94	293.35	287.82	296.6
CH$_3$–F	465.64	468.50	470.12	459.17	459.52	459.57	460.2
H–CH$_2$F	425.71	426.18	430.35	426.81	426.25	426.20	423.8
CH$_2$F–F	505.81	506.64	510.54	500.35	499.46	498.24	496.2
H–CHF$_2$	426.82	428.52	431.83	429.18	429.41	427.36	431.8
CHF$_2$–F	537.13	538.00	542.79	533.08	532.14	529.41	533.9
H–CF$_3$	447.78	449.51	452.62	450.85	451.52	446.94	445.2
CF$_3$–F	550.08	550.46	555.70	546.35	545.37	540.67	546.8
CH$_3$–CH$_3$	376.80	379.58	379.95	369.70	370.99	372.44	377.4
H–CH$_3$CH$_2$	425.51	425.48	429.32	423.24	422.53	421.25	420.5
CH$_3$–OCH$_3$	355.27	356.18	359.45	348.58	348.21	347.10	351.9
H–CH$_2$OCH$_3$	404.87	405.95	408.83	403.29	403.26	400.56	402.1
CH$_3$–COOH	401.69	404.12	404.40	397.81	398.18	394.70	384.9
H–CH$_2$COOH	414.37	414.45	418.34	412.01	412.12	409.41	398.7
CH$_3$–CN	517.21	517.51	520.31	514.30	510.52	514.15	521.7
H–CH$_2$CN	401.44	402.73	409.59	402.14	402.68	402.88	405.8
CH$_3$–CHO	353.60	356.75	357.19	349.43	350.41	349.78	354.8
H–CH$_2$CHO	401.49	398.55	405.94	399.18	398.22	397.02	394.5
CH$_3$–OH	387.40	389.85	391.60	378.77	380.32	381.79	384.93
H–CH$_2$OH	404.57	405.32	408.72	402.89	402.77	401.52	401.92
CH$_3$–NO$_2$	251.87	257.29	262.52	250.77	252.50	251.85	260.7
H–CH$_2$NO$_2$	425.22	423.92	429.40	423.11	423.98	420.90	415.4
CH$_3$–NH$_2$	354.80	356.80	358.20	347.28	348.06	350.13	356.1
H–CH$_2$NH$_2$	387.90	390.85	395.64	389.36	389.37	387.79	392.9

[c] From Ref. [35].

Table 7
Computed and experimental GPAs for the molecules at 298.15 K (kJ mol^{-1}).

	CBS-Q	CBS-QB3	G2	G3	G3B3	G4	Exp[b]	AVG
CH$_3$Cl	1661.43	1664.10	1664.38	1659.63	1665.10	1665.35	1672 ± 10;1657 ± 13;1674 ± 8.4;1670 ± 17	1668.25
CH$_2$Cl$_2$	1576.82	1578.29	1581.94	1576.76	1580.80	1581.88	1572 ± 9.2;1567 ± 13	1569.5
CHCl$_3$	1500.58	1503.35	1507.93	1501.88	1507.68	1508.02	1496 ± 8.8;1494 ± 26	1495
CHF$_3$	1724.50	1721.22	1716.92	1720.21	1720.69	1718.11	1711 ± 17	1711
CH$_2$F$_2$	1675.51	1672.93	1668.76	1671.04	1671.24	1669.21	1628 ± 15	1628
CHF$_3$	1590.56	1592.75	1589.45	1591.34	1592.29	1589.53	1582 ± 5.9;1577 ± 8.8; 1573 ± 19	1554.25
CH$_3$CH$_3$	1762.61	1759.63	1759.11	1760.06	1759.30	1755.46	1758 ± 8.4;1761 ± 8.4	1759.5
CH$_3$OCH$_3$	1730.13	1728.43	1726.96	1727.57	1726.86	1724.02	1703 ± 8.4	1703
CH$_3$COOH	1553.23	1553.21	1554.14	1551.59	1551.12	1549.44	1540 ± 13;1539 ± 19	1539.50
CH$_3$CN	1569.24	1569.12	1568.52	1567.59	1567.99	1566.30	1560 ± 8.8;1562 ± 11;1568 ± 8.4	1553.6
CH$_3$CHO	1536.24	1536.65	1536.55	1534.21	1534.12	1532.58	1531 ± 9.2;1533 ± 12	1517.75
CH$_3$OH	1736.95	1737.49	1734.13	1734.10	1734.20	1731.98	N	N
CH$_3$NO$_2$	1496.25	1493.69	1495.43	1493.61	1494.75	1492.11	1498 ± 21;1491 ± 9.2;1495 ± 12	1494.67
CH$_3$NH$_2$	1755.11	1753.04	1751.68	1752.46	1751.38	1748.02	1682 ± 11;1687.0 ± 3.3	1684.5

N means none.
[b] From Ref. [46].

Table 8
The six methods and the corresponding RMS, MAD, AVD, MND and MPD for the HOFs (from isodesmic reactions and atomization energies), BDEs and GPAs at 298.15 K for all the species (kJ mol^{-1}).

ID&IG	CBS-Q	CBS-QB3	G2	G3	G3B3	G4	AE	CBS-Q	CBS-QB3	G2	G3	G3B3	G4
RMS	12.74	9.83	8.01	5.61	5.32	4.65	RMS	5.98	5.73	5.18	1.88	1.71	1.62
MAD	8.23	6.97	5.77	3.93	3.94	3.43	MAD	10.06	8.47	7.35	2.76	2.34	2.05
AVD	−6.78	−4.65	−3.17	−1.93	−1.61	−1.14	AVD	−3.25	−3.88	−2.55	−0.02	0.33	−0.28
MPD	5.91	12.06	7.02	6.97	9.98	6.89	MPD	8.99	8.88	14.43	7.22	6.36	4.87
MND	−46.21	−30.04	−23.50	−16.26	−14.45	−15.92	MND	−42.32	−30.47	−23.33	−7.48	−3.00	−3.69

BDE	CBS–Q	CBS-QB3	G2	G3	G3B3	G4	GPA	CBS–Q	CBS–QB3	G2	G3	G3B3	G4
RMS	7.05	6.56	8.49	5.79	5.88	5.39	RMS	6.48	5.04	3.75	5.12	4.31	3.61
MAD	5.44	5.02	6.85	4.69	4.68	4.56	MAD	5.86	4.32	3.45	4.32	3.32	3.36
AVD	3.33	3.89	6.74	−0.60	−0.77	−2.19	AVD	3.59	2.61	2.03	1.09	2.20	0.19
MPD	16.79	19.22	19.64	13.31	13.42	10.71	MPD	13.49	10.22	5.92	9.21	9.69	7.11
MND	−8.83	−4.19	−1.39	−9.93	−11.18	−9.58	MND	−6.82	−4.15	−3.87	−8.62	−3.15	−4.05

Acknowledgements

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