Ab Initio Studies of Halogenated Methyl and Methylene Radicals: Molecular Structure, Vibrational Frequencies, and Enthalpies of Formation

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Fluorine- and chlorine-substituted methyl and methylene radicals have been studied by ab initio quantum chemical methods in order to determine the molecular structure and vibrational frequencies as well as the enthalpies of formation. The equilibrium geometries of radicals have been optimized at various levels, and the vibrational frequencies have been calculated at the optimized geometries. The calculated results, particularly at the MP2/ 6-311G(d) level, are in good agreement with the experimental data reported previously, suggesting that the present levels of theory can yield reasonably accurate estimates for the molecular properties of halogenated radicals when the experimental data are lacking. The standard enthalpies of formation at 298 K, $\Delta H_f°$(298 K), of these radicals have been obtained, utilizing the electronic energies calculated by the G2 or the CBS method. Enthalpies of formation for methyl radicals calculated with the original G2 method are close to the experimental values although the claimed accuracy of 2 kcal/mol is not quite achieved, but the errors in enthalpies of formation from other methods are rather high. For methylene radicals whose enthalpies of formation show large discrepancies among the values reported, some assessments have been made based on the calculated enthalpies of formation.

I. Introduction

Small halogen-substituted hydrocarbon radicals are important in many industrial processes such as combustion, fire suppression, plasma etching of semiconductor surfaces, and reprocessing of burnt nuclear fuel, and many of them, especially methylene radicals or carbenes, are important intermediates or precursors in many organic reactions.[1−3] Recently these halogenated radicals have received much attention because of fundamental roles that they play in the atmospheric chemistry.[2,3] For example, the fates of chlorofluorocarbons (CFC) and halons in the upper atmosphere have been extensively investigated in relation to the destruction of ozone layer in the stratosphere.[4] Fluorine- or chlorine-substituted methyl and methylene radicals are believed to be generated in the upper atmosphere by photolysis of CFC or by reactions of OH radicals with hydrochlorofluorocarbons (HCFC) or hydrofluorocarbons (HFC), which are used as replacements for CFC.[5] These radicals are expected to undergo subsequently various chemical processes with other radicals or ions in the atmospheric environment.

While knowledge of the electronic structures and the accurate thermochemical data of these radicals are required for better understanding of the processes aforementioned, available information is still fragmentary for majority of the halogenated radicals, particularly for methyl radicals. The geometrical structures and vibrational frequencies of halogenated methylene radicals have been determined experimentally,[6] and several high-level ab initio studies have been reported for CF_2 and CCl_2.[7−15] In fact, these methylene radicals have been the subject of numerous theoretical investigations in light of the nature of low-lying electronic states, in particular, the relative ordering of singlet and triplet states.[7,8] On the other hand, the enthalpies of formation have not been established conclusively, experimental values showing a quite large scatter.[16] For halogenated methyl radicals, much less information is available. The experimental geometrical structures and vibrational frequencies have been determined partially only for a few methyl radicals,[6] and the thermochemical properties are less well-known. Only limited ab initio calculations to determine the geometrical parameters and vibrational frequencies have been reported,[17−23] mostly conducted at the Hartree−Fock (HF) level using small to medium size basis sets. It is fairly recent that calculations at correlated levels have been reported.[23]

We employed here ab initio quantum mechanical methods to study the electronic structures and to compute the enthalpies of formation of fluorine- and chlorine-substituted methyl and methylene radicals, thereby providing a means for predicting unknown electronic and thermochemical properties. These radicals are small enough to be amenable to high-level ab initio calculations with consideration of electron correlation using larger basis sets than in previous studies. By comparison of the calculated results with the experimental ones for which rather accurate experimental data are available, it is expected that better estimates may be obtained for the uncertainties involved in calculations of electronic and thermochemical properties for the methyl radicals, especially for CF_2Cl and $CFCl_2$.

II. Computational Methods

Ab initio quantum mechanical calculations were carried out using the Gaussian 92 and Gaussian 94 suites of programs.[24,25] The equilibrium geometries of radicals were optimized by the analytical gradient technique at the HF and the second-order Møller−Plesset (MP2) levels, with the standard 6-31G(d) and 6-311G(d) basis sets. All calculations were done using the spin unrestricted theory (UHF or UMP2) for both open-shell and closed-shell species. For spin unrestricted calculations, it turned out that the spin contamination was relatively minor ($\langle S^2 \rangle <$ 0.77). In calculations of inversion barriers, the MP2 energies corrected with the spin projection scheme[26] were utilized. A few calculations for methylene radicals, which have a closed-shell configuration, were proceeded employing the spin restricted theory (RHF or RMP2), but essentially the same results were obtained as in spin unrestricted calculations. For the MP2

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TABLE 1: Optimized Equilibrium Structures[a] and Total Energies[b] of Halogenated Methylene and Methyl Radicals; Values in Parentheses Are the Fixed Parameters in Geometry Optimization

(a) Methylene Radicals

	level	energy	*R*(C−F)	*R*(C−Cl)	θ(XCX) (X = F, Cl)	θ(FCCl)
CF_2 ($^1A_1$)	HF/6-31G(d)	−236.660 744	1.2833		104.47	
	HF/6-311G(d)	−236.725 172	1.2755		104.97	
	MP2/6-311G(d)	−237.304 319	1.2994		104.95	
	MP2/6-311+G(d)	−237.315 912	1.3016		104.90	
	expt[c,d]		1.30		104.9	
CFCl ($^1A'$)	HF/6-31G(d)	−596.681 977	1.2758	1.7429		106.22
	HF/6-311G(d)	−596.742 627	1.2674	1.7428		106.61
	MP2/6-311G(d)	−597.287 624	1.2940	1.7386		106.75
	MP2/6-311+G(d)	−597.299 441	1.3016	1.7251		106.84
	expt[e]		1.32	(1.714)		107.6
	expt[f]		1.307	1.706		107.6
CCl_2 ($^1A_1$)	HF/6-31G(d)	−956.712 261		1.7112	110.32	
	HF/6-311G(d)	−956.769 964		1.7116	110.34	
	MP2/6-311G(d)	−957.282 831		1.7126	110.32	
	MP2/6-311+G(d)	−957.292 391		1.7079	110.36	
	expt[g]			1.7157	109.2	

(b) Methyl Radicals

	level	energy	R(C−F)	R(C−Cl)	θ(XCX) (X = F, Cl)	θ(FCCl)	Φ
CF_3 ($^2A_1$)	HF/6-31G(d)	−336.131 183	1.3008		111.28		49.97
	HF/6-311G(d)	−336.223 312	1.2954		111.33		49.83
	MP2/6-311G(d)	−337.017 373	1.3169		111.34		49.82
	MP2/6-311+G(d)	−337.033 744	1.3181		111.32		49.87
	expt[h]		1.318		110.7		51.6
planar ($^2A_2''$)	HF/6-311G(d)	−336.171 758	1.2928		(120)		(0)
	MP2/6-311G(d)	−336.968 284	1.3113		(120)		(0)
CF_2Cl ($^2A'$)	HF/6-31G(d)	−696.163 286	1.3031	1.7255	110.62	113.58	45.35
	HF/6-311G(d)	−696.251 758	1.2975	1.7267	110.72	113.62	45.19
	MP2/6-311G(d)	−697.013 351	1.3195	1.7268	110.60	113.70	45.09
	MP2/6-311+G(d)	−697.031 312	1.3227	1.7189	110.24	113.97	44.72
planar ($^2B_1$)	HF/6-311G(d)	−696.223 704	1.2992	1.6802	115.95	122.02	(0)
	MP2/6-311G(d)	−696.986 167	1.3191	1.6717	116.01	122.00	(0)
$CFCl_2$ ($^2A'$)	HF/6-31G(d)	−1056.201 588	1.3090	1.7184	117.68	112.93	41.16
	HF/6-311G(d)	−1056.286 336	1.3026	1.7209	117.47	113.02	41.10
	MP2/6-311G(d)	−1057.016 398	1.3260	1.7184	117.49	112.99	41.16
	MP2/6-311+G(d)	−1057.032 884	1.3305	1.7143	117.76	112.91	41.14
planar ($^2B_1$)	HF/6-311G(d)	−1056.273 905	1.3055	1.6932	124.30	117.85	(0)
	MP2/6-311G(d)	−1057.004 033	1.3277	1.6838	124.23	117.89	(0)
CCl_3 ($^2A_1$)	HF/6-31G(d)	−1416.248 160		1.7142	117.14		29.00
	HF/6-311G(d)	−1416.328 722		1.7172	116.89		30.22
	MP2/6-311G(d)	−1417.028 062		1.7120	116.86		30.34
	MP2/6-311+G(d)	−1417.039 772		1.7127	116.53		31.86
	expt[i]				116.7		31.1
planar ($^2A_2''$)	HF/6-311G(d)	−1416.325 374		1.7039	(120)		(0)
	MP2/6-311G(d)	−1417.024 634		1.6951	(120)		(0)

[a] Bond lengths are in angstroms, and angles in degrees. [b] Energies are in hartrees. [c] Reference 31. [d] Reference 32. [e] Reference 35. [f] Reference 36. [g] Reference 33. [h] Reference 34. [i] Reference 22.

correlated methods, all electrons were included in computations. Each optimized structure was characterized by harmonic vibrational frequency calculations and was verified to be an energy minimum.

Enthalpies of formation were computed employing the Gaussian-2 (G2) theory of Pople and co-workers[27] and the complete basis set (CBS) theory of Petersson and co-workers.[28] These theories are designated to yield estimates of the electronic energy with large basis sets and a high degree of electronic correlation using a series of lower level calculations. In the original G2 method, several corrections are applied to the MP4/6-311G(d,p) energy in order to obtain effectively the QCISD-(T)/6-311+G(3df,2p) energy.[27a] The G2(MP2) method, which is the simpler version of the G2 method, replaces the MP4/6-311G(2df,p) energy with the one evaluated at the MP2 level.[27b] The CBS methods intend to recover the errors that result from incomplete convergence with respect to the one-particle (basis set) and the *n*-particle expansions of the wave function, and they incorporate the extrapolation of the second-order pair energies calculated with natural orbitals to the infinite-order pair energies at the limit of the complete basis set.

To obtain the standard enthalpy of formation at 298 K, $\Delta H_f°$(298 K), the atomization energies, $\sum D_0$, were computed from the calculated energies for the species and their constituent atoms. Enthalpies of formation at 0 K, $\Delta H_f°$(0 K), were then computed from the atomization energies and the experimental enthalpies of formation of the constituent elements.[29] Standard temperature corrections were applied to $\Delta H_f°$(0 K) in order to obtain $\Delta H_f°$(298 K).[30]

Major calculations were performed on a Cray C90 supercomputer, with supplementary calculations on a Pentium computer using the Windows version of the Gaussian package.

III. Results and Discussion

The optimized equilibrium geometries and the total electronic energies at the several levels of theory are given in Table 1.

The geometrical parameters of CF_2, CCl_2, and CF_3 have been determined definitely from various experimental studies including microwave spectroscopy,[6,31−34] and therefore the reliability of the ab initio structures may be evaluated directly against the experimental data. Comparisons of the ab initio structures with the experimental ones indicate that the optimized geometries of CF_2, CCl_2, and CF_3 at the MP2/6-311G(d) level reproduce quite well the experimental structures. In fact, examination of the calculated results for these radicals in Table 1 indicates that at least the MP2/6-311G(d) level of theory is necessary for obtaining accurate structural parameters. Although the bond angles are quite well reproduced within 1° at both the HF and MP2 levels and the C−Cl bond lengths are rather insensitive to the levels of theory, it appears that accurate determination of the C−F bond length requires inclusion of electron correlation. That is, the C−F bond lengths calculated at the HF level are consistently shorter (~0.02 Å) than the experimental values or those calculated at the MP2 level. At the MP2 level, however, the 6-31G(d) basis set overelongates the C−F bond lengths significantly, and in order to obtain the values close to the experimental ones, the 6-311G(d) basis set should be used. The effects of adding the diffuse functions have also been tested; it elongates C−F bonds very slightly and contracts C−Cl bonds, notably for those radicals containing both F and Cl.

For CFCl, there are some discrepancies between the calculated and the experimental structures. Karolczak, Joo, and Clouthier have obtained the electronic spectrum of CFCl under the jet-cooled conditions.[35] Without isotope data, it was not possible to determine a precise structure of CFCl, and they had to fix the C−Cl bond length at the value of CCl_2 (1.714 Å) to obtain the FCCl angle and the C−F bond length. Schlachta, Lask, and Bondybey have also studied jet-cooled LIF spectra of CFCl.[36] But they were only able to obtain relatively high rotational temperatures and thus extracted structural information from a simulation of band contours. Considering the errors inherent in the two methods, both sets of geometrical parameters should contain large uncertainties. On the basis of the geometries obtained here, it may be presumed that the C−F bond length be ~1.30 Å for CFCl and the C−Cl bond length ~1.74 Å, the C−Cl bond being distinctively longer than that of other chlorine-containing radicals.

As mentioned above, the experimental geometries for CF_2Cl and $CFCl_2$ are not available, and some of geometrical parameters of CCl_3 are lacking. However, on the basis of the excellent agreements between the ab initio and experimental structures for CF_2, CCl_2, and CF_3 radicals, it is expected that the geometries of other radicals obtained at the MP2/6-311G(d) level provide reasonably good estimates for the exact (unknown) structures. As in the case of methylene radicals, while the bond angles are rather insensitive to the basis set employed or electron correlation, the C−F bond lengths show large variation depending on the level of calculations: the HF level predicts consistently shorter bond lengths than the MP2 level does, and at the MP2 level, the 6-31G(d) basis produces the C−F bond lengths considerably larger than the 6-311G(d) basis does. Many of ab initio studies for halogenated methyl radicals have conducted geometry optimization at the HF level using medium size basis sets such as 6-31G,[17−22] and the deficiency of these levels of theory for predicting the C−F bond length should be noted.

The present results suggest that all methyl radicals studied here have nonplanar, pyramidal geometry, the same conclusion as observed in experimental studies.[22,34,37,38] The out-of-plane angle Φ of CX_2Y (where X, Y = F or Cl), which is defined as an angle between the CX_2 plane and the C−Y bond (when planar, Φ = 0°), is listed in Table 1b as well as in Table 2. This degree of nonplanarity is found to be insensitive to the level of calculations except for CCl_3, where an addition of the diffuse functions increases the out-of-plane angle more than 1°. Various factors, for example, the interaction between the unpaired electron on carbon and the nonbonding electrons of halogen, the electrostatic repulsion between the halogen atoms, and the change in hybridization of the carbon atom, will affect the degree of nonplanarity.[17,22] Although the combined effects of these factors are hard to predict, a prior ab initio study has determined that fluorine destabilizes a planar geometry more than chlorine does.[17] Table 1b shows that the out-of-plane angle Φ increases as the number of C−F bonds increases, in accord with earlier prediction. Also obtained are the structures of planar forms of methyl radicals. The vibrational frequency analysis at this configuration of geometry results in one imaginary frequency, indicating that the planar form is the transition structure during the out-of-plane bending motion.

TABLE 2: Inversion Barriers (cm^{-1}) and Out-of-Plane Angles, Φ (degrees), for Halogenated Methyl Radicals

	level	barrier	Φ
CF_3 ($^2A_1$)	HF/6-31G(d)[a]	11542	
	HF/6-311G(d)	11315	49.8
	MP2/6-311G(d)	10774	49.8
	PMP2/6-311G(d)	10352	
CF_2Cl ($^2A'$)	HF/6-31G(d)	6242	
	HF/6-311G(d)	6157	45.2
	MP2/6-311G(d)	5966	45.1
	PMP2/6-311G(d)	5529	
$CFCl_2$ ($^2A'$)	HF/6-31G(d)	2689	
	HF/6-311G(d)	2728	41.1
	MP2/6-311G(d)	2714	41.2
	PMP2/6-311G(d)	2342	
CCl_3 ($^2A_1$)	HF/6-31G(d)	608	
	HF/6-311G(d)	735	30.2
	MP2/6-311G(d)	752	30.3
	PMP2/6-311G(d)	513	
	expt[b]	460 ± 40	

[a] Reference 17. [b] Reference 22.

Table 2 presents the inversion barriers, defined as the difference in energy between the pyramidal and the planar forms, along with the out-of-plane angle Φ. It is seen that the inversion barrier increases as the out-of-plane angle increases or as the number of C−F bonds increases. The magnitude of inversion barriers varies depending on the levels of calculation. However, for open-shell systems such as halogenated methyl radicals, the effects due to the size of basis sets or inclusion of electron correlation are hard to predict without correction for spin contamination. As shown in Table 2, increasing the size of basis sets or including electron correlation does not necessarily lower the inversion barriers, but the inversion barriers calculated using the MP2 energies after spin projection scheme (denoted as PMP2 in Table 2) are significantly lower than the values before elimination of spin contamination. Hudgens et al.[22] have obtained a inversion barrier of 460 cm^{-1} for CCl_3 from the analysis of REMPI spectra, which is rather close to the value of 513 cm^{-1} calculated using the spin-projected energies.

Table 3 lists the harmonic vibrational frequencies. It is well-known that the levels of theory employed in the present study overestimate the harmonic vibrational frequencies due to insufficient corrections for electron correlation and the anharmonicity.[39] Thus, the vibrational frequencies are scaled by a factor of 0.8929 for HF/6-31G(d) and 0.95 for MP2/6-311G(d), and the scaled frequencies are listed in parentheses. The scale factor for the MP2/6-311G(d) frequencies is chosen so that the differences between the calculated and the experimental frequencies for methylene radicals are minimized in a linear

TABLE 3: Harmonic Vibrational Frequencies (cm^{-1})

(a) Methylene Radicals

	level	sym str (a_1)	bend (a_1)	asym str (b_2)
CF_2 ($^1A_1$)	HF/6-31G(d)	1390 (1241)[a]	729 (651)	1295 (1156)
	HF/6-311G(d)	1383	742	1280
	MP2/6-311G(d)	1282 (1218)	685 (651)	1174 (1115)
	expt[b]	1225.08	666.25[c]	1114.44
CCl_2 ($^1A_1$)	HF/6-31G(d)	793 (708)	367 (328)	847 (756)
	HF/6-311G(d)	788	364	834
	MP2/6-311G(d)	771 (733)	354 (336)	795 (755)
	expt[d]	730.0	335.2	748[b] (Ar)

	level	CF str (a′)	bend (a′)	CCl str (a′)
CFCl ($^1A'$)	HF/6-31G(d)	1347 (1202)	488 (436)	817 (730)
	HF/6-311G(d)	1335	491	810
	MP2/6-311G(d)	1223 (1162)	467 (444)	793 (753)
	expt[e]	1156	449	759

(b) Methyl Radicals

	level	CX_3 sym str (a_1)	out-of-plane (a_1)	CX str (e)	def (e)
CF_3 ($^2A_1$)	HF/6-31G(d)	1217 (1086)	758 (677)	1441 (1286)	549 (491)
	HF/6-311G(d)	1210	765	1420	561
	MP2/6-311G(d)	1124 (1067)	717 (681)	1302 (1237)	520 (494)
	expt[b]	1089	701	1260.16	512 (Ar)
CCl_3 ($^2A_1$)	HF/6-31G(d)	542 (484)	351 (314)	1001 (893)	296 (264)
	HF/6-311G(d)	539	360	979	296
	MP2/6-311G(d)	521 (495)	366 (348)	939 (892)	293 (278)
	expt[b]		251	898 (Ar)	

	level	CF_2 sym str (a′)	CCl str (a′)	CF_2 scissors (a′)	out-of-plane (a′)	CF_2 asym str (a″)	rocking (a″)
CF_2Cl ($^2A'$)	HF/6-31G(d)	1308 (1168)	863 (771)	459 (409)	641(572)	1407 (1256)	396 (354)
	HF/6-311G(d)	1295	856	463	650	1385	400
	MP2/6-311G(d)	1196 (1136)	811 (771)	438 (416)	613 (582)	1265 (1202)	379 (360)
	expt[b](Ar)	1148	761	599		1208	

	level	CF str (a′)	CCl_2 sym str (a′)	CCl_2 scissors (a′)	out-of-plane (a′)	CCl_2 asym str (a″)	rocking (a″)
$CFCl_2$ ($^2A'$)	HF/6-31G(d)	1331 (1188)	687 (613)	307 (274)	492 (439)	1026 (916)	414 (370)
	HF/6-311G(d)	1314	680	308	494	1009	418
	MP2/6-311G(d)	1200 (1140)	650 (618)	301 (286)	481 (457)	958 (910)	397 (377)
	expt[b](Ar)	1143	747			919	

[a] The values in parentheses are the scaled frequencies; the scale factors are 0.8929 for HF/6-31G(d) and 0.95 for MP2/6-311G(d). [b] Reference 6. [c] Reference 41. [d] Reference 42. [e] Reference 35.

least-squares sense. Also, it should be noted that the out-of-plane bending vibration for methyl radicals is not harmonic,[22,23,40] although the calculated vibrational frequencies are obtained assuming the harmonic potential. Instead, the potential for this mode possesses two potential energy minima, and therefore the frequencies listed in Table 3 for this out-of-plane bending mode should be taken with caution.

As shown in Table 3, the ab initio frequencies calculated both at the HF and the MP2 levels for methylene radicals match the experimental frequencies quite well,[6,35,41,42] once the appropriate scale factor is applied. The scaled MP2/6-311G(d) frequencies show particularly excellent agreement with the experimental values, suggesting that scaling of the MP2/6-311G(d) frequencies may be used for estimating the unknown frequencies of methyl radicals. However, two notable discrepancies are observed. For CF_2Cl, four vibrational frequencies have been reported from a matrix-isolation study.[43] Although other three vibrational frequencies are in good agreement with the ab initio frequencies, the experimental vibrational frequency assigned to the CF_2 scissors mode is in large deviation from the calculated one (599 cm^{-1} vs 416 cm^{-1}). Also for $CFCl_2$, three vibrational frequencies have been reported.[43] Again, while other two vibrational frequencies are in good agreement with the ab initio ones, the experimental frequency assigned to the CCl_2 symmetric stretch mode deviates considerably from the calculated one (747 cm^{-1} vs 618 cm^{-1}). For these two radicals, only the frequencies evaluated at the HF/3-21G level have been reported,[18] but the frequencies calculated at this level are not accurate enough to allow a direct comparison with experiment. Since only the particular vibrational frequencies show large discrepancies, assignments of these two experimental frequencies are in doubt, and reexamination of the vibrational frequencies of CF_2Cl and $CFCl_2$ seems to be warranted.

TABLE 4: Calculated and Experimental Enthalpies of Formation (kcal/mol) at 298 K and 1 Atm

	G2	G2(MP2)	CBS-Q	CBS-4	expt
			Methylene Radicals		
CF_2	−49.32	−50.44	−47.54	−44.62	−39.4 ± 3.4,[a] −49 ± 3[b] −43.5 ± 1.5[c]
CFCl	5.01	3.40	5.80	7.69	−2 ± 7,[b] 7 ± 6[d]
CCl_2	53.49	51.13	52.23	53.14	51.0 ± 2.0,[e] 52.4 ± 3.1,[a] 39 ± 3[b]
			Methyl Radicals		
CF_3	−114.41	−115.50	−113.74	−112.08	−111.4 ± 0.9,[f] −112 ± 1[d]
CF_2Cl	−67.78	−69.26	−68.33	−68.40	−66.7 ± 2.0,[g] −67 ± 3[d]
$CFCl_2$	−23.69	−25.72	−26.02	−27.42	−21.3 ± 2.4,[h] −22 ± 2[d]
CCl_3	17.18	14.50	12.21	9.48	17.0 ± 0.6,[i] 17 ± 1[d]

[a] Reference 52. [b] Reference 16. [c] Reference 53. [d] Reference 44. [e] Reference 54. [f] Reference 45. [g] Reference 47. [h] Reference 48. [i] Reference 49.

The ground-state electronic energies have been calculated by the G2, G2(MP2), CBS-Q, and CBS-4 methods, and Table 4 displays the calculated enthalpies of formation at 298 K, $\Delta H_f°$(298 K), obtained according to the procedures described

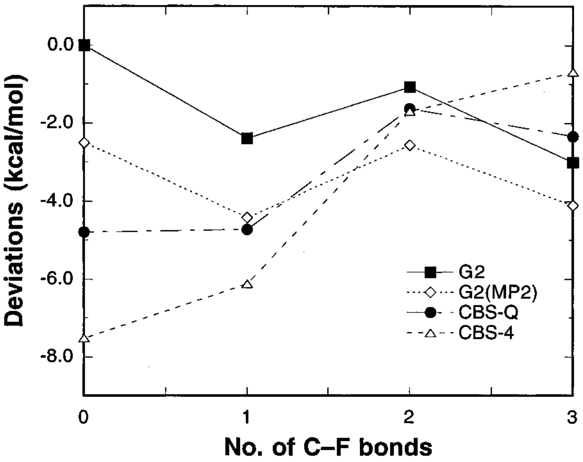

Figure 1. A plot of deviations of the calculated $\Delta H_f°$(298 K) from the experimental $\Delta H_f°$(298 K) for methyl radicals as a function of the number of C−F bonds.

in section II. As mentioned earlier, the experimental $\Delta H_f°$(298 K) values for halogenated methylene radicals exhibit a wide spread,[16] and therefore a direct comparison of the calculated values with the experimental ones is difficult. On the other hand, consistency among the experimental $\Delta H_f°$(298 K) values for methyl radicals is much higher.[44−50] Accordingly, a comparison of the calculated values with the experimental ones can be made more concretely.

The calculated values of $\Delta H_f°$(298 K) for methyl radicals using the G2 electronic energies, in general, match the experimental ones within the reported experimental uncertainties, but the values based on the G2(MP2) energies give consistently a little lower estimates than the G2 method. The G2 theory claims an accuracy of less than 2 kcal/mol in the evaluation of thermochemical data.[27] However, assuming that the $\Delta H_f°$(298 K) values quoted are accurate enough, the claimed accuracy for the G2 theory is not satisfactorily achieved in the present calculations, some cases showing deviations greater than 2 kcal/mol. The $\Delta H_f°$(298 K) values based on the G2(MP2) energies deviate the target accuracy to an even larger degree, producing the values up to 4.4 kcal/mol lower. The CBS theory also yields less satisfactory prediction. Although both CBS-Q and CBS-4 methods yield somewhat better estimates for CF_3 than the G2 methods, they show larger deviations particularly for $CFCl_2$ and CCl_3.

In contrast to the systems where the G2 or CBS calculations of $\Delta H_f°$ have yielded excellent agreement with experiment, the deficiency of these methods in predicting $\Delta H_f°$ of halogen-substituted hydrocarbons has been observed previously. Berry et al. have calculated $\Delta H_f°$(298 K) for the halomethane compounds using the same procedures as in the present study.[51] They have found that the values of $\Delta H_f°$(298 K) for those molecules based on the G2 or the CBS theory are significantly lower than the experimental estimates, and the discrepancy tends to increase as the number of C−F and C−Cl bonds increases. Figure 1 displays the deviations of the calculated $\Delta H_f°$(298 K) values in the present study from the experimental ones as a function of the number of C−F bonds for methyl radicals. As shown in Figure 1, the calculated values are consistently lower than the experimental ones. Because of the limited number of data set calculated here, it is not possible to examine the deviations as a function of the number of C−F bonds at each fixed number of C−Cl bonds. Still, it can be readily seen that the deviations are closely related to the number of C−F and C−Cl bonds. Furthermore, it is observed that the G2 methods exhibit greater errors with increasing number of C−F bonds, while the CBS methods much greater errors with increasing number of C−Cl bonds. One can conjecture that the reason for this discrepancy is partly related to the high degree of polarization of the C−F and C−Cl bonds. A related observation is that the G2 methods exhibit a particularly large deviation when the molecule possesses a single C−F bond as in $CFCl_2$ (Figure 1) or CH_3F (Figure 1 of ref 50a). In these cases, the polarization of electron density is expected to be higher compared to the cases of other molecules in series with two or more C−F bonds.

There are large uncertainties in $\Delta H_f°$(298 K) of CF_2 and CCl_2. The experimental $\Delta H_f°$(298 K) of CF_2 ranges from −34 to −56 kcal/mol.[16] A collision-induced dissociation threshold measurement of CF_3^- has established an upper limit of −39.4 ± 3.4 kcal/mol,[52] and a proton affinity bracketing experiment yields a value of −49 ± 3 kcal/mol.[16] In JANAF tables, evaluation of thermal equilibrium data leads to recommendation of 43.5 ± 1.5 kcal/mol as $\Delta H_f°$(298 K) of CF_2.[53] The calculated $\Delta H_f°$(298 K) values based on the G2 methods are quite close to the value by proton affinity bracketing, while the CBS-Q method predicts a little higher value, and the CBS-4 method yields a value close to that obtained from analysis of thermal equilibrium data. However, considering the tendency of the G2 method producing a lower estimate of $\Delta H_f°$(298 K) as the number of C−F bonds increases, the actual $\Delta H_f°$(298 K) value may well be higher than −49 kcal/mol, probably close to the CBS prediction. For CCl_2, too, there is a wide spread in the experimental $\Delta H_f°$(298 K), ranging from 30 to 59 kcal/mol.[16] Collision-induced dissociation of CCl_3^- yields a value of 52.4 ± 3.1 kcal/mol,[52] while proton affinity bracketing a value of 39 ± 3 kcal/mol.[16] But the value of 51.0 ± 2.0 kcal/mol extracted from the photoelectron spectrum of CCl_2 [54] lends supports to the value greater than 50 kcal/mol. The $\Delta H_f°$(298 K) values calculated here all exceed 50 kcal/mol, supporting the value obtained from the collision-induced dissociation. For CFCl, the experimental $\Delta H_f°$(298 K) suggests a negative value,[16] while the calculated $\Delta H_f°$(298 K)'s are of positive values. Nevertheless, the $\Delta H_f°$(298 K) values determined by the G2 and G2(MP2) methods are within the experimental error due to the large experimental uncertainties. Moreover, the 1994 NASA tables reports a value of 7 ± 6 kcal/mol,[44] which is more consistent with the present calculated results.

IV. Conclusions

In the present study, ab initio quantum chemical methods have been applied to obtain the equilibrium geometries and harmonic vibrational frequencies as well as enthalpies of formation for halogenated methyl and methylene radicals. The optimized geometries for CF_2, CCl_2, and CF_3 obtained at the MP2/6-311G(d) level are in good agreement with the experimental geometries. Thus, it is expected that the optimized geometries of other halogenated radicals represent closely the actual structures of those radicals, and the results obtained here can be served as a guideline for determining the unknown geometrical parameters of fluorine- or chlorine-substituted radicals. It is also observed that, in order to reproduce the C−F bond lengths, the optimization of geometries should be conducted, at least, at the MP2/6-311G(d) level. The calculated vibrational frequencies of methylene radicals match the experimental frequencies quite well, once the appropriate scale factors are applied. However, for methyl radicals, discrepancies between the calculated and the experimental frequencies have been observed for some of the vibrational modes, and reexamination of the experimental frequencies is suggested. The G2 and CBS theories were applied to compute $\Delta H_f°$(298 K) of halogenated radicals. It appears that the claimed accuracy of 2 kcal/mol of the G2 and CBS theories is not quite fulfilled for the halogenated radicals, showing deficiencies in estimating ΔH_f° for compounds containing C−F or C−Cl bonds. Also, a tendency has been observed that the G2 methods exhibit large errors as the number of C−F bonds whereas the CBS methods are more susceptible to errors as the number of C−Cl bonds increases.

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