A computational study of chlorofluoro-methyl radicals

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Chlorine- and fluorine-containing methyl radicals have been investigated by *ab initio* methods. Geometries and vibrational frequencies were derived with quadratic configuration methods at the QCISD/6-311G(*d,p*) level of theory, and energies via QCISD(T)/6-311+G(3*df,2p*) and Gaussian 3 theory. Anharmonicity of the out of plane bending mode was taken into account by numerical integration of the Schrödinger equation with a potential derived from a relaxed scan of this mode. The results are in good accord with experimental data where available. For the radicals CHF₂, CF₃, CH₂Cl, CHCl₂, and CCl₃, we compute $\Delta_f H_{298}^0$ values of -241.2, -465.9, 117.0, 91.1, and 72.2 kJ mol⁻¹, respectively, which agree with well-established experimental values to within 2.2 kJ mol⁻¹. For the more poorly characterized molecules CH₂F, CHClF, CClF₂, and CCl₂F we compute $\Delta_f H_{298}^0$ values of -29.0, -63.8, -274.7, and -94.3 kJ mol⁻¹, respectively, with recommended confidence limits of ± 4.1 kJ mol⁻¹. © 2003 American Institute of Physics.
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I. INTRODUCTION

Halocarbons are widely used as fire suppressants, solvents, and refrigerants. Some play a significant role in atmospheric ozone depletion and have high global warming potentials.¹ Modeling combustion processes, such as flame inhibition or waste incineration, or atmospheric chemistry involving halocarbons, requires accurate values of the thermodynamic parameters (enthalpies of formation, entropies, and heat capacities) of these molecules and their decomposition products. Halomethyl radicals are important products of radical attack (reaction with H or OH) on halomethanes.^{2,3}

Because of their transient nature, it is difficult to obtain accurate direct determinations of the structures, vibrational frequencies, or thermodynamics of halomethyl radicals. Kinetics investigations have proven useful in deriving enthalpies of formation of these species. When one can determine both forward and reverse rate constants, often for reaction with atomic halogens, then an equilibrium constant involving the halomethyl radical is known. Second-law analysis, based on differences between forward and reverse activation energies, and/or third-law analysis, based on ΔG and a separately determined ΔS , lead to accurate enthalpies of formation. In other cases, the kinetics results must be coupled with various assumptions, resulting in only rough approximations of the formation enthalpies.

There have also been previous computational studies of halogenated methyl radicals. Zachariah *et al.*⁴ studied fluoromethyl radicals by means of BAC-MP4 theory, where en-

ergies at fourth-order perturbation theory (MP4) with the 6-31G(*d,p*) basis set are modified with empirical bond additivity corrections (BAC). These species were also investigated by Haworth *et al.*,⁵ who combined Gaussian-3 (G3) theory with isodesmic reactions. CF₃ has been the subject of particular focus, based on G3 theory by Ruscic *et al.*⁶ and on extrapolation of coupled-cluster [coupled-cluster single double (triple) CCSD(T)] results to the complete basis set limit by Dixon *et al.*⁷ Rodriguez *et al.*⁸ analyzed chlorinated methyl radicals with quadratic configuration interaction (QCI) methods and large basis sets, in conjunction with atomization reactions. McGivern *et al.*⁹ derived bond strengths in fluoro-, chloro-, and bromomethanes by means of second-order Møller–Plesset (MP2) theory with basis sets up to cc-pV5z and with corrections for higher-level electron correlation based on CCSD(T) results.

In recent years, we have been able to employ high level quantum calculations to obtain enthalpies of formation of haloalkanes,^{10–12} halomethylidenes,¹³ and halocarbenes¹⁴ which are in very close agreement to accurate experimental data, where available. In this study, we utilize similar procedures to obtain accurate structures, vibrational frequencies, and enthalpies of formation of the series of nine chloro-, fluoro-, and chlorofluoromethanes. It is expected that the results will prove useful in accurate thermodynamic modeling of these species in combustion and atmospheric chemical processes.

II. COMPUTATIONAL METHODS

Calculations on CH₃ and the nine halomethyl radicals were performed using the GAUSSIAN 98¹⁵ and MOLPRO¹⁶

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FIG. 1. Effects of substituent electronegativities on molecular geometry: Sum of interbond angles ($\Sigma\theta_i$) vs sum of electronegativities (ΣX_i).

quantum mechanical packages. In order to obtain accurate structural and frequency data, the geometries were optimized at the QCISD/6-311G(*d,p*) level, and vibrational frequencies were computed at the same level. Frequencies were scaled by the factor 0.955¹⁴ (*vide infra*). The structural parameters and scaled frequencies are contained in Tables I and II, respectively. To facilitate statistical mechanical calculation of thermodynamic parameters such as entropies and heat capacities, products of the three components of the inertia tensor are also listed in Table I. Single point QCISD(T)/6-311+G(3*df*,2*p*) energies were then computed at the optimized QCISD/6-311G(*d,p*) geometries. For comparison, energies were also calculated using the G3 protocol,¹⁷ which approximates the QCISD(T) energy with the G3Large basis set via a series of additive calculations at MP2(full)/6-31G(*d*) geometries and uses scaled HF/6-31G(*d*) frequencies. QCISD(T) and G3 energies, E_0 [QCISD(T)] and E_0 [G3], are given in Table IV; values in Table IV include vibrational zero-point energies (ZPEs).

To facilitate analysis of the anharmonic "Umbrella" or "Out of plane large amplitude" (OPLA) vibrational modes, relaxed scans of the relevant coordinates corresponding to this bending vibration were performed at the QCISD/6-311G(*d,p*) level.

III. RESULTS AND DISCUSSION

A. Structures

To the authors' knowledge, there are as yet no accurate measurements of the molecular geometries of any chloro- or

FIG. 2. Effects of substituent electronegativities on molecular geometry: Bond lengths vs $X_Y + X_Z$ (sum of electronegativities of the "other" two bonding atoms) $R(C-F)$: circles; $R(C-Cl)$: squares.

fluoro-substituted methyl radicals. Approximate methods, usually based upon correlations with known data for other radicals and parent halomethanes, are generally used to obtain estimates of the bond lengths and angles, and hence the inertia tensor components, required for estimation of the rotational contributions to thermodynamic properties, are given here.

In our earlier investigation of the halocarbenes,¹⁴ it was found that computed QCISD/6-311G(*d,p*) geometries agreed with the available accurate experimental data to within approximately ± 0.01 Å and $\pm 1^\circ$. Therefore, we believe that the geometrical parameters contained in Table I provide reasonably accurate estimates of the halomethyl structures. The computed CH_3 bond length is in excellent agreement with the experimental value, 1.079 ± 0.005 Å.¹⁸ The computed inertia product, $I_a I_b I_c$, agrees with the value for CH_3 (for which accurate structural data are available) to within 2.5%,¹⁹ but ranges from 2% to 16% lower than estimates based on approximate structures.¹⁹

The radicals CH_2F and CH_2Cl deserve special attention. Our calculations, and those of Levchenko and Krylov,²⁰ yield a pyramidal equilibrium structure for CH_2F , although experiments yield a planar geometry.¹⁹ Levchenko and Krylov point out that the ZPE of the inversion or umbrella mode is higher than the inversion barrier, so that the effective geometry is planar. In the case of CH_2Cl our QCISD/6-311G(*d,p*) results are consistent with a slightly pyramidal structure, with a very small barrier to inversion, of about 0.01 kJ mol^{-1} . Levchenko and Krylov obtained a planar geometry

TABLE I. Structural parameters.

Radical	$R(\text{C-H})$ (Å)	$R(\text{C-F})$ (Å)	$R(\text{C-Cl})$ (Å)	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)	$\Sigma \theta_i$ (deg)	$I_a I_b I_c$ ($10^{-138} \text{ kg}^3 \text{ m}^6$)
CH_3	1.083	...	...	120.0 (HCH)			360.0	0.0511
CH_2F	1.084	1.342	...	122.9 (HCH)	114.4 (HCF)		351.8	2.64
CHF_2	1.090	1.328	...	113.8 (HCF)	111.4 (FCF)		338.9	83.4
CF_3	...	1.317	...	111.3 (FCF)			333.8	890
CH_2Cl	1.080	...	1.710	124.0 (HCH)	117.5 (HCCl)		358.9	9.35
CHCl_2	1.081	...	1.713	116.7 (HCCl)	119.2 (ClCCl)		352.5	1.27×10^3
CCl_3	...	...	1.721	117.0 (ClCCl)			351.0	3.30×10^4
CHClF	1.086	1.333	1.719	116.9 (HCF)	114.5 (HCCl)	114.5 (FCCl)	348.4	330
CClF_2	...	1.321	1.732	110.5 (FCF)	113.7 (FCCl)		338.0	3.21×10^3
CCl_2F	...	1.328	1.726	113.0 (FCCl)	117.6 (ClCCl)		343.6	1.08×10^4

using CCSD(T)/6-311++G(3df,2pd) theory,²⁰ and our QCISD(T)/6-311+G(3df,2p) data confirm that the planar form is the lowest energy conformation.

In order to obtain a semiquantitative measure of the departure from planarity of the halomethyl radicals, the sum of the three interbond angles, $\Sigma \theta_i$, are listed in the penultimate column of Table I. This quantity may vary from 360° (sp^2 bonding orbitals with the unpaired electron in a pure p orbital) to 328.4° (sp^3 bonding and nonbonding orbitals). One observes from Table I that replacement of a hydrogen by a chlorine atom causes a modest decrease in $\Sigma \theta_i$, with a significantly greater reduction when fluorine substituents replace the hydrogens.

A relatively simple interpretation, first proposed by Bent^{21,22} to explain the effects of substituent electronegativity upon molecular geometry, is that when substituents are bound to a central hybridized orbital, the fractional p character of the bonding orbital is increased by an amount approximately proportional to the substituent electronegativity. Displayed in Fig. 1 is a plot of $\Sigma \theta_i$ versus ΣX_i (representing the sum of the Pauling electronegativities^{23,24} of the three substituents) for CH_3 and the halomethyl radicals. One finds that the correlation between the two parameters is remarkably good, indicating the degree of pyramidalization of halomethyl radicals can be explained almost entirely by the increase in p character of the bonding orbitals with rising substituent electronegativity. Indeed, in CF_3 the sum of the F–C–F bond angles is quite close to that expected for purely sp^3 hybridized orbitals.

One may also attempt to apply Bent's rule to rationalize observed trends in C–F and C–Cl bond lengths in the halomethyl radicals. If one considers fluorine containing species, YZC-F , then, as seen in Fig. 2 (circles), there is a clear decrease in $R(\text{C-F})$ with the increased sum of electronegativities of the ancillary Y and Z ligands. This is consistent with expectations because increasing X_Y (or X_Z) will induce

a greater p character in the corresponding C–Y (or C–Z) bonding orbital, which must then increase the fractional s character of the remaining C–F orbital, which should lead to a decreased bond length. Indeed, the trend of shorter C–F bonds with increasing number of fluorines is found experimentally in the parent fluoromethanes ($\text{CH}_x\text{F}_{4-x}$),²² similar to that found here in the halomethyl radicals.

On the same arguments, one would expect that in chlorine-containing radicals, YZC-Cl , $R(\text{C-Cl})$ should decrease with rising $X_Y + X_Z$. The expected shortening of the C–Cl bond with additional chlorines has been reported experimentally in the chloromethanes ($\text{CH}_x\text{Cl}_{4-x}$),²² although, not surprisingly, the effect is smaller than in the fluoromethanes. However, in contrast both to expectations based upon Bent's rule and observations in the parent chloromethanes, $R(\text{C-Cl})$ is actually found to rise modestly with increasing electronegativity of the other two substituents (squares in Fig. 2).

A plausible, although not definitive, explanation for the apparently anomalous C–Cl bond length behavior is that as the sum, $X_Y + X_Z$, rises, this increases the s character of both the C–Cl bonding and unpaired electron hybrid orbitals. This, in turn, will increase the repulsive interaction between the unpaired electron and the chlorine lone-pairs, which may be sufficient to overcome the natural bond length decrease expected purely upon the basis of Bent's rule. While such a repulsive interaction can, in principle, also influence C–F bond lengths, both the significantly lower spatial delocalization of the fluorine lone-pair electrons and the greater pyramidalization of the fluoromethyl radicals should diminish the repulsive interaction with the radical's unpaired electron.

B. Vibrational frequencies

Not surprisingly, considering their transient existence, there is limited experimental data on the vibrational frequen-

TABLE II. Calculated and experimental vibrational frequencies.^a

Radical		ν_a	ν_b	ν_c	ν_d	ν_e	ν_f
CH ₃	Calc. ^b	416	1372	1372	2984	3158	3158
	Expt.	607	1398	1398	3004	3161	3161
	Diff. ^{c,d}	Umb (-191)	(-26)	(-26)	(-20)	(-3)	(-3)
CH ₂ F	Calc. ^b	648	1147	1147	1439	3014	3156
	Expt.	260	1170				
	Diff. ^{c,d}	Umb	(-16)				
CHF ₂	Calc. ^b	531	1008	1142	1173	1327	3037
	Expt.		949	1164	1173	1317	
	Diff. ^{c,d}		Umb (59)	(-22)	(0)	(10)	
CF ₃	Calc. ^b	496	496	681	1069	1256	1256
	Expt.	508	508	701	1089	1260	1260
	Diff. ^{c,d}	(-12)	(-11)	Umb (-20)	(-20)	(-4)	(-4)
CH ₂ Cl	Calc. ^b	200	821	986	1393	3056	3197
	Expt.	402	827		1391		
	Diff. ^{c,d}	Umb (-202)	(-4)		(2)		
CHCl ₂	Calc. ^b	301	496	740	884	1245	3114
	Expt.				902	1226	
	Diff. ^{c,d}		Umb		(-18)	(19)	
CCl ₃	Calc. ^b	274	274	326	487	893	893
	Expt.		290	251		898	898
	Diff. ^{c,d}		(-16)	Umb (-75)	Umb	(-5)	(-5)
CHClF	Calc. ^b	396	751	841	1146	1292	3073
	Expt.	540	757		1151	1283	
	Diff. ^{c,d}	Umb (-144)	(-6)		(-5)	(9)	
CClF ₂	Calc. ^b	359	415	579	767	1148	1218
	Expt.			599	761	1148	1208
	Diff. ^{c,d}			Umb (-20)	(6)	(0)	(10)
CCl ₂ F	Calc. ^b	283	375	448	611	913	1155
	Expt.				747	919	1143
	Diff. ^{c,d}				Umb (-136)	(-6)	(12)

^aFrequencies are in cm⁻¹.^bFrequencies calculated at QCISD/6-311G(*d*) level, and scaled by 0.955 (see the text).^cDiff = $\nu(\text{calc}) - \nu(\text{expt})$.^dThe notation, **Umb**, indicates that the mode has been assigned to the “umbrella” vibration.

cies of halomethyl radicals, other than CF₃.²⁵ Because these data are essential for estimation of the vibrational contributions to thermodynamic properties, approximate estimates have been given for the many unknown frequencies.¹⁹

It is well established that *ab initio* vibrational frequencies are typically greater than experimental values, in part because of the assumption of a harmonic force field; the discrepancies are approximately 5% when electron correlation is included in the calculation. In our recent study of the halocarbenes,¹⁴ it was determined that multiplication of QCISD/6-311G(*d*) frequencies by a scale factor of 0.955 gave close agreement to experimental data on a series of reference halomethanes, with a resultant rms error of <16 cm⁻¹. It was satisfying to find that a nearly identical scale factor (0.954) gave the best agreement to the limited experimental data in halocarbenes. The rms error was ~28 cm⁻¹, with the larger error most likely due to the greater uncertainty in the experimental frequencies of the carbenes. Thus, the 0.955 scale factor was used here to correct the QCISD frequencies for anharmonicity. The scaled frequencies for

CH₃ and the halomethyl radicals, together with the available experimental values,²⁵ are contained in Table II.

In general, the agreement between calculated and the limited experimental data is quite good, with five “pathological” exceptions (in CH₃, CHF₂, CH₂Cl, CHClF, and CCl₂F), where deviations between theory and experiment ranging from 60 to 200 cm⁻¹ for a single frequency are observed.

It is well known that the “inversion” mode in CH₃, at 607 cm⁻¹ (190 cm⁻¹ greater than ν_{cal}) is such a pathological case. This results from the extremely anharmonic inversion potential of this mode, which cannot be accounted for by the standard *ab initio* harmonic force field analyses. Because of the relatively low barrier to planarity, it is not unreasonable to expect comparatively large anharmonicities (leading to spurious frequencies) in the analogous “umbrella” modes of some of the pyramidal halomethyl radicals. We have located the umbrella frequencies in the halomethyl radicals by visualization of the various modes, aided in two cases by an anharmonic vibrational analysis (see the following); these

TABLE III. Anharmonic parameters of the halomethyl radical umbrella modes.

Radical	ν_{Umb}^a (Expt.)	ν_{Umb}^a (Harm)	ν_{Umb}^a (Anharm)	$\Delta(\text{ZPE})^{b,c}$	$\Delta(H_{298}-H_0)^{b,d}$	Potential fit parameters ^a				μ	Barrier ^{b,g}
						C_2	C_4	C_6	C_8		
CH ₃	607	416	588	0.7	-0.4	7 400	80 000	-58 300	32 900	2.415 ^e	0
CH ₂ F	260	648	216	-1.4	0.5	-3 080	12 500	-17 600	10 700	0.541 ^f	2.5
CHF ₂	949	1008	915	-0.3	0.0	-11 100	15 400	-10 500	4 790	1.197 ^f	33.6
CF ₃	701	681	587	2.8	-0.3	-177 000	1 070 000	-2 740 000	2 890 000	9.91 ^e	122
CH ₂ Cl	402	200	363	0.7	-0.7	-1 460	10 300	-14 300	8 910	0.518 ^f	0.01
CHCl ₂	...	496	386	-1.0	0.4	-2 490	7 580	-6 020	3 430	1.178 ^f	2.5
CCl ₃	251	326	241	-0.1	0.1	-9 390	53 700	-29 800	6 150	10.77 ^e	7.0
CHClF	540	396	617	2.8	-0.5	-4 710	104	15 500	-8 010	1.189 ^f	13.6
CClF ₂	599	579	819	-3.5	-0.5	-102 000	781 000	-3 220 000	5 920 000	10.31 ^e	66.0
CCl ₂ F	747	611	510	-3.7	-0.4	-54 900	574 000	-2 950 000	5 760 000	10.57 ^e	28.8

^aIn cm⁻¹.^bIn kJ mol⁻¹.^c(ZPE)_{Anharm} - (ZPE)_{Harm}.^d[H(298) - H(0)]_{Anharm} - [H(298) - H(0)]_{Harm}.^eReduced mass in u, x coordinate is distance in Å.^fReduced moment of inertia in u Å²; x coordinate is angle in radians.^gBarrier height from difference in planar and equilibrium QCISD/6-311G(d,p) energies. There are small differences between these barriers and those derived from the fit parameters.

vibrations are denoted by **Umb** in Table II. Not surprisingly, the radicals in which the deviations between theory and experiment for this mode are very large (>100 cm⁻¹), correspond to species which are closer to planar, with $\Sigma \theta_i$ ranging from 344° (CCl₂F) to 359° (CH₂Cl).

Excluding the anharmonic umbrella vibrations from the analysis reveals that the agreement between the scaled QCISD/6-311G(d) and available experimental frequencies is excellent, with a rms deviation of only 13 cm⁻¹ (the deviation rises to 86 cm⁻¹ if umbrella modes are included in the analysis). Thus, it is recommended that, with the exception of these highly anharmonic vibrations, the computed halomethyl vibrational frequencies in Table II furnish significantly more accurate estimates of the missing vibrational data in these species than the approximations based upon correlation with the parent halomethanes which have been used heretofore.¹⁹

We now consider the umbrella or OPLA modes in more detail. For methyl radicals of the type CHXY, the umbrella mode was approximated as bending of the angle between the C-H bond and the CXY plane. The reduced moment of inertia was taken to be that of H pivoting around C. For CH₂X radicals, the angle between the C-X bond and the CH₂ plane was followed, and the reduced moment of inertia was approximated from a mass of 2 u centered between the H atoms and pivoting around the C atom. For CH₃ and CCl₃, the umbrella mode was approximated as a change in distance between C and the H₃ or Cl₃ planes, and the reduced mass was derived from the sum of the masses of the substituents and the mass of C. The umbrella modes were investigated by carrying out relaxed scans of the umbrella motion and the results were fit to the form

$$V(x) = C_2x^2 + C_4x^4 + C_6x^6 + C_8x^8,$$

where x is a coordinate that describes the umbrella mode. The fitted $V(x)$ matches QCISD/6-311G(d,p) data to within about 200 cm⁻¹. Energy levels were obtained by solving the one-dimensional Schrödinger equation via the Fourier Grid

Hamiltonian method of Balint-Kurti and Martson²⁶ as implemented by Johnson.²⁷ Table III summarizes the anharmonic analysis, and its impact on the thermochemistry, derived from the explicit energy levels,²⁷ where the zero-point energies and integrated heat capacities $H_{298}-H_0$ are affected by up to about 3 and 1 kJ mol⁻¹, respectively. The calculated transition frequencies correspond to $v=1 \leftarrow v=0$ for the potentials with a single minimum and $v=2 \leftarrow v=0$ for the double well potentials, where the lower levels form closely spaced pairs. These transition frequencies match the observed values for these seven radicals (all species containing at least one hydrogen) better than the harmonic values, as seen in Table III, and the rms deviation between the calculated and experimental frequencies for all modes drops from 86 to 31 cm⁻¹.

There are high barriers to inversion for CF₃, CF₂Cl, and CFCI₂, as noted by Cheong and Cho²⁸ and seen in Table III. These barriers make the harmonic approximation useful, and we find that the simple anharmonic treatment as used for CCl₃ here is *less* accurate than harmonic analysis for these three species. This is likely because of the approximate description of the umbrella mode and reduced mass, neglect of changes in reduced mass with geometry during umbrella motion, and neglect of possible coupling with other modes. For these three molecules the harmonic results are employed for the thermochemistry.

C. Enthalpies of formation

In a recent publication, Louis *et al.*^{29,30} compiled a list of the most recent and accurate data on enthalpies of formation of the halomethyl radicals. The experimental enthalpies of formation given in Table IV are taken from the sources given in their article,^{6,31-35} and from a recent study by Litorja and Ruscic³⁶ for CH₃.

As noted in Sec. I, direct thermochemical measurement of the formation enthalpies is not possible for these transient

TABLE IV. *Ab initio* energies, and experimental and computed enthalpies of formation.^a (A) Reference compounds. (B) Fluoro-, chloro-, and chlorofluoromethyls.

Radical	$E_0(\text{G3})$	$E_0[\text{QCISD(T)}]$	$\Delta_f H^0(298)$ Experiment	Expt. Ref. ^b	$\Delta_f H_{298}^0$ [G3]	$\Delta_f H_{298}^0$ ^c [QCISD(T)]
(A)						
CH ₄	-40.457 629	-40.389 944 2	74.6 ± 0.3	19	...	...
CF ₄	-437.307 809	-436.984 939	-933.2 ± 0.75	19	...	...
CH ₃ Cl	-499.913 026	-499.518 601	-81.9 ± 0.6	19	...	...
CH ₂ Cl ₂	-959.371 223	-958.649 122	-95.00 ± 0.3	19	...	...
CH ₃	-39.793 287	-39.728 895	146.6 ± 0.4	36	...	...
(B)						
CH ₂ F	-138.989 675	-138.861 900	-32 ± 8.4	31	-27.2 (4.8)	-29.0 (3.0)
CHF ₂	-238.201 319	-238.009 770	-239 ± 4.2	31	-239.8 (-0.8)	-241.2 (-2.2)
CF ₃	-337.417 369	-337.162 530	-465.7 ± 2.1	6	-463.5 (2.2)	-465.9 (-0.2)
CH ₂ Cl	-499.256 308	-498.865 983	117.3 ± 3.1	32	118.8 (1.5)	117.0 (-0.3)
CHCl ₂	-958.719 539	-958.001 259	89.0 ± 3.0	32	91.8 (2.8)	91.1 (2.1)
CCl ₃	-1418.181 09	-1417.135 079	71.1 ± 2.5	33	70.3 (-0.8)	72.2 (1.1)
CHClF	-598.456 716	-598.002 247	-60.7 ± 10	34	-64.4 (-3.7)	-63.8 (-3.1)
CClF ₂	-697.666 788	-697.148 839	-279 ± 8.4	35	-272.1 (6.9)	-274.7 (4.3)
CCl ₂ F	-1057.921 06	-1057.139 307	-89.1 ± 10	34	-93.4 (-4.3)	-94.3 (-5.2)

^a*Ab initio* energies are in hartrees; enthalpies are in kJ mol⁻¹.^bNumbers correspond to references to experimental data (see the text).^cComputed using anharmonic umbrella mode parameters for all radicals except CF₃, CClF₂, and CCl₂F. See the text.

species, but estimates of varying accuracy are available by combining kinetics and other relevant data.

Table IV shows that the experimental values for CH₂Cl, CHCl₂, and CCl₃, obtained from kinetics investigations of CH_{3-x}Cl_x + HBr ⇌ CH_{4-x}Cl_x + Br,^{32,33} are known with a good degree of accuracy, as is CF₃, obtained from a network of thermochemical cycles.⁶ We do note that there is an unresolved discrepancy between the experimental entropy of CH₂Cl found by Seetula³² and that tabulated by Gurvich *et al.*,¹⁹ which we confirm. The estimate for CHF₂, based on data for CHF₂ + CH₄ ⇌ CH₂F₂ + CH₃, is known with a somewhat lower, but still reasonable degree of certainty.³¹ We denote the set of these five well-characterized halomethyl radicals as group A. On the other hand, as may be seen from the large quoted uncertainties of at least 8 kJ mol⁻¹, values of heats of formation of CH₂F, CHClF, CClF₂, and CCl₂F are less precise. CH₂F data are based on CH₃F + I → CH₂F + HI kinetics and *assumed* information on the reverse reaction, while CHClF, CClF₂, and CCl₂F values involve uncertainties both in bromination kinetics and the enthalpies of formation of the parent halomethanes.^{34,35} We denote these four radicals as group B.

It is well-established that the standard direct determination of enthalpies of formation from computed molecular atomization energies leads to unacceptably large systematic errors in haloalkanes (particularly those containing fluorine).¹⁰⁻¹⁴ A straightforward method for eliminating these

systematic errors is via the use of isodesmic reactions,^{37,38} in which the numbers of each type of bond are conserved. In the past, we have utilized this procedure successfully to obtain accurate *ab initio* enthalpies of formation in halomethanes,¹⁰ halomethylidynes,¹³ and halocarbenes,¹⁴ and apply it here in our investigation of the halomethyl radicals.

Application of this method to the chloro- and fluoromethyls requires accurately measured heats of formation of CH₄, CH₃, and at least one chloromethane and fluoromethane. Whereas $\Delta_f H^0(\text{CH}_3\text{Cl})$ and $\Delta_f H^0(\text{CH}_2\text{Cl}_2)$ are both known to high precision, there are no good measurements on CH₃F. Therefore, we use CF₄, whose heat of formation has been measured accurately, as the fluorine reference compound. The required experimental enthalpies of formation (and *ab initio* energies) of the reference compounds are given in Table IV.³⁹

If one uses CH₃Cl as a reference compound, then *ab initio* energies are computed for all species in reactions of the type

Vibrational zero-point energies and standard thermal corrections⁴⁰ are added to obtain H^0 (298.15 K) for each specie, from which one computes ΔH^0 (298.15 K) for the above-given reaction. One combines this computed reaction

enthalpy with the experimental data to determine $\Delta_f H^0$ for the desired radical, $\text{CH}_x\text{Cl}_y\text{F}_{3-x-y}$. If CH_2Cl_2 is used as a reference, the same procedure is used with an equation analogous to the above-given one.

Calculated enthalpies of formation of the halomethyl radicals, obtained both with G3 and QCISD(T) energies, are contained in the penultimate two columns of Table IV. It was found that computed values for chlorine-containing radicals using CH_2Cl_2 as a reference were uniformly above those with CH_3Cl by $0.2 \text{ kJ mol}^{-1}/\text{Cl}$ atom using G3 energies, and $1.0 \text{ kJ mol}^{-1}/\text{Cl}$ atom below CH_3Cl -based results using QCISD(T) energies. This small discrepancy suggests a minor inconsistency between the experimental heats of formation of these two references. The values in Table IV represent the average of the two determinations for the chlorinated species.

The values of $\Delta_f H^0$ using the two theoretical methods are close, to within 2.6 kJ mol^{-1} or less. The G3 results are even closer (maximum difference 2.2 kJ mol^{-1}) to the QCISD(T) data when anharmonicity is ignored in the latter. A comparison of the computed enthalpies with experimental determinations for the five radicals for which accurate data are available (*vide supra*) reveals that, with one exception, the theoretical values agree with experiment to within the quoted experimental confidence limits. The exception is the G3 value for CF_3 which is only 0.1 kJ mol^{-1} outside these limits. For the group A radicals (whose enthalpy of formation is given to better than 4.2 kJ mol^{-1}) to which we apply anharmonic corrections, namely CH_2Cl , CHCl_2 , CCl_3 , and CHF_2 , the corrections yielded minor improvements of between 0.3 and 1 kJ mol^{-1} in the accord with experiment for the first three, and a decrease in accord of 0.7 kJ mol^{-1} for the last. Inclusion of anharmonicity improved the accord more significantly, by 1 – 2 kJ mol^{-1} , for CH_2F and CHClF , although their experimental uncertainties are large.

The close agreement between the G3 and QCISD(T) methods and with the accurate experimental data provides confidence that, as in our earlier studies on halomethylidynes and halocarbenes, these calculations yield excellent estimates of enthalpies of formation in the halomethyl radicals for which accurate data are not available. The computed enthalpies using both methods are close. We suggest $\Delta_f H^0$ [QCISD(T)] results with anharmonic corrections be used as the recommended enthalpies, primarily because they are based on higher-level calculations of geometry and frequency. The agreement with the five accurate experimental enthalpies of the group A radicals in Table IV is to within 2.2 kJ mol^{-1} or better, with a mean deviation of 0.1 kJ mol^{-1} and a root mean square deviation of 1.5 kJ mol^{-1} . There is therefore negligible systematic error, and statistical 95% confidence limits based on this comparison and using Student's *t* to allow for the small sample size are $\pm 4.1 \text{ kJ mol}^{-1}$. This is our error estimate for the recommended heats of formation of the group B halomethyl radicals.

IV. CONCLUSIONS

QCISD/6-311G(d) geometric parameters, inertia products and vibrational frequencies, and isodesmic

QCISD(T)/6-311+G(3df,2p) enthalpies of formation of the halomethyl radicals determined here, provide more accurate data on these quantities than has been available heretofore. It is expected that these data will prove useful in the determination of the thermodynamic and kinetic parameters required to model these important decomposition products in simulations of the role of halomethanes in atmospheric chemistry and combustion processes.

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