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A Computational Study of the Thermochemistry of Bromine- and Iodine-Containing Methanes and Methyl Radicals

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Bromo- and iodomethanes and the corresponding halogenated methyl radicals have been investigated by ab initio methods. Geometries and vibrational frequencies were derived with quadratic configuration interaction methods at the QCISD/6-311G(d,p) level of theory, and energies via QCISD(T)/6-311+G(3df,2p). Core electrons were represented with relativistic effective potentials. Anharmonicity of the out-of-plane bending modes in the methyl radicals was taken into account by numerical integration of the Schrödinger equation with potentials derived from relaxed scans of these modes. The results are in good accord with experimental data where available. Thermochemistry derived via isodesmic reactions referenced to CH_3, CH_4, and monohalomethanes yields excellent accord with new experiments on dihalomethanes and provides recommendations for the more poorly characterized tri- and tetrahalomethanes and halomethyl radicals. For the methanes CH_2Br_2, $CHBr_3$, CBr_4, CH_2I_2, CHI_3, CI_4, CH_2BrI, $CHBr_2I$, and $CHBrI_2$ we compute $\Delta_f H^\circ_{298}$ values of 4.3, 51.6, 110.6, 108.1, 208.5, 321.3, 56.8, 104.8, and 157.1 kJ mol^{-1}, respectively. For the methyl radicals CH_2Br, $CHBr_2$, CBr_3, CH_2I, CHI_2, CI_3, CHBrI, CBr_2I, and $CBrI_2$ we compute $\Delta_f H^\circ_{298}$ values of 166.6, 191.7, 224.0, 217.2, 290.4, 369.1, 241.6, 320.8, and 272.3 kJ mol^{-1}, respectively. Recommended confidence limits are ±3 kJ mol^{-1} per Br or I atom. Trends in these values and the corresponding C−H bond strengths are discussed and compared with prior experiments, empirical estimation schemes, and ab initio calculations.

I. Introduction

Halogenated methanes are an important class of halogen compounds which are used to modify flames and which enter the atmosphere from natural and man-made sources. Their degradation via thermal decomposition, radical attack, or photolysis creates halogenated methyl radicals.

The important role of halogen compounds in stratospheric ozone depletion is well-known, especially for chlorine and bromine species.[1] Attention has also been drawn to potentially important iodine interactions with stratospheric ozone.[2] Bromine- and iodine-containing compounds, including mixed species such as CH_2BrI, may also play roles in the tropospheric chemistry of ozone and mercury.[3,4] Halogen compounds are employed as fire extinguishers, and CF_3Br is notably effective as a fire suppressant.[5] However, this compound has a high ozone depletion potential. One avenue for CF_3Br replacement is directed toward iodine compounds, which exhibit short atmospheric lifetimes with respect to photolysis.

A critical first step in quantitative modeling of atmospheric and combustion chemistry is to establish the thermochemistry of reactants and transient intermediates. While there is considerable thermochemical information available[6−8] for the lighter halogens, experimental data are sparse for bromine- and especially iodine-containing species. There are also some extraordinarily large discrepancies in the literature, which in the case of the enthalpy of formation of CI_4 exceeds 200 kJ mol^{-1}.[9−11] For the halomethanes, empirical estimation schemes have often been employed to complete data series. Much of the data come from equilibrium studies[12,13] and calorimetry, where a potential challenge is attaining complete combustion, and where the heat of combustion may be a small part of the total energy release when the halogen is absorbed in solution.[14] Threshold energies for dissociative ionization, induced by electon impact[15,16] or photoionization,[17] also yield thermochemical information. Not surprisingly there are fewer experiments on the transient halomethyl radicals R$^\bullet$, many based on kinetic studies of the equilibria[6]

$$R^\bullet + X_2 = RX + X \tag{1}$$

$$R^\bullet + HX = RH + X \tag{2}$$

where X is a halogen. Often the activation energy in one direction must be estimated, which is a source of uncertainty. It should be noted that the work of Gutman and co-workers, who were able to measure forward and reverse rate constants directly,[18,19] led to surprising R$^\bullet$ + HX activation energies and reassessment of some earlier alkyl radical thermochemistry.

There have also been computational studies of some of these systems. Seetula investigated the barrier for iodomethyl reactions with HBr, and combined the results with experimental data to assess the thermochemistry.[20] Bromomethanes and bromomethyl radicals have been investigated several times. Paddison and Tschuikow-Roux applied many-body perturbation (MP4) theory with small basis sets,[21] Chandra and Uchimaru applied density functional theory,[22] and McGivern et al. applied MP2 theory with corrections to approximate results with large basis sets and coupled cluster [CCSD(T)] theory.[23] Most recently, Oren et al. applied a variation of W2 theory to these bromo compounds.[24] There has been less work with iodine-containing species: Lazarou et al. surveyed a large number of species containing up to two halogen atoms with approximate extrapolation of

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CCSD(T) results to the complete basis set limit,[25] and Feller et al. extended this approach with very large basis sets and estimation of full configuration interaction for several species including CH_3Br and CH_3I.[26] The most recent studies have made explicit allowances for relativistic contributions to the molecular energy.[24−26] Discrepancies have not been entirely resolved by these computational studies, as may be seen in the case of CBr_4 where proposed $\Delta_f H°_{298}$ values of 119.2 ± 4.2 and 105.6 ± 3.3 kJ mol^{-1} are significantly different.[21,24]

As part of our research on the kinetics and thermodynamics of halocarbons important in atmospheric and flame chemistry,[27] we have utilized high level quantum mechanical methods to determine enthalpies of formation in haloalkanes,[28−30] halomethylidenes,[31] halocarbenes,[32] and chlorofluoromethyl radicals.[33] Our results were in excellent agreement with accurate experimental data, where available, and permitted estimation of formation enthalpies in systems where data either have large experimental uncertainties or are nonexistent.

To provide a set of consistent, reasonably accurate estimations of enthalpies of formation in bromo- and iodomethanes and their corresponding halomethyl radicals, required for thermodynamic and kinetic modeling of atmospheric and flame chemistry, we have extended our studies to these species. New data are presented for systems containing up to four iodine atoms, and special attention is paid to vibrational anharmonicity in the radical species. These systems are also prototypes for larger halogenated alkanes and alkyl radicals.

II. Computational Methods

Calculations were performed with the Gaussian 98 program suite.[34] The systems investigated were the eleven bromo- and iodomethanes, $CH_{4-n}X_n$ ($X = Br, I$; $n = 1-4$), and the nine bromo-, iodo-, and bromoiodomethyl radicals, $CH_{3-m-n}X_mY_n$ ($X = Br$, $Y = I$; $n = 1-3$).

Geometries were optimized and vibrational frequencies computed at the QCISD/6-311G(d,p) level. This relatively high level was used both to maintain consistency with our earlier studies of the thermochemistry of halocarbons and because we wanted to use a suitable level of theory to compute the potential energy surfaces and vibrational frequencies of the inversion modes of the halomethyl radicals (vide infra). Thus, it was most appropriate to compute other vibrational frequencies at the same level. It should be noted that in larger systems where this level of calculation is too computationally intensive, lower level geometry and frequency determinations may be suitable, but their accuracy remains to be tested. Preliminary results for bromomethanes with geometries and frequencies derived at the B3LYP/6-31G(d) level are in excellent agreement with the higher level QCISD-based results here. However, accord for iodomethanes is worse, with deviations up to 9 kJ mol^{-1} for CI_4. The accuracy of DFT and other low level methods has yet to be investigated for the characterization of inversion barriers in radicals.

Ab initio energies were computed by single point QCISD(T)/6-311+G(3df,2p) calculations on the optimized structures. There was little spin contamination in any of the radical calculations as revealed by values of $\langle S^2 \rangle$ in the range 0.77−0.79 (close to the expected value of 0.75 for doublets). Further, values of the T1 diagnostic of Lee and Taylor[35] were less than 0.022 for all radicals, an indication of the validity of QCISD theory based upon a single-reference wave function.

Computed frequencies were scaled by the factor 0.955, which has been found to yield excellent agreement with experiment in earlier studies.[32,33] Hay−Wadt relativistic effective core potentials (ECPs)[36] were used to represent the [Ar] core and 3d orbitals in bromine, and the [Kr] core and 4d orbitals in iodine, and to allow partly for relativistic effects. To test the effect of using ECPs on the computed frequencies, calculations were also performed on the bromomethanes using an all-electron basis. The values were generally within 0−3 cm^{-1} (and in no cases greater than 10 cm^{-1} different) of the frequencies using the ECP. For the mixed halomethane, CH_2BrI, switching to an all-electron basis changed the frequency by at most 4 cm^{-1}.

The optimized structures and scaled frequencies for the halomethanes and halomethyl radicals are contained in Tables 1 and 2, respectively, together with experimental data, where available. Values of the inertia products, required for statistical mechanical calculation of the rotational contributions to thermodynamic properties, are given in the last column of Table 1.

To characterize the anharmonic "umbrella" modes in the halomethyl radicals, relaxed scans at the QCISD/6-311G(d,p) level were performed on the relevant coordinates corresponding to this vibration.

III. Results and Discussion

A. Geometries and Vibrational Frequencies. Computed bond lengths and angles in the halomethanes and halomethyl radicals are presented in Table 1, together with available experimental data on the former species.[8,9,37] To the authors' knowledge, no geometries have been reported for the radicals to date. The agreement of calculated geometric parameters with experiment is good, with bond lengths accurate to within 0.01−0.03 Å (computed lengths are higher) and bond angles to within 1°.

To characterize the degree of deviation from planarity in the radicals, the sum of the three angles about the central carbon ($\sum\theta_I$) is tabulated in Table 1B. One expects this parameter to lie in the range 328.4° (tetrahedral) $\leq \sum\theta_I \leq$ 360° (planar). As observed in the table, all values are ≥353°, indicating near-planar structures. This is not surprising since, as shown in our earlier chlorofluoromethyl radical study,[33] the degree of pyramidalization is approximately proportional to the sum of substituent electronegativities, which are much lower for the heavier halogens studied here.

It is well established that ab initio vibrational frequencies, even those derived via correlated methods, are generally higher than experimental results, due primarily to the neglect of vibrational anharmonicity. In earlier studies on halocarbenes[32] and chlorofluoromethyl radicals,[33] it was found that application of a scale factor of 0.955 to QCISD/6-311G(d,p) frequencies yielded excellent agreement with experiment. We therefore applied the same scale factor to our computed results for the systems studied here. The results, together with available measured frequencies,[9,10,38−46] are displayed in Table 2.

One may observe from the table that agreement between theory and experiment on the halomethanes (Table 2A) is excellent. The mean error of the computed frequencies is only +3.0 cm^{-1}, indicating that the scale factor developed in our earlier work[32] extends well to the current study. The mean absolute deviation is 14.0 cm^{-1}. One also finds comparatively good agreement with the limited data on the halomethyl radicals (Table 2B) for all vibrations except a single low-frequency mode, assigned to the "umbrella" (OPLA: out-of-plane large amplitude) vibration. With the exception of the umbrella modes, the mean absolute deviation is 18.4 cm^{-1}.

It is well established that harmonic calculations on the umbrella (or inversion) mode in CH_3 yield very poor results (~200 cm^{-1} below experiment), and we found similar deviations

TABLE 1: Structural Parameters Computed at the QCISD/6-311G(d,p) Level

A. Halomethanes

molecule	R(C−H) [Å]	R(C−X)^a [Å]	$\theta_1{}^a$ [deg]	$\theta_2{}^a$ [deg]	$\theta_3{}^a$ [deg]	$I_aI_bI_c$ [10^{-135} kg^3 m^6]
CH_4	1.093		109.5			1.51×10^{-4}
	[1.091]^b		[109.5]^b			
CH_3Br	1.089	1.953	110.7	108.2		4.23×10^{-2}
	[1.095]^c [1.082]^d	[1.939]^c [1.934]^d	[111.6]^c [111.2]^d	[107.2]^c		
CH_2Br_2	1.086	1.945	111.6	107.8	114.2	16.2
	[1.097]^c	[1.925]^c	[110.9]^c		[112.9]^c	
$CHBr_3$	1.083	1.949		106.9	112.0	659
	[1.068]^c	[1.930]^c		[107.9]^c	[111.0]^c	
CBr_4		1.962			109.5	2.43×10^{3}
		[1.942]^b			[109.3]^b	
		[1.942]^c			[109.5]^c	
CH_3I	1.088	2.146	110.9	108.0		6.79×10^{-2}
	[1.084]^c [1.084]^d	[2.132]^c [2.136]^d	[111.2]^c	[107.6]^c [107.5]^d		
CH_2I_2	1.086	2.143	111.2	107.5	115.9	73.3
	[1.09]^c	[2.12]^c	[111.3]^c		[114.7]^c	
CHI_3	1.084	2.155		105.7	113.0	5.11×10^{3}
	[1.09]^c	[2.12]^c		[105.7]^c	[113.0]^c	
CI_4		2.180			109.5	1.90×10^{4}
		[2.135]^c			[109.5]^c	
CH_2BrI	1.086	1.945	111.3	107.9	114.9	33.1
		2.144		107.4		
$CHBrI_2$	1.083	1.949		106.6	111.9	1.29×10^{3}
		2.154		106.2	112.4	
$CHBr_2I$	1.084	1.952		106.4	112.3	2.58×10^{3}
		2.155		106	113.1	

B. Halomethyl Radicals

radical	R(C−H) [Å]	R(C−X)^a [Å]	$\theta_1{}^a$ [deg]	$\theta_2{}^a$ [deg]	$\theta_3{}^a$ [deg]	$\Sigma\theta_i$ (deg)	$I_aI_bI_c$ [10^{-135} kg^3 m^6]
CH_3	1.083		120.0			360.0	5.11×10^{-5}
	[1.079]^b		[120.0]^b				
CH_2Br	1.081	1.867	123.4	117.6		358.6	0.0179
$CHBr_2$	1.082	1.876		116.3	120.8	353.4	11.0
CBr_3		1.892			117.7	353.1	651
CH_2I	1.081	2.049	122.9	118.6		360.0	0.0283
CHI_2	1.082	2.062		116.8	123.7	357.2	48.6
CI_3		2.084			119.3	357.9	5.07×10^{3}
$CHBrI$	1.082	1.876	116.0^e	117.1^e	122.1^e	355.2	22.2
		2.064					
$CBrI_2$		1.892		118.3^f	119.7	356.3	2.56×10^{3}
		2.085					
CBr_2I		1.892		118.6^f	117.4	354.6	1.28×10^{3}
		2.086					

[a] X = Br or I; θ_1 = HCH, θ_2 = HCX, and θ_3 = XCX angles. [b] From reference (experimental values are from NIST-JANAF tables). [c] Reference 9. [d] Reference 36. [e] θ_1 = HCBr, θ_2 = HCI, and θ_3 = BrCI angles. [f] θ_2 = BrCI angle.

in our recent chlorofluoromethyl radical study,[33] as well as in this work for the two radicals (CH_2Br and CH_2I) for which experimental umbrella frequencies have been reported. Following our recent work, we performed relaxed QCISD/6-311G(d,p) scans along the inversion coordinate, and the potentials were fit with an eighth order even polynomial out to energies about 25 kJ mol^{-1} above the minimum. The Schrödinger equation was then solved numerically by using the FGH method of Balint-Kurti and Martson[47] as implemented by Johnson[48] to obtain the energy levels and, thus, the anharmonic frequencies.

Contained in Table 3 is a comparison of the anharmonic frequencies with values obtained from the standard harmonic analysis. As found in the earlier chlorofluoromethyl study, one observes that values of ν_{Umb}(Anharm) are vastly different from ν_{Umb}(Harm) values and much closer to experiment in the two halomethyl radicals for which experimental frequencies are available.

Also contained in the table are the corrections to the ZPE and thermal contributions to the enthalpy (required for calculation of $\Delta_f H°_{298}$), as well as the potential fit parameters, the estimated reduced masses, and the computed barrier heights. One notes that the inversion barrier heights are low, below 4 kJ mol^{-1}, as would be expected for nearly planar systems.

The CH_2I radical provides a clear example of errors involved in assuming a harmonic potential for the inversion modes. The calculated harmonic frequency of 21 cm^{-1} for out-of-plane motion is in extremely poor accord with the measured value of 375 cm^{-1} (Table 2B) but the simple anharmonic treatment here yields an improved value of 335 cm^{-1}. The thermochemical significance of anharmonicity is not restricted to an apparent error of $^1/_2(21-375)$ cm^{-1} = −177 cm^{-1} or −2.1 kJ mol^{-1} in ZPE. First, the lowest energy level is not at half the spacing between the first and second levels, and so the ZPE error is reduced to −1.4 kJ mol^{-1}. Compared to an anharmonic analysis with the parameters in Table 3, harmonic calculations of entropy and heat capacity for the umbrella mode at 298 K are in error by 22.6 and 2.8 J K^{-1} mol^{-1}, respectively, and the integrated heat capacity to 298 K is in error by +1.5 kJ mol^{-1}. At room temperature this error in $H_{298}-H_0$ fortuitously cancels with the ZPE error in $\Delta_f H°_{298}$, but this will not be the case in general.

TABLE 2: Calculated and Experimental Vibrational Frequencies[a]

A. Halomethanes

molecule		ν_a	ν_b	ν_c	ν_d	ν_e	ν_f	ν_g	ν_h	ν_i
CH_3Br	calc^b	599	937	937	1314	1429	1429	2963	3064	3064
	expt^c	*611*	*955*	*955*	*1306*	*1443*	*1443*	*2935*	*3056*	*3056*
	diff^j	(−12)	(−18)	(−18)	(8)	(−14)	(−14)	(28)	(8)	(8)
CH_2Br_2	calc^b	167	562	646	791	1094	1206	1400	3020	3094
	expt^c	*169*	*588*	*653*	*812*	*1095*	*1195*	*1382*	*3009*	*3073*
	diff^j	(−2)	(−26)	(−7)	(−21)	(−1)	(11)	(18)	(11)	(21)
$CHBr_3$	calc^b	150	150	217	515	654	654	1153	1153	3084
	expt^c	*155*	*155*	*222*	*541*	*669*	*669*	*1149*	*1149*	*3042*
	diff^j	(−5)	(−5)	(−5)	(−26)	(−15)	(−15)	(4)	(4)	(42)
CBr_4	calc^b	124	124	180	180	180	259	658	658	658
	expt^c	*122*	*122*	*182*	*182*	*182*	*267*	*672*	*672*	*672*
	diff^j	(2)	(2)	(−2)	(−2)	(−2)	(−8)	(−14)	(−14)	(−14)
CH_3I	calc^b	516	873	873	1269	1421	1421	2971	3076	3076
	expt^c	*533*	*882*	*882*	*1252*	*1436*	*1436*	*2933*	*3060*	*3060*
	diff^j	(−17)	(−9)	(−9)	(17)	(−15)	(−15)	(38)	(16)	(16)
CH_2I_2	calc^b	117	469	568	705	1043	1136	1375	3018	3095
	expt^d	*127*	*484*	*570*	*716*	*1031*	*1108*	*1350*	*2967*	*3047*
	diff^k	(−10)	(−15)	(−2)	(−11)	(12)	(28)	(25)	(51)	(48)
CHI_3	calc^b	103	103	152	417	568	568	1082	1082	3070
	expt^d	*111*	*111*	*153*	*427*	*573*	*573*	*1065*	*1065*	*2974*
	diff^k	(−8)	(−8)	(−1)	(−10)	(−5)	(−5)	(17)	(17)	(96)
CI_4	calc^b	85	85	123	123	123	177	560	560	560
	expt^c	*90*	*90*	*125*	*125*	*125*	*178*	*555*	*555*	*555*
	diff^k	(−5)	(−5)	(−2)	(−2)	(−2)	(−1)	(5)	(5)	(5)
CH_2BrI	calc^b	141	502	621	745	1072	1171	1388	3018	3094
	expt^c	*144*	*517*	*616*	*754*	*1065*	*1150*	*1374*	*2978*	*3053*
	diff^k	(−3)	(−15)	(5)	(−9)	(7)	(21)	(14)	(40)	(41)
$CHBrI_2$	calc^b	110	123	174	443	576	621	1087	1124	3076
	expt									
	diff^k									
$CHBr_2I$	calc^b	128	134	197	474	613	646	1113	1148	3078
	expt									
	diff^k									

B. Halomethyl Radicals[l]

radical		ν_a	ν_b	ν_c	ν_d	ν_e	ν_f
CH_3	calc^b	416	1372	1372	2984	3158	3158
	expt^c	*607*	*1398*	*1398*	*3004*	*3161*	*3161*
	diff^{k,l}	**Umb (−191)**	(−26)	(−26)	(−20)	(−3)	(−3)
CH_2Br	calc^b	228	679	904	1358	3049	3191
	expt^e	368	*693*	953	1355		
	diff^{k,l}	**Umb(−140)**	(−14)	(−49)	(3)		
$CHBr_2$	calc^b	179	420	594	755	1167	3105
	expt^f			*633*	*778*	*1165*	
	diff^{k,l}			(−39)	(−23)	(2)	
CBr_3	calc^b	155	155	224	305	756	756
	expt^g	—	—	—	—	*773*	—
	diff^{k,l}			**Umb**		(−17)	
CH_2I	calc^b	21	591	835	1336	3047	3188
	expt^h	*375*	*611*		*1330*	*3050*	
	diff^{k,l}	**Umb (−354)**	(−20)		(6)	(−3)	
CHI_2	calc^b	125	255	486	679	1118	3098
	expt^i				*716*	*1106*	
	diff^{k,l}		**Umb**		(−37)	(12)	
CI_3	calc^b	108	108	123	190	670	670
	expt^i					*693*	*693*
	diff^{k,l}			**Umb**		(−23)	(−23)
$CHBrI$	calc^b	151	340	533	725	1145	3100
	expt						
	diff^{k,l}		**Umb**				
$CBrI_2$	calc^b	114	129	163	223	679	721
	expt						
	diff^{k,l}			**Umb**			
CBr_2I	calc^b	132	142	197	263	713	746
	expt						
	diff^{k,l}			**Umb**			

[a] Frequencies are in cm^{-1}. [b] Frequencies calculated at the QCISD/6-311G(d,p) level, and scaled by 0.955 (see text). [c] References 38 and 39. [d] Reference 42. [e] Reference 9. [f] Reference 44. [g] Reference 43. [h] Reference 40. [i] Reference 46. [j] Reference 41. [k] Diff = ν(calc) − ν(expt). [l] The notation **Umb** indicates that the mode has been assigned to the "umbrella" vibration.

TABLE 3: Anharmonic Parameters of the Halomethyl Radical Umbrella Modes

radical	ν_{Umb}[a] [exp]	ν_{Umb}[a] [Harm.]	ν_{Umb}[a] [Anharm.]	Δ[ZPE][b,c]	$\Delta[H_{298}-H_0]$[b,d]	potential fit parameters[a] C_2	C_4	C_6	C_8	μ	barrier[b,g]
CH_3	607	416	588	0.7	−0.4	7400	80000	−58300	32900	2.415[e]	0.0
CH_2Br	368	228	323	0.1	−0.5	−190	2017	−91	−98	0.530[f]	0.1
$CHBr_2$		420	349	−1.1	0.3	−1456	3774	−1167	229	1.180[f]	1.8
CBr_3		224	354	1.0	−0.5	−26323	571172	−1505301	267427	12.01[e]	3.9
CH_2I	375	21	335	1.4	−1.5	−2	1888	−170	−61	0.538[f]	0.0
CHI_2		255	165	−0.7	−0.1	−495	2661	−716	121	1.181[f]	0.3
CI_3		123	198	0.2	−0.7	−5222	395164	−990114	324808	12.01[e]	0.0
CHBrI		340	382	−1.0	0.1	−936	3180	−927	172	1.181[f]	0.9
$CBrI_2$		163	81	−0.4	−0.3	−1453	6646	−3082	986	12.01[e]	1.0
CBr_2I		197	106	−0.3	−0.1	−2331	8048	−4009	1242	12.01[e]	2.2

[a] In cm^{-1}. The empirical parameters are valid only for energies up to 25 kJ mol^{-1} (∼2100 cm^{-1}) above the minimum. [b] In kJ mol^{-1}. [c] $[ZPE]_{Anharm} - [ZPE]_{Harm}$. [d] $[H(298)-H(0)]_{Anharm} - [H(298)-H(0)]_{Harm}$. [e] Reduced mass in amu, *x* coordinate is distance in Å. [f] Reduced moment of inertia in amu Å^2; *x* coordinate is angle in radians. [g] Barrier height from the difference between planar and equilibrium QCISD/6-311G(d,p) energies. There are small differences between these barriers and those derived from the fit parameters.

Such errors are likely to increase as the temperature is raised, and become significant when accuracies in the subkilocalorie range are sought.[24]

To better understand the nature of the errors involved in using a harmonic approximation to characterize the umbrella vibration in halomethyl radicals, it is illustrative to view plots of the potential energy as a function of the inversion coordinate and the computed vibrational levels. These are displayed for CH_2I and CBr_2I in Figure 1. One can see from Figure 1A that the inversion potential in CH_2I is actually closer to a purely quartic function than to a parabola. Indeed, the harmonic potential corresponding to the computed harmonic frequency is virtually a flat horizontal line in the figure, reflecting the near-zero curvature of the actual potential in the planar conformation ($x = 0$). The anharmonic vibrational levels are not only much greater than predicted by a harmonic potential, but the spacing between levels is seen to increase with quantum number.

A very different situation is found for CBr_2I (Figure 1B), which exhibits a double-well potential with a small, but nonnegligible barrier in the planar conformation. As one expects, the two lowest vibrational levels are a nearly degenerate doublet, and the doublet structure may still be observed in the next pair of levels. In this radical, the harmonic potential determined at the bottom of either well is seen to have a greater curvature (and higher level spacing). This yields higher frequencies than the pattern obtained from the actual inversion potential because it does not reflect the asymmetry resulting from the finite barrier.

It is important to note from the irregular vibrational energy patterns found for these and other radicals that it is **not** sufficient simply to use the corrected anharmonic frequency (spacing between the first two levels) to compute the vibrational contributions to the enthalpy, entropy, heat capacity, and other quantities using formulas derived from the harmonic oscillator approximation. Rather, it is necessary to use the actual vibrational partition function to calculate thermodynamic properties. Our tabulated anharmonic potentials are valid up to energies of 25 kJ mol^{-1} and it is important not to exceed this range if determining energy levels for use at other temperatures.

B. Enthalpies of Formation. Reported data on a series of bromo- and iodomethanes and analogous halomethyl radicals, taken from critical reviews[6−10,49,50] and individual investigations,[14−17,20,51−53] are contained in Table 4 (together with computed results). To the authors' knowledge, with one exception,[17] there have been no experimental enthalpies reported for the mixed bromoiodomethanes.

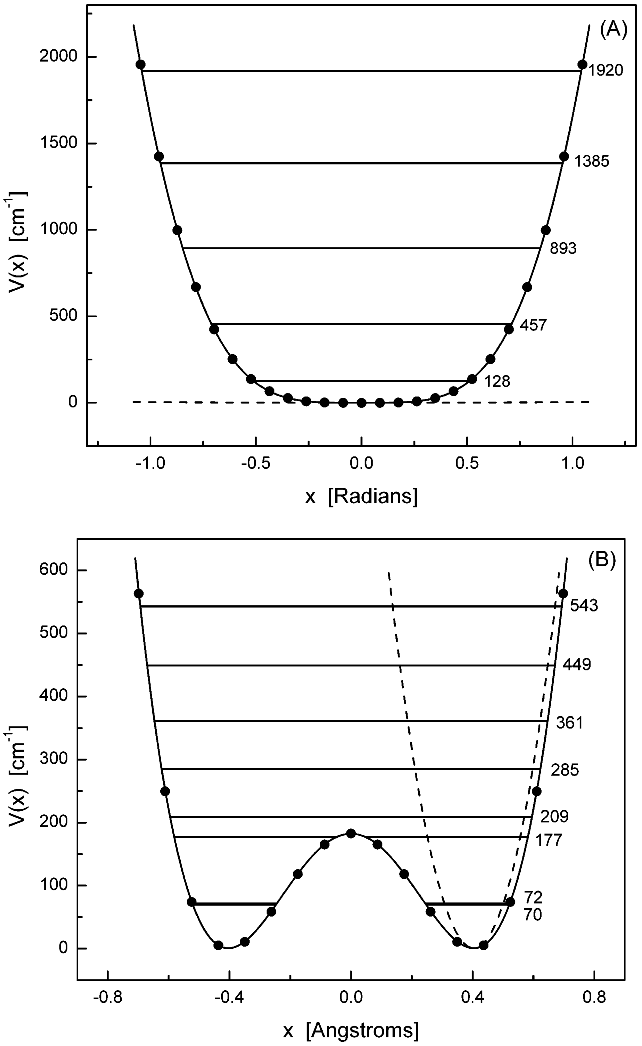

Figure 1. Potential energy surface and vibrational levels of the umbrella mode. Energies given relative to minimum: (A) the CH_2I−inversion coordinate is the angle between the CI bond and the CH_2 plane (in radians); (B) the CBr_2I−inversion coordinate is the distance of the carbon atom from the Br_2I plane (in Å). Energies are from the relaxed scan of the inversion coordinate. Symbols: solid curve, eighth order parametric fit; dashed line, parabolic potential that yields the computed harmonic frequencies (Table 3); horizontal lines, computed vibrational energy levels.

Among the halomethanes, one observes that there is close agreement between the multiple determinations of $\Delta_fH°$ for CH_3Br, CH_3I, and CH_2I_2, but that there are considerable discrepancies among reported values for the other molecules, with spreads ranging from 25 (CH_2Br_2) to over 200 kJ mol^{-1} (CI_4). One observes also from the table that, although determinations

TABLE 4: Ab Initio Energies + Computed and Experimental Enthalpies of Formation[a]

A. Halomethanes

species	E[QCISD(T)][b]	$\Delta_f H°_{298}$(calc)	$\Delta_f H°_{298}$(expt)[d]	D_{298}(calc)
CH_4	−40.433004	*c*	−74.6 ± 0.3 (7)	439.2[e]
CH_3Br	−52.962065	*c*	−36.4 ± 0.5 (7), −38.1 ± 1.3 (17), −37.8 ± 1.5 (9,10), −35.5 ± 1.1 (14), −34.3 ± 0.8 (51)	421.0
CH_2Br_2	−65.489433	4.3	−14.8 ± 3.3 (9,10), −11.1 ± 5.0 (14), 5.9 ± 1.7 (50), 10 ± 15 (7), 3.2 ± 3.4 (17)	405.4
$CHBr_3$	−78.013575	51.6	16.7 ± 3.3 (9,10), 23.8 ± 4.5 (14), 55.3 ± 3.3 (50), 60 ± 15 (7)	390.4
CBr_4	−90.532651	110.6	50.2 (8), 79.5 ± 4.2 (9,10), 83.9 ± 3.4 (14), 116.0 ± 3.9 (50), 120 ± 15 (7)	
CH_3I	−51.168270	*c*	14.4 ± 0.5 (7), 13.8 ± 1.0 (9,10), 14.2 ± 1.3 (48), 14.4 ± 1.4 (11)	420.8
CH_2I_2	−61.901140	108.1	117.6 ± 4.2 (9,10), 119.5 ± 2.2 (11), 122.2 ± 4.2 (13), 107.5 ± 4.5 (17)	400.3
CHI_3	−72.631070	208.5	211.0 ± 4.2 (9,10), 251.0 ± 1.4 (11)	378.6
CI_4	−83.355891	321.3	268.0 (9,10), 474 ± 13 (11)	
CH_2BrI	−63.695033	56.8	57.2 (45), 60 ± 25 (7), 55.0 ± 3.4 (17)	402.8
$CHBr_2I$	−76.219084	104.8	93.5 (45), 110 ± 25 (7)	385.5
$CHBrI_2$	−74.424899	157.1	158.2 (45), 165 ± 35 (7)	381.7

B. Halomethyl Radicals[f]

species	E[QCISD(T)][b]	$\Delta_f H°_{298}$(cal)	$\Delta_f H°_{298}$(exp)[d]
CH_3	−39.757236	*c*	146.6 ± 0.4 (56)
CH_2Br	−52.293361	166.6	168.3 (15), 169.1 ± 4.2 (53), 173.7 (6), 162.7 (16)
$CHBr_2$	−64.827484	191.7	185.9 (15), 188.4 ± 8.4 (53), 227.3 (6)
CBr_3	−77.358666	224.0	205.1 (15), 235 ± 25 (7)
CH_2I	−50.499834	217.2	228.0 ± 2.8 (20), 228.4 ± 8.4 (52), 230.2 ± 6.7 (6), 219.2 (16)
CHI_2	−61.241310	290.4	314.4 ± 3.3 (20), 334 ± 9.2 (6)
CI_3	−71.980646	369.1	424.9 ± 2.8 (20)
CHBrI	−63.034153	241.6	
$CBrI_2$	−73.773113	320.8	
CBr_2I	−75.565803	272.3	

[a] Ab initio energies are in hartrees; enthalpies are in kJ mol^{-1}. [b] QCISD(T)/6-311+G(3df,2p)//QCISD/6-311G(d,p) energies. [c] Reference compounds. [d] Numbers in parentheses refer to experimental reference. [e] Experimental: ref 56. [f] Computed with use of anharmonic umbrella mode parameters.

of the experimental enthalpies of the radicals CH_2Br and CH_2I are in very good agreement with each other, for the heavier radicals the results are sparse and deviate widely.

Although it is well established that direct calculation of enthalpies of formation of haloalkanes from quantum mechanical atomization energies is often subject to unacceptably high systematic errors, these errors can be eliminated via use of isodesmic reactions,[54,55] together with accurately known enthalpies of suitable reference compounds. Earlier calculations in our laboratories on bromo- and iodomethylidenes,[31] carbenes,[32] and chlorofluoromethyl radicals[33] at the QCISD(T)/6-311+G(3df,2p)//QCISD/6-311G(d,p) level have yielded excellent agreement with experimental data for those species where accurately measured enthalpies are available.

To determine enthalpies of formation of the halomethanes, we used computed enthalpies for isodesmic reactions of the form

$$x\mathrm{CH_3Br} + y\mathrm{CH_3I} \rightarrow \mathrm{CH}_{4-x-y}\mathrm{Br}_x\mathrm{I}_y + (x + y - 1)\mathrm{CH_4} \quad (3)$$

Values of $\Delta_f H°$ of the radicals were determined from equations of the type

$$\mathrm{CH_3} + x\mathrm{CH_3Br} + y\mathrm{CH_3I} \rightarrow \mathrm{CH}_{3-x-y}\mathrm{Br}_x\mathrm{I}_y + (x + y)\mathrm{CH_4} \quad (4)$$

Reference enthalpies of formation of CH_4, CH_3Br, and CH_3I were taken from ref 7, and for CH_3 from ref 56. For the radicals, the anharmonic umbrella mode data (Table 3) were included in the thermal corrections. These isodesmic reactions have the advantage of partial cancellation with respect to deficiencies in basis set size and completeness of the treatment of electron correlation. Furthermore, errors in vibrational treatments also tend to cancel, as do relativistic effects. For example, the scalar-relativistic terms calculated by Lazarou et al. reached 6 kJ mol^{-1} per halogen atom.[25] Their contribution to the overall energy change of reaction 3 for CH_2I_2 is reduced to −2.7 kJ mol^{-1}, and is reduced to −1.7 kJ mol^{-1} for reaction 4 with CH_2I. As will be seen below, application of such isodesmic reactions enabled Paddison and Tschuikow-Roux to obtain fairly high quality thermochemistry from modest MP4/6-31G(d,p) calculations.[21]

The ab initio energies, together with computed enthalpies, $\Delta_f H°_{298}$(cal), are contained in Table 4. The calculated data are also plotted (filled circles and solid lines) in Figure 2 [halomethanes, parts A, B; halomethyl radicals, parts C and D] as a function of number of halogens. The reported experimental enthalpies of formation are also plotted in the figure. Error bars are drawn in cases where they are reported and are larger than the symbol size. To discern trends in values of $\Delta_f H°$ with increasing number of halogens, we have also included the reference compounds [CH_3Br and CH_3I in Figure 2A,B; CH_3 in Figure 2C,D]. Because all experimental measurements on these species are closely clustered (Table 4), we have included only the reference values used in the isodesmic calculations.[7,56]

(*i*) *Bromomethanes.* As may be seen in Figure 2A, the enthalpies of formation of bromomethanes fall into two groups, "high" values preferred by Papina et al.[50] and Gurvich and Alcock[7] and "low" values proposed by Bickerton et al.[14] and Kudchadker and Kudchadker.[9,10] Like previous calculations,[21,24] our results are more consistent with the "high" values, although somewhat lower. In the case of CBr_4 the "high" values are 116.0 ± 3.9 and 120.0 ± 15.0 kJ mol^{-1}, respectively, while we compute 110.6 kJ mol^{-1}. This molecule is important because it anchors the contrasting interpolation schemes of Papina et al.[50] and Bickerton et al.,[14] where the latter authors use 83.9± 3.4 kJ mol^{-1}. The JANAF tables[8] give an even lower value of 50.2 kJ mol^{-1}, which must be in error. Our calculated value lies between contradictory earlier calculations of 119.2 ± 4.2 and 105.6 ± 3.3 kJ mol^{-1}, where presumably at least one set of error limits has been underestimated.[21,24] "Experimental" data for the remaining bromomethanes, $CHBr_3$ and CH_2Br_2, are

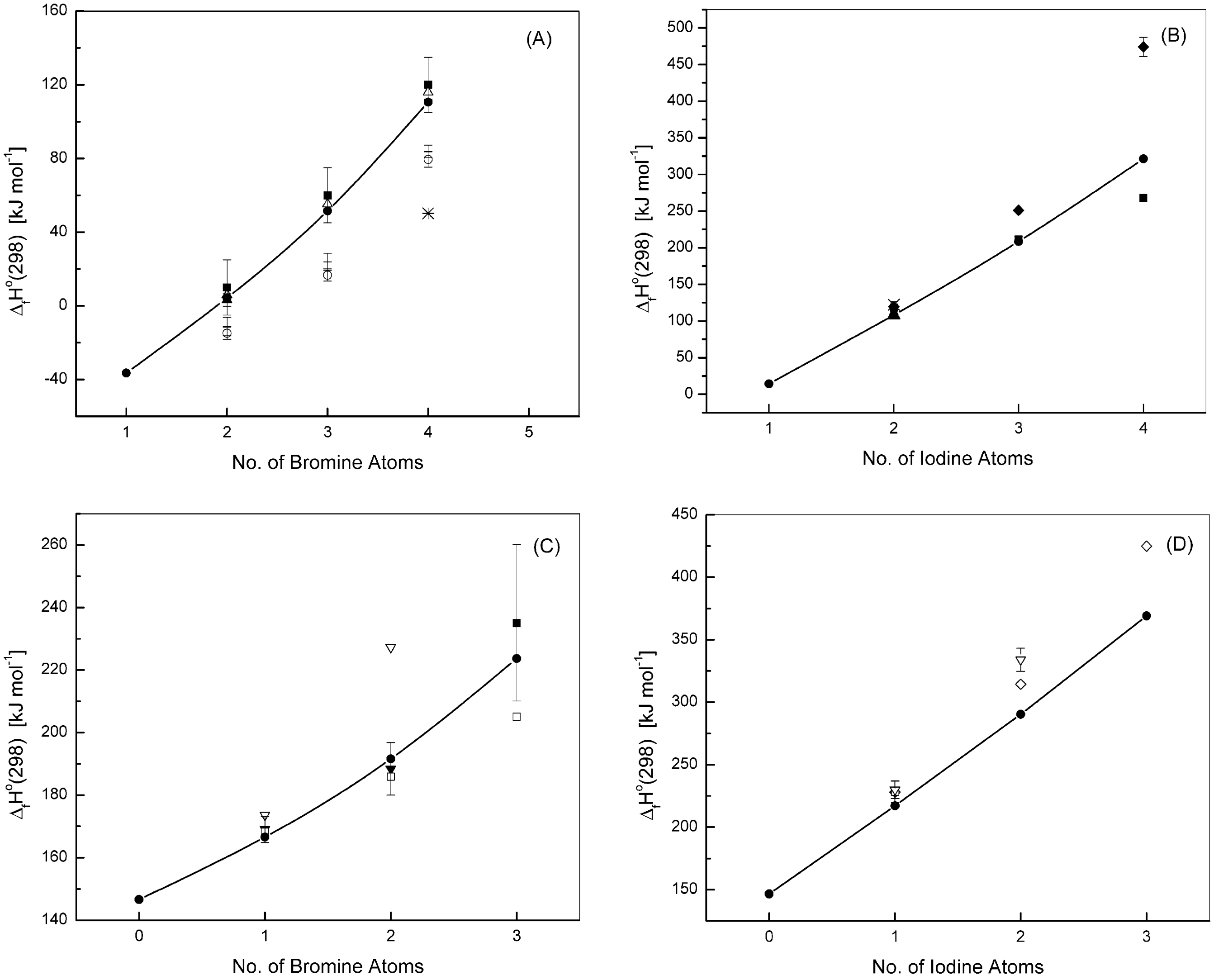

Figure 2. Dependence of enthalpy of formation on number of halogen atoms: (A) bromomethanes, (B) iodomethanes, (C) bromomethyl radicals, (D) iodomethyl radicals. Symbols: ●, calculated (this work); ○, refs 9 and 10; ◆, ref 11; ◇, ref 20; ■ , ref 7; □ , ref 15; +, ref 14; △, ref 50; ×, ref 13; ▼, ref 53; ▽, ref 6; ∗, ref 8; ▲, ref 17; and ⊕, ref 16.

essentially interpolated between CH_3Br and CBr_4, and again we find our results support the "higher" estimation scheme of Papina et al.[50] For $CHBr_3$ we compute 51.6 kJ mol^{-1}, which compares well with values from Oren et al.[24] and Paddison and Tschuikow-Roux[21] of 54.3 ± 4.2 and 50.9 ± 2.9 kJ mol^{-1}. For CH_2Br_2 we obtain 4.3 kJ mol^{-1}, which is in excellent accord with prior computations of 4.8 ± 4.2 and 4.5 ± 2.5 kJ mol^{-1},[21,24] and a very recent photoionization determination of 3.2 ± 3.4 kJ mol^{-1} by Lago et al.[17] We note that our selected reference enthalpy for CH_3Br[7] of −36.4 ± 0.5 kJ mol^{-1} is very close to two recent calculations. Oren et al.[24] obtained the same value, and Feller et al.[26] obtained −36.8 kJ mol^{-1}. A less demanding set of calculations by Lazarou et al.[25] yielded −41.6 kJ mol^{-1}.

(*ii*) *Iodomethanes.* As may be seen in Figure 2B there is general accord between earlier experimental values for CH_2I_2, whereas our calculation of 108.1 kJ mol^{-1} lies about 10 kJ mol^{-1} lower. While this paper was in preparation the photoionization results of Lago et al.[17] appeared in print, and their value of 107.5 ± 4.5 kJ mol^{-1} closely supports our calculations. The computational result of Lazarou et al.[25] of 99.3 kJ mol^{-1} is a further 8 kJ mol^{-1} lower. However, these authors also underestimated the enthalpy of CH_3I at 8.0 kJ mol^{-1}, cf. our reference value of 14.4 ± 0.5 kJ mol^{-1}.[7] Even the more sophisticated calculations of Feller et al.[26] for CH_3I are approximately 3.7 kJ mol^{-1} too small, indicating that high-accuracy CCSD(T)-based complete basis set extrapolations remain a challenge for these iodine species. Our data for CHI_3 support the Kudchadker and Kudchadker[9,10] estimate over the calorimetric value from Carson et al., despite the high accuracy claimed.[11] We also disagree with their value for CI_4 by about −150 kJ mol^{-1}, and suggest there may be unrecognized difficulties with calorimetry for these highly substituted iodomethanes. For this species our enthalpy is 53 kJ mol^{-1} above the extrapolation by Kudchadker and Kudchadker.[9,10] In the absence of unequivocal measurements it is hard to prove our estimates are the most accurate, but we note first that the trend of our enthalpies shown in Figure 2B indicates similar increments per C−I bond unlike the other data sets where CI_4 is either more or less stable than expected from extrapolation from the less substituted species. Second, in the one case where new, high-quality experimental data are available (CH_2I_2) our calculations are in excellent agreement. While an unfavorable steric interaction might be expected for four iodine atoms around one carbon atom (qualitatively consistent with Carson's data rather than Kudchadker and Kudchadker's), such repulsions are of course included in our own calculations.

(*iii*) *Bromomethyl Radicals.* Computed enthalpies for CH_2Br by Lazarou et al.[25] and by Paddison and Tschuikow-Roux,[21] 165.5 and 174.2 ± 1.7 kJ mol^{-1}, respectively, bracket experimental values (see Table 4 and Figure 2C). Our value of 166.6 kJ mol^{-1} also lies in this range. A trend is that the newer determinations are somewhat lower, and closer to our calculation. A similar trend applies to the $CHBr_2$ data, although the value of 227.3 kJ mol^{-1} is clearly too high.[6] Our computed enthalpy of 191.7 kJ mol^{-1} is up to 6 kJ mol^{-1} higher than the most recent measurements,[15,53] but lower than other calculated values of 194.0, 198.5 ± 4.2, and 201.3 ± 2.5 kJ mol^{-1}.[21,24,25] For CBr_3 our result of 224.0 kJ mol^{-1} lies within the broad uncertainty of Gurvich and Alcock's recommendation[7] and is about 19 kJ mol^{-1} above the value of 205.1 kJ mol^{-1} derived by Holmes and Lossing.[15] However, our value is closer than the prior calculated values of 232.2 ± 4.2 and 231.6 ± 2.9 kJ mol^{-1}.[21,24]

(*iv*) *Iodomethyl Radicals.* Our value of 217.2 kJ mol^{-1} for CH_2I is close to the electron impact result of de Corpo et al.,[16] but about 12 kJ mol^{-1} smaller than other experimental determinations (see Table 4 and Figure 2D). It is supported also by the calculation of Lazarou et al.,[25] who obtained 217.8 kJ mol^{-1}. Our enthalpy of 290.4 kJ mol^{-1} for CHI_2 is about 44 kJ mol^{-1} below the recommendation of Golden et al.[6] but again is supported by the result of 284.5 kJ mol^{-1} by Lazarou et al.[25] There is a systematic deviation between our results and those of Seetula.[20] He measured the activation energy for $CH_2I + HBr = CH_3I + Br$ and computed the reverse barrier height using MP2 theory. The difference yields the thermochemistry. While this approach appears to work well for CH_2I, we would argue that MP2 theory generally cannot be relied on for accurate barrier heights, and that the energy computed at a minimum on the potential energy surface is likely to be more reliable than the energy of a transition state. Furthermore, for CHI_2 and CI_3 the activation energies in the forward direction were themselves estimated empirically, and then the resulting thermochemistry was combined with data from Carson et al.[11] (which may be suspect as noted above in subsection iii) to obtain the enthalpy of formation of the radicals.

(*v*) *Mixed Bromine and Iodine Species.* Few experimental data are available for the mixed species so both Kudchadker and Kudchadker[45] and Gurvich et al.[7] used empirical estimation schemes for the substituted methanes. For $CHBrI_2$ they proposed 158.2 and 165 ± 35 kJ mol^{-1}, respectively, for the enthalpy of formation at 298 K. Our computed value of 157.1 kJ mol^{-1} is consistent with these estimates. Similarly for $CHBr_2I$, they estimated 93.5 and 110 ± 25 kJ mol^{-1}, respectively, while we derive 104.8 kJ mol^{-1}. In the case of CH_2BrI the corresponding estimates are 57.2 and 60 ± 25 kJ mol^{-1}, respectively. The accuracy of our computed value of 56.8 kJ mol^{-1} is confirmed by the very recent measurement of Lago et al.,[17] who obtained 55.0 ± 3.4 kJ mol^{-1}.

There appear to be no measured enthalpies of formation for the mixed substituted methyl radicals CHBrI, $CBrI_2$, and CBr_2I with which to compare our computed values of 241.6, 320.8, and 272.3 kJ mol^{-1}, respectively.

(*vi*) *C−H Bond Dissociation Enthalpies.* The thermochemistry summarized in Table 4 can be used to derive a wealth of carbon−hydrogen and carbon−halogen bond strengths. Here we focus on C−H bonds and list the results for D_{298} in the same table. These were obtained from the computed enthalpies of formation of methane and the corresponding methyl radical and the experimental value for an H atom (218.0 kJ mol^{-1}).[8] The data reveal a consistent trend of C−H bond weakening with increasing Br or I substitution. Figure 3 indicates that the number of halogen atoms is more important than their nature, and the trend line drawn corresponds to a weakening of 18.3 kJ mol^{-1} per halogen atom. The di- and trisubstituted methanes have a slightly greater effect for iodine rather than bromine substitution. Although the electronegative halogen atoms might be expected to destabilize the electron-deficient methyl radicals through σ withdrawal, one interpretation is that this is more than overcome by π donation to the half-occupied p orbital on carbon, leading to stabilization of the radicals.

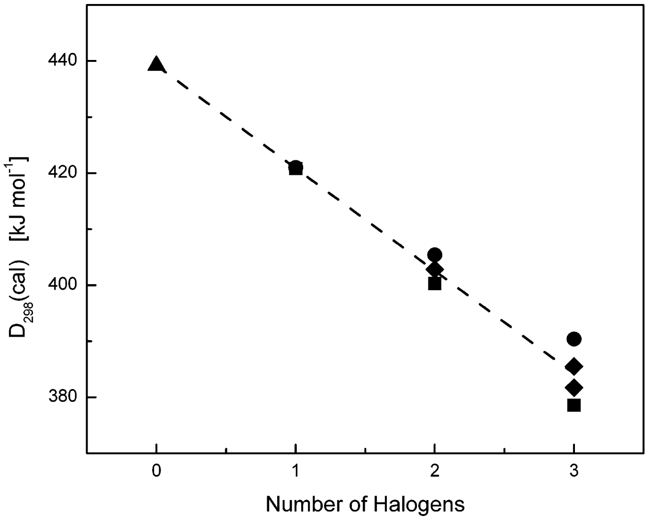

Figure 3. Dependence of bond dissociation enthalpy on the number of halogen atoms: ▲, methane; ●, bromomethanes; ■, iodomethanes; and ◆, bromoiodomethanes. The dashed line represents a linear fit constrained to pass through the reference (CH_4).

Seetula measured $D_{298}(CH_2Br{-}H)$ of 427.2 ± 2.4 kJ mol^{-1}.[57] Bond dissociation enthalpies in the bromomethanes have also been the target of past computational studies. Espinosa-Garcia and Dobe[58] applied a variety of methods and concluded that $D_{298}(CH_2Br{-}H) = 425.5 \pm 5.9$ kJ mol^{-1}. Chandra and Uchimaru applied density functional theory, and their highest level, (RO)B3LYP/6-311++G(3df,2p), yielded 422.2, 405.0, and 386.6 kJ mol^{-1} for CH_3Br, CH_2Br_2, and $CHBr_3$, respectively.[22] These values are in close accord with ours. McGivern et al. applied additive corrections to MP2/cc-pVtz results to extend the basis set to cc-pV5z and the correlation treatment to CCSD(T).[23] They obtained 413.8, 402.9, and 389.9 kJ mol^{-1} for the bromomethane series. Their result for $D_{298}(CH_2Br{-}H)$ seems about 7 kJ mol^{-1} too low (a larger discrepancy from experiment was reported in their work[23]) and implies a less consistent variation of D_{298} with increasing Br substitution. Their values for the more substituted bromomethanes are in better accord with our recommendations (Table 4). We employed isodesmic rather than direct dissociation reactions to estimate the relevant energy changes, because they are expected to converge quickly with respect to basis set size, leading to higher computational efficiency and greater accuracy.

(*vii*) *Confidence Intervals.* Previously we have proposed uncertainties from 4 to 10 kJ mol^{-1}, depending on the species, for the formation enthalpies of halogenated methylidynes, carbenes, and lighter methanes and methyl radicals. Our predictions for bromine-containing 2 and 3 atom species have been confirmed within these limits by the more sophisticated calculations of Oren et al.[24] Here, approximate confidence intervals which are consistent with the higher quality experimental determinations and prior calculations are ±3 kJ mol^{-1} per heavy halogen atom. These error limits encompass the likely influence of neglected relativistic effects as well.

IV. Conclusions

Enthalpies of formation have been computed for bromine- and iodine-containing methanes and methyl radicals, based on QCISD(T)/6-311+G(3df,2p) calculations with Hay−Wadt effective core potentials combined with isodesmic reactions. Geometries and frequencies were obtained via QCISD/6-311G-(d,p) theory, with a special focus on the anharmonic umbrella modes of the substituted methyl radicals. It is proposed that, until further accurate experiments resolve some of the large discrepancies in enthalpies of formation on bromo- and iodomethanes and methyl radicals, values for the formation enthalpies obtained in this study furnish a consistent set of good estimates for the thermodynamic and kinetic modeling of these species.

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