

BAC-MP4 Predictions of Thermochemical Data for C₁ and C₂ Stable and Radical Hydrofluorocarbons and Oxidized Hydrofluorocarbons

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An *ab initio* bond additivity corrected quantum chemistry procedure has been applied to the development of a data base for thermochemistry of C/H/F/O species. This information has been used to construct a chemical kinetic mechanism for the prediction of the behavior of fluorocarbons as flame suppressants, with clear applications to plasma and atmospheric chemistry as well. Bond additivity corrected (BAC) Moller–Plesset fourth-order perturbation theory (MP4) calculations have been performed to obtain a large body of thermochemical data on about 100 closed and open shelled fluorocarbon species. For about 70 of these species, literature values for enthalpies of formation were available for comparison to the calculated values. The average difference between the calculated and literature values was about 9 kJ/mol. The results indicate that the BAC-MP4 procedure can provide energies that are comparable in accuracy to most experimentally derived values, at lower computational costs relative to other more computationally expensive *ab initio* molecular orbital methods. This work provides a substantial data base of thermochemical data for fluorinated hydrocarbons constructed in a self-consistent manner.

Introduction

Fluorocarbon chemistry has importance in a variety of areas including atmospheric chemistry, combustion/flame suppression, and plasma etching in the microelectronics industry. This work has been motivated by the need to find a replacement for CF₃-Br. Halon 1301 (CF₃Br) is a highly effective agent for the suppression of flames, whose activity is generally considered to be derived from the activity of bromine atoms for catalytically removing hydrogen atoms in flames. However, the environmental impact of CF₃Br (its ozone depletion potential) has prompted a search for alternative agents for flame suppression. The most promising replacement candidates seem to be fluorocarbons and hydrofluorocarbons, which have recently been evaluated in a critical study conducted at NIST under the auspices of the Air Force and other agencies.¹ As an aid to the testing and subsequent selection procedure, a theoretical model based on the application of detailed chemical kinetics has been developed.^{2–4} Because the available thermochemical and kinetic data were not sufficient to the task, we have undertaken to calculate thermochemical data for a large set of stable and radical species along with a critical evaluation against experiment. The relevance of the data, however, goes beyond the application to flame suppression, since there are clear needs in the atmospheric chemistry and plasma etching communities for high-quality thermochemical and kinetic data. The ability to provide quality data in a timely fashion is clearly of value to the user community. In this study, we have generated a large body of thermochemical data for C₁ and C₂ fluorinated hydrocarbons and made a critical comparison with literature values.

Calculation Methodology

All calculations were performed using the BAC-MP4 procedure outlined by Melius.⁵ This procedure involves *ab initio*

molecular orbital calculation using the Gaussian series of programs,⁶ followed by application of a bond additivity correction (BAC) procedure to the calculated energy. The essence of the BAC procedure is to enable one to calculate energies at accuracies sufficient for chemical applications, without the need to resort to large basis sets or configuration interaction terms. This is a particularly important issue where the goal is generation of a sufficiently complete data set necessary for detailed chemical modeling. *Ab initio* methods have been used previously to calculate equilibrium geometries and energies for the fluoroethanes by Martell and Boyd⁷ and the fluoroethyl radicals by Chen *et al.*^{8–11} This work presents data for most of the stable, radical, fluorinated, and oxidized fluorinated hydrocarbons with one (C₁) or two (C₂) carbon atoms.

Equilibrium geometries, vibrational frequencies, and zero-point energies were calculated at the HF/6-31G(d) level. Single-point energies were calculated at the MP4/6-31G(d,p) level, to which the BAC procedure was applied. In the BAC method, errors in the electronic energy of a molecule are treated as bondwise additive and depend on bonding partner, distance, and next nearest neighbors. The energy per bond is corrected by calibration at a given level of theory against molecules of known energy.

Melius⁵ has shown that for any molecule with bond connectivity A_k–A_i–A_j–A_l that the error in calculating the electronic energy can be estimated through use of an empirical correction E_{BAC} to each bond A_i–A_j, where

$$E_{\text{BAC}}(A_i-A_j) = f_{ij}g_{kij}g_{ijl} \quad (1)$$

and

$$f_{ij} = A_{ij} \exp(-\alpha_{ij}r_{ij}) \quad (2)$$

A_{ij} and α_{ij} are calibration constants that depend on bond type. r_{ij} is the bond length at the Hartree–Fock level. g_{kij} is a correction to each second-nearest neighbor A_k, where

$$g_{kij} = (1 - h_{ik}h_{ij}) \quad (3)$$

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TABLE 1: Bond Additivity Correction Parameters

bond	calibration species	MP4/6-31G(d,p)//HF/6-31G(d)			
		A_{ij}	α_{ij}	atom type	B_k
C–H	CH ₄	38.61	2.0	H	0
C–C	C ₂ H ₆ , C ₂ H ₂	1444.1	3.8	C	0.31
O–H	H ₂ O	72.45	2.0	O	0.225
C–O	CH ₃ OH, CH ₂ O	175.6	2.14	F	0.33
H–F	HF	84.21	2.0		
C–F	CF ₄	143.29	2.1		
H–H	H ₂	18.98	2.0		

and

$$h_{jk} = B_k \exp(-\alpha_{ik}(r_{ik} - 1.4 \text{ \AA})) \quad (4)$$

B_k is a calibration constant that depends on the atom type. The bond additivity correction parameters used in this work are given in Table 1. For open shell molecules, an additional correction is needed due to contamination from higher spin states. This

error E_{spin} is estimated using an approach developed by Schlegel in which the spin energy correction is obtained from the difference between the energy at the MP2 level using the UHF wave function and the projected energy,¹² or

$$E_{\text{spin}} = E(\text{UMP3}) - E(\text{PUMP3}) \quad (5)$$

For closed shell species having a UHF instability, the spin correction is

$$E_{\text{spin}} = KS(S + 1) \quad \text{where } K = 41.8 \text{ kJ/mol} \quad (6)$$

Results

The primary focus of this work was to accurately predict molecular energies for fluorinated hydrocarbon species and to compare these values with those in the literature. We will also present the calculated geometries (bond distances and angles), vibrational frequencies, and moments of inertia. These data are necessary for calculation of ideal gas thermodynamic functions,

TABLE 2: C₁ Fluorinated Hydrocarbons: *Ab Initio* (hartrees) and Calculated and Literature Enthalpies of Formation (kJ/mol)^a

species	$E(\text{HF})$	$E(\text{MP4})$	$E(\text{ZP})$	$H(\text{MP4})$	$H(\text{BAC})$	$H(\text{S})$	$\Delta H_f^\circ(298)$	unc	lit	unc	diff	ref
CH ₄	-40.201 706	-40.388 611	0.047 777	-0.87	73.97		-74.8	4.2	-74.9	0.3	0.1	20
CH ₃ F	-139.039 734	-139.385 818	0.042 440	-143.98	89.83		-233.8	4.2	-232.6	8.4	-1.2	21
CH ₂ F ₂	-237.899 811	-238.406 677	0.035 981	-351.69	99.37		-451.1	4.2	-452.2	1.8	1.1	21
CHF ₃	-336.773 376	-337.441 589	0.028 135	-599.62	99.83		-699.5	4.2	-697.6	2.7	-1.9	21
CF ₄	-435.645 203	-436.473 877	0.019 176	-843.26	90.88		-934.1	4.3	-933.0	0.4	-1.1	21
*CH ₃	-39.564 457	-39.714 718	0.030 971	205.67	59.71	0.71	146.0	5.1	145.7	0.7	0.3	20
*CH ₂ F	-138.406 067	-138.719 345	0.026 899	45.38	76.82	0.58	-31.4	4.4	-32.6	8.4	1.2	22
*CHF ₂	-237.765 182	-237.740 921	0.021 029	-162.84	84.43	0.37	-247.3	4.3	-247.7	8.4	0.4	22
*CF ₃	-336.131 195	-336.767 975	0.013 564	-389.06	82.84	0.29	-471.9	4.3	-467.4	8.4	-4.5	22
:CH ₂	-38.876 305	-39.011 696	0.017 966	496.35	66.57	7.30	429.8	15.9	424.7	4.2	5.1	23
:CHF	-137.756 210	-138.064 362	0.013 589	188.94	57.24	5.04	131.7	11.6	163.2	12.6	-31.5	24
:CF ₂	-236.660 751	-237.137 375	0.007 776	-133.08	70.25	0.87	-203.3	16.3	-186.6	6.3	-16.7	25
*CH	-38.226 694	-38.369 346	0.006 967	632.91	19.20	0.38	613.7	4.6	594.1	0.4	19.6	20
*CF	-137.171 005	-137.447 723	0.003 214	280.68	44.35	0.59	236.3	11.5	240.5	10.0	-4.2	26
CH ₂ =O	-113.869 736	-114.206 276	0.029 204	-13.93	94.60		-108.5	4.2	-108.6	6.3	0.1	27
CHF=O	-212.749 634	-213.249 512	0.023 149	-279.48	102.80		-382.3	4.4	-376.6	15.0	-5.7	20
CF ₂ =O	-311.615 295	-312.273 987	0.015 788	-498.93	99.45		-598.4	7.0	-638.9	1.7	40.5	20
*CH=O	-113.249 687	-113.561 111	0.014 386	121.2	82.3	0.76	38.9	7.1	37.2	5.0	1.7	22
*CF=O	-212.112 061	-212.585 648	0.009 258	-92.8	90.0	1.08	-182.9	7.4	-171.5	15.0	-11.4	20
CH ₃ OH	-115.046 684	-115.410 896	0.055 341	-67.18	137.65		-204.8	4.2	-201.2	0.4	-3.7	28
CF ₂ FOH [fcoh gauche]	-213.909 058	-214.433 838	0.049 058	-280.03	150.29		-430.3	4.9				
CHF ₂ OH [hcoh trans]	-312.783 966	-313.469 513	0.041 106	-530.05	154.26		-684.3	7.4				
CF ₃ OH	-411.654 816	-412.500 610	0.032 018	-770.66	148.78		-919.4	10.1	-893.3	12.6	-26.2	29
CH ₃ OF	-213.770 233	-214.309 219	0.046 572	41.27	133.26		-92.0	4.9	-72.4	12.6	-19.6	29
CH ₂ FOF	-312.617 523	-313.316 559	0.039 579	-131.47	145.60		-277.1	5.3				
CHF ₂ OF	-411.486 969	-412.348 450	0.031 818	-371.34	150.08		-521.4	7.1				
CF ₂ OF	-510.354 462	-511.377 197	0.022 918	-605.49	144.64		-750.1	8.8	-764.8	12.6	14.7	20
CH ₃ O*	-114.425 580	-114.743 907	0.040 274	123.76	96.15	0.68	27.6	4.6	16.7	2.9	10.9	30
CH ₂ FO*	-213.285 492	-213.765 732	0.034 366	-85.20	109.20	0.72	-194.4	5.9				
CHF ₂ O*	-312.147 064	-312.786 407	0.027 076	-294.16	111.46	0.59	-405.6	8.8				
CF ₃ O*	-411.013 245	-411.813 477	0.018 226	-523.23	105.10	0.53	-628.3	9.1	-655.6	6.3	27.3	29
*CH ₂ OH	-114.418 732	-114.750 832	0.040 204	106.35	125.85	0.59	-19.5	4.6	-9.0	4.0	-10.5	31
*CHFOH	-213.279 205	-213.772 720	0.034 092	-103.32	136.31	0.40	-239.6	5.5				
*CF ₂ OH [fcoh trans]	-312.143 646	-312.797 791	0.026 418	-324.60	138.49	0.33	-463.1	8.3				
*CH ₂ OF	-213.227 127	-213.707 077	0.030 708	62.19	104.56	0.90	-42.4	9.8				
*CHFOF	-312.115 723	-312.749 756	0.023 347	-203.36	105.73	0.27	-309.1	4.6				
CH ₃ OOH	-189.807 548	-190.360 342	0.059 834	64.18	175.69		-124.6	4.2	-131.0	8.4	6.4	27
CF ₃ OOH	-486.402 740	-487.438 110	0.036 460	-621.04	186.44		-807.5	8.2				
CH ₃ O*	-189.207 061	-189.724 301	0.046 682	175.48	140.00	0.80	25.3	8.2	28.0	12.6	-2.7	32
CF ₃ OO*	-485.793 976	-486.790 710	0.022 951	-470.74	149.79	0.77	-627.5	6.9	-602.5	12.6	-25.0	29
HC(O)OH [trans]	-188.770 538	-189.286 346	0.037 052	-231.65	155.64		-387.3	5.2	-378.6	0.4	-8.7	27
FC(O)OH [trans]	-287.639 526	-288.313 629	0.029 603	-458.62	156.23		-614.9	14.0				
HC(O)O*	-188.083 944	-118.602 008	0.018 636	-3.15	121.75	0.76	-124.9	4.8	-150.6	8.4	25.7	32
FC(O)O*	-286.998 169	-287.630 585	0.015 303	-222.89	114.01	0.70	-336.9	10.3				
CH ₂ (OH) ₂	-189.165 420	-190.459 718	0.062 306	-190.25	199.53		-404.4	4.6	-391.2	8.4	-13.2	32
CF ₂ (OH) ₂	-387.663 544	-388.527 222	0.044 988	-697.53	205.52		-903.1	16.0				
*OCH ₂ (OH)	-114.419 093	-114.751 268	0.040 230	112.34	125.81	0.71	20.6	5.9				
*OCF ₂ (OH)	-387.025 391	-387.843 719	0.031 379	-459.60	161.84	0.58	-621.4	14.9				

^a All geometries using the Hartree–Fock method with a 6-31G(d) basis set. $E(\text{HF})$, total energy using Hartree–Fock method with 6-31G(d,p) basis set (hartrees); $E(\text{MP4})$, total energy using fourth-order Moller–Plesset theory with 6-31G(d,p) basis set (hartrees); $E(\text{ZP})$, zero-point correction (hartrees); $H(\text{MP4})$, calculated enthalpy of formation at 0 K (kJ/mol); $H(\text{BAC})$, bond additivity correction (kJ/mol); $H(\text{S})$, spin correction (kJ/mol); $\Delta H_f^\circ(298)$, calculated enthalpy of formation at 298.15 K (kJ/mol); lit, literature value for $\Delta H_f^\circ(298)$ (kJ/mol); unc, reported uncertainty in value (kJ/mol); diff, difference between calculated and literature values (kJ/mol); ref, literature reference.

TABLE 3: C₂ Fluorinated Hydrocarbons: *Ab Initio* Energies (hartrees) and Calculated and Literature Enthalpies of Formation (kJ/mol)^k

species	<i>E</i> (HF)	<i>E</i> (MP4)	<i>E</i> (ZP)	<i>H</i> (MP4)	<i>H</i> (BAC)	<i>H</i> (S)	$\Delta H_f^\circ(298)$	unc	lit	unc	diff	ref
C ₂ H ₆	-79.238 235	-79.584 023	0.079 755	41.80	128.74		-86.9	4.3	-84.1	0.4	-2.8	33
CH ₃ -CH ₂ F	-178.085 403	-178.591 492	0.073 137	-130.76	141.59		-272.4	4.2	-263.2	1.6	-9.2	17
CH ₂ F-CH ₂ F	-276.928 894	-277.594 635	0.066 316	-292.07	153.89		-446.0	4.4	-433.9	11.8	-12.1	a
CH ₃ -CHF ₂	-276.950 928	-277.618 652	0.065 525	-357.52	147.82		-505.3	4.4	-500.8	6.3	-4.5	17
CH ₂ F-CHF ₂	-375.791 065	-376.618 820	0.058 551	-511.25	160.25		-671.5	4.9	-664.8	4.2	-6.7	35
CH ₃ -CF ₃	-375.825 409	-376.654 694	0.056 881	-610.09	145.35		-755.4	4.8	-745.6	1.6	-9.9	17
CHF ₂ -CHF ₂	-474.647 705	-475.637 939	0.050 704	-716.87	166.44		-883.3	5.6	-877.8	17.6	-5.5	b
CH ₂ F-CF ₃	-474.661 774	-475.651 672	0.049 873	-755.38	157.95		-913.3	5.2	-895.8	4.2	-17.5	17
CHF ₂ -CF ₃	-573.517 883	-574.670 288	0.041 861	-960.14	163.97		-1124.1	5.9	-1104.6	4.6	-19.5	17
CF ₃ -CF ₃	-672.384 460	-673.699 768	0.032 955	-1195.56	161.42		-1357.0	6.4	-1342.7	6.3	-14.3	17
C ₂ H ₅ *	-78.605 522	-78.914 810	0.063 352	236.80	116.23	0.76	120.6	5.6	118.5	4.0	2.1	33
CH ₂ F-CH ₂ *	-177.450 180	-177.919 434	0.056 810	71.89	128.11	0.73	-56.2	5.8	-47.7	1.0	-8.5	c
CH ₃ -CHF*	-177.454 727	-177.927 460	0.057 857	53.14	128.78	0.60	-75.6	4.9	-76.3	5.9	0.6	d
CH ₂ F-CHF*	-276.296 204	-276.929 932	0.051 227	-106.20	141.08	0.65	-247.3	5.4	-238.5	12.5	-8.8	e
CHF ₂ -CH ₂ *	-276.313 385	-276.943 878	0.049 267	-147.24	133.64	0.71	-280.9	6.4	-285.8	15.0	4.9	f
CH ₃ -CF ₂ *	-276.317 749	-276.952 942	0.050 932	-167.65	132.59	0.40	-300.2	5.1	-302.5	8.4	2.3	25
CH ₂ F-CF ₂ *	-375.154 449	-375.950 958	0.044 204	-315.00	145.14	0.47	-460.1	5.8	-449.8	15.0	-10.4	g
CHF ₂ -CHF*	-375.154 053	-375.949 524	0.043 553	-312.90	146.94	0.61	-459.8	6.2	-456.1	15.0	-3.8	h
CF ₃ -CH ₂ *	-375.186 554	-375.978 546	0.040 761	-395.95	130.67	0.69	-526.6	6.7	-517.1	4.2	-9.5	25
CHF ₂ -CF ₂ *	-474.011 444	-474.969 727	0.036 297	-520.06	151.00	0.43	-671.1	6.4	-664.8	18.7	-6.3	i
CF ₃ -CHF*	-474.025 970	-474.982 941	0.034 739	-558.83	144.14	0.59	-703.0	6.5	-680.7	9.6	-22.2	13
CF ₃ -CF ₂ *	-572.879 883	-574.000 549	0.027 442	-759.20	148.36	0.41	-907.6	6.7	-891.2	4.2	-16.4	25
C ₂ H ₄	-78.038 841	-78.353 065	0.054 771	167.19	115.65		51.5	4.2	52.5	0.6	-1.0	20
CH ₂ =CHF	-176.887 573	-177.364 426	0.047 658	-17.12	122.09		-139.2	6.5	-140.1	2.5	0.9	26
CHF=CHF [Z]	-275.725 342	-276.364 990	0.040 441	-172.67	128.62		-301.3	10.3	-297.1	10.0	-4.2	38
CHF=CHF [E]	-275.725 769	-276.365 173	0.040 042	-173.98	128.20		-302.2	10.2	-292.9	10.0	-9.3	38
CH ₂ =CF ₂	-275.743 744	-276.382 446	0.039 896	-220.35	119.79		-340.1	11.0	-336.4	4.0	-3.7	26
CHF=CF ₂	-374.574 188	-375.376 312	0.032 238	-358.87	126.69		-485.6	14.0	-491.0	9.0	5.4	26
CF ₂ =CF ₂	-473.415 680	-474.381 287	0.023 980	-528.22	125.44		-653.7	16.9	-658.6	2.9	4.9	20
C ₂ H ₃ *	-77.395 897	-77.662 048	0.038 711	419.63	122.55	6.55	297.1	14.8	299.6	3.3	-2.5	39
CHF=CH* [Z]	-176.238 495	-176.667 862	0.032 184	251.43	128.32	6.24	123.1	15.4				
CHF=CH* [E]	-176.238 068	-176.667 999	0.032 319	251.55	127.44	6.03	124.1	16.0				
CH ₂ =CF*	-176.241 196	-176.674 622	0.032 635	234.95	125.85	5.50	109.1	14.1				
CHF=CF* [Z]	-275.074 615	-275.670 288	0.025 824	93.37	134.47	5.81	-41.1	16.8				
CHF=CF* [E]	-275.075 653	-275.669 495	0.025 232	94.05	136.57	6.38	-42.5	17.9				
CF ₂ =CH*	-275.089 600	-275.684 387	0.025 013	53.72	121.38	4.92	-67.7	16.9				
CF ₂ =CF*	-373.919 556	-374.678 314	0.017 846	-83.56	132.80	5.66	-216.4	19.4	-192.1	8.4	-24.2	40
C ₂ H ₂	-175.625 519	-176.072 235	0.021 900	316.01	89.24		226.8	4.2	226.7	0.8	0.0	33
C ₂ H ₂ F	-175.645 203	-176.093 704	0.022 588	213.28	95.48		117.8	15.9	125.5	22.0	-7.7	20
C ₂ F ₂	-274.459 065	-275.070 500	0.015 287	120.42	88.62		31.8	27.3	20.9	21.0	10.9	20
*C ₂ H	-76.152 107	-76.379 669	0.013 740	681.26	130.79	12.33	550.5	26.8	564.8	4.2	-14.4	22
*C ₂ F	-174.968 506	-175.366 791	0.008 401	565.41	111.55	8.74	453.9	25.6	460.2	22.0	-6.3	j
CH ₂ =C=O	-151.728 760	-152.195 602	0.034 208	84.72	125.35		-40.6	7.2	-47.7	2.5	7.1	41
CHF=C=O	-250.544 434	-251.176 208	0.027 736	-16.90	130.29		-147.2	9.8				
CF ₂ =C=O	-349.374 939	-350.172 302	0.019 748	-162.11	128.32		-290.4	13.2				
*CH=C=O	-151.084 306	-151.516 846	0.019 066	308.83	121.55	3.00	187.3	15.2	175.3	8.4	12.0	39
*CF=C=O	-249.903 534	-250.485 458	0.012 340	237.02	167.99	13.59	69.0	31.1				
CH ₃ -CHO	-152.922 577	-153.417 847	0.059 931	-15.76	145.35		-161.1	0.8	-166.2	0.4	5.1	27
CH ₂ F-CHO [fcco trans]	-251.763 474	-252.418 655	0.053 052	-171.23	157.49		-328.7	4.7				
CHF ₂ -CHO [hecco cis]	-350.619 751	-351.437 500	0.045 629	-375.40	163.55		-539.0	5.1				
CF ₃ -CHO [fcco cis]	-449.486 938	-450.467 773	0.037 013	-612.84	161.46		-774.3	5.4				
CH ₃ -CO*	-152.302 949	-152.771 808	0.046 545	124.89	132.34	0.70	-7.5	4.4	-10.2	1.7	2.8	33
CH ₂ F-CO* [fcco trans]	-251.141 815	-251.771 545	0.039 782	-27.34	145.27	0.71	-172.6	6.6				
CHF ₂ -CO* [hecco cis]	-349.995 270	-350.788 055	0.032 308	-225.60	151.75	0.83	-377.4	8.2				
CF ₃ -CO* [fcco cis]	-448.861 084	-449.817 200	0.023 686	-460.18	149.70	0.90	-609.9	9.4				

^a This work, from ΔH_f° for CH₂F²² and C-C BDE (368.6 kJ/mol) for CH₂F-CH₂F.³⁴ ^b This work, from ΔH_f° for CHF₂²² and C-C BDE (382.4 kJ/mol) for CHF₂-CHF₂.³⁶ ^c This work, from ΔH_f° for CH₃-CH₂F¹⁷ and estimated C-H BDE (433.5 kJ/mol). ^d This work, average of enthalpies of formation from refs 13 and 37. ^e This work, from ΔH_f° for CH₂F-CH₂F⁹ and C-H BDE (413.4 kJ/mol).¹³ ^f This work, from ΔH_f° for CH₃-CHF₂¹⁷ and estimated C-H BDE (433.0 kJ/mol). ^g This work, from ΔH_f° for CH₂F-CHF₂³⁵ and estimated C-H BDE (433.0 kJ/mol). ^h This work, from ΔH_f° for CH₂F-CHF₂³⁵ and estimated C-H BDE (426.7 kJ/mol). ⁱ This work, from ΔH_f° for CHF₂-CHF₂^b and C-H BDE (431.0 kJ/mol).¹³ ^j This work, estimated assuming BDE(FCC-F) = BDE(HCC-F). ^k For definitions of other notation, see Table 2.

such as entropies at standard state, heat capacities, and Gibbs energy of formation.

Enthalpies of Formation. Table 2 lists calculated total energies (Hartrees) and both calculated and literature values for enthalpies of formation at 298.15 K (kJ/mol) for C₁ fluorinated hydrocarbons, including partially oxidized species and unsubstituted hydrocarbon analogues. Table 3 lists calculated and literature values for the C₂ fluorinated hydrocarbons.

The literature values for enthalpies of formation consist of a number of different types of data, including experimental,

calculated, and estimated values. Many are high-quality, experimentally derived values based on heat of combustion or heat of reaction data, where the other reactants and products have well-established enthalpies of formation. The uncertainty in these data is typically less than 4 kJ/mol. Some of the data, although experimentally derived, have somewhat higher uncertainties due to side reactions or due to the fact that other reactants or products have somewhat uncertain enthalpies of formation. Typically, these values have enthalpies of formation with uncertainties of about 4–8 kJ/mol.

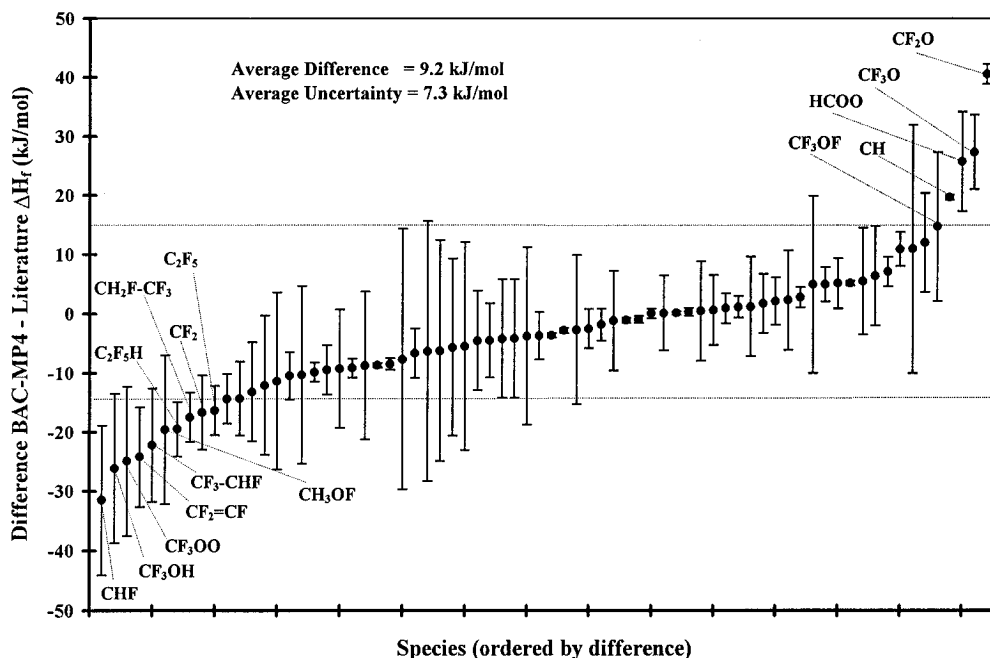


Figure 1. BAC-MP4 enthalpies of formation: difference from literature values.

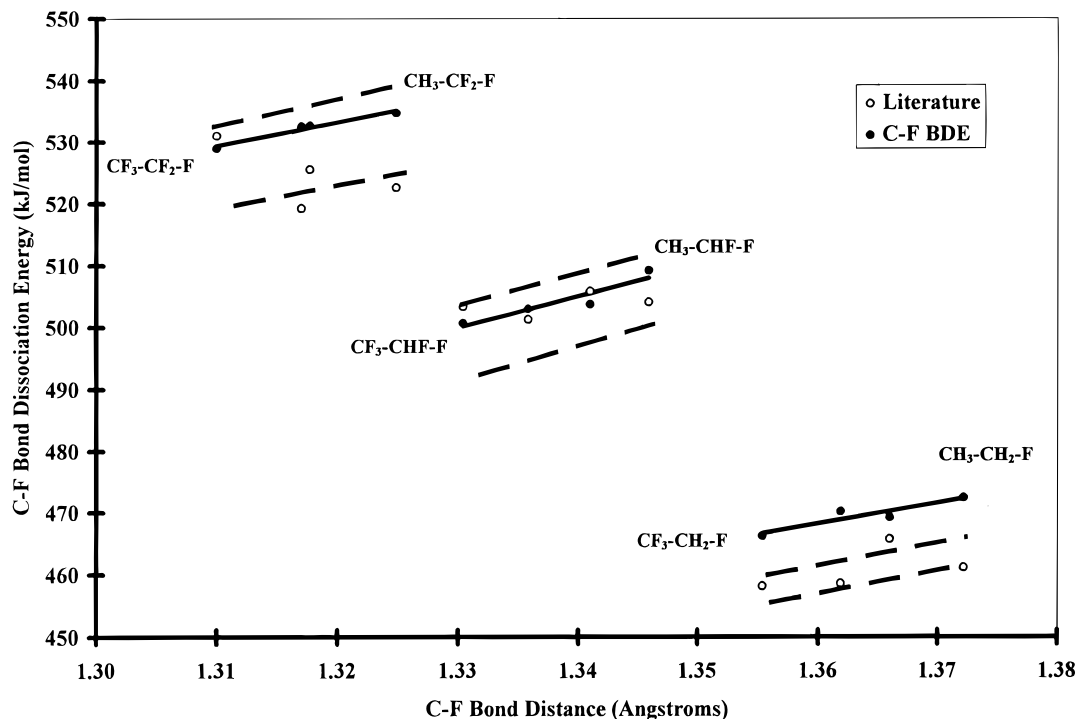


Figure 2. BAC-MP4 C–F bond dissociation energies: comparison with literature values. Dashed lines are a visual aid for bracketing the bounds of the literature values.

In some cases, the literature values are based, in whole or part, on bond additivity, group additivity, or other trends in enthalpies of formation of related species. Typically, these values have enthalpies of formation with uncertainties of about 8–12 kJ/mol. Many of the radicals have literature values for their enthalpies of formation that were determined using the enthalpies of formation of the parent species and bond dissociation energies that were either indirectly measured or were reasonable estimates based on trends in other molecules. For example, Martin and Paraskevopoulos¹³ have estimated C–H bond strengths in fluoromethanes and fluoroethanes (and consequently, enthalpies of formations for the fluoromethyl and fluoroethyl radicals) through correlations between the rates of H atom abstraction by OH radicals, C–H vibrational frequen-

cies, and known C–H bond strengths. We have supplemented these data with our own estimates in order to provide enthalpies of formation for the other fluoroethyl radicals in the absence of other literature values.

Of the roughly 100 species shown in Tables 2 and 3, about 70 species have literature values for enthalpies of formation. The differences between the BAC-MP4 and the literature values are shown in Figure 1 (ordered by difference from low to high). The average difference between the calculated and literature values is 9.2 kJ/mol. The average uncertainty of the literature values is 7.3 kJ/mol.

From Figure 1 and Tables 2 and 3, one can conclude that for the fluorinated hydrocarbon system enthalpies of formation calculated using the BAC-MP4 method have accuracies that are

TABLE 4: C₁ and C₂ Fluorinated Hydrocarbons: Moments of Inertia (10⁻⁴⁷ kg m²)

species	I _A	I _B	I _C	species	I _A	I _B	I _C
CH ₄	5.24	5.24	5.24	CH ₃ -CF ₃	148.76	158.76	158.79
CH ₃ F	5.25	31.84	31.84	CHF ₂ -CHF ₂	155.94	287.94	327.62
CH ₂ F ₂	16.50	77.20	88.32	CH ₂ F-CF ₃	152.80	292.75	296.90
CHF ₃	78.98	78.98	144.03	CHF ₂ -CF ₃	221.90	338.10	408.22
CF ₄	142.55	142.55	142.55	CF ₃ -CF ₃	288.03	442.91	442.91
•CH ₃	2.89	2.89	5.78	C ₂ H ₅ •	8.00	37.13	39.93
•CH ₂ F	3.15	26.82	29.53	CH ₂ F-CH ₂ •	20.06	82.42	96.41
•CHF ₂	12.20	74.78	85.62	CH ₃ -CHF•	17.80	87.43	99.26
•CF ₃	75.31	75.31	145.53	CH ₂ F-CHF•	39.75	174.04	189.67
:CH ₂ [sing]	1.34	2.47	3.80	CHF ₂ -CHF•	84.43	85.02	155.35
:CHF	1.72	22.40	24.12	CH ₃ -CF ₂ •	81.02	90.62	162.04
:CF ₂	9.35	64.95	74.30	CH ₂ F-CF ₂ •	103.85	201.05	249.68
•CH	0.00	1.90	1.90	CHF ₂ -CHF•	103.74	195.77	241.53
•CF	0.00	19.60	19.60	CF ₃ -CH ₂ •	146.37	150.57	154.14
CH ₂ =O	2.86	20.91	23.76	CHF ₂ -CF ₂ •	152.33	288.44	336.57
CHF=O	8.84	68.99	77.83	CF ₃ -CHF•	148.39	291.61	296.93
CF ₂ =O	68.97	69.00	137.97	CF ₃ -CF ₂ •	217.96	339.92	414.26
•CH=O	1.07	18.30	19.37	C ₂ H ₄	5.60	27.34	32.93
•CF=O	4.19	70.99	75.18	CH ₂ =CHF	12.50	77.57	90.08
CH ₃ O•	5.24	30.41	130.49	CHF=CHF [Z]	38.51	139.95	178.47
CH ₂ FO•	15.36	75.54	85.58	CHF=CHF [E]	14.20	204.30	218.50
CHF ₂ O•	76.21	78.48	141.68	CH ₂ =CF ₂	74.41	78.63	153.04
CF ₃ O•	136.13	139.58	144.70	CHF=CF ₂	76.88	212.39	289.27
CH ₃ OH	6.40	33.01	34.19	CF ₂ =CF ₂	148.83	252.80	401.63
CH ₂ FOH [fcoh gauche]	18.02	78.78	89.64	C ₂ H ₃ •	3.61	26.06	29.68
CHF ₂ OH [hcoh trans]	80.43	81.32	144.72	CHF=CH• [Z]	9.65	75.95	85.60
CF ₃ OH	143.10	144.11	145.53	CHF=CH• [E]	12.29	71.42	83.71
CH ₃ OF	18.09	75.51	88.30	CH ₂ =CF•	7.56	81.01	88.57
CH ₂ FOF	20.43	187.87	202.93	CHF=CF• [Z]	32.42	146.49	178.91
CHF ₂ OF	83.34	198.65	263.27	CHF=CF• [E]	10.31	207.95	218.26
CF ₃ OF	145.41	261.40	265.21	CF ₂ =CH•	70.89	76.08	146.97
•CH ₂ OH	4.27	27.83	31.52	CF ₂ =CF•	72.80	217.89	290.68
•CHFOH	13.77	75.64	87.24	C ₂ H ₂	0.00	81.78	81.78
•CF ₂ OH [fcoh trans]	74.69	78.29	147.91	C ₂ HF	0.00	84.53	84.53
•CH ₂ OF	13.45	125.19	138.01	•C ₂ H	0.00	19.16	19.16
•CHFOF	52.48	308.48	356.54	•C ₂ F	0.00	75.82	75.82
CF ₃ OOH	146.17	260.61	262.43	CH ₂ =C=O	2.92	79.95	82.87
CF ₃ OO•	144.76	249.01	251.97	CHF=C=O	14.45	180.24	194.69
HC(O)OH [trans]	10.52	67.38	77.90	CF ₂ =C=O	76.39	209.01	285.39
FC(O)OH [trans]	67.70	71.33	139.04	•CF=C=O	5.47	195.70	201.18
HC(O)O•	5.01	69.84	74.85	CH ₃ -CHO	14.46	81.55	90.89
FC(O)O•	63.38	69.89	133.27	CH ₂ F-CHO [fcco trans]	20.71	190.45	205.95
CF ₂ (OH) ₂	144.48	145.04	148.32	CHF ₂ -CHO [hcco cis]	87.24	211.96	272.48
•OCF ₂ (OH)	138.11	139.22	147.20	CF ₃ -CHO [fcco cis]	148.91	273.72	278.81
C ₂ H ₆	10.28	41.83	41.83	CH ₃ -CO	9.67	83.88	88.42
CH ₃ -CH ₂ F	22.84	88.06	100.54	CH ₂ F-CO• [fcco gauche]	36.25	139.26	170.32
CH ₂ F-CH ₂ F	25.87	212.05	227.51	CHF ₂ -CO• [hcco cis]	82.99	209.20	274.09
CH ₃ -CHF ₂	86.33	92.27	159.20	CF ₃ -CO• [fcco cis]	144.25	275.19	275.38

comparable to the majority of experimentally derived values. We believe the precision of the BAC-MP4 values for any homologous series to be significantly better than that which is typically obtainable from experimental measurements. For example, in Figure 2 we show the C-F bond dissociation energies for the fluoroethanes as calculated and literature (or estimated) values. It would appear that the calculated values provide a more consistent set of data. On the other hand, one could argue that the calculations using limited basis sets may be insensitive to some types of interactions. Although we believe this not to be the case, an analysis of the difference between experimental and calculated data as a function of larger basis sets and higher order theories would be useful for a more accurate definition of the accuracy of the calculations used in this work. In any case, these calculations are clearly comparable in accuracy to most experimentally derived values, with the added benefit of a self-consistent procedure for all species.

A number of species shown in Figure 1 have significant differences (> 15 kJ/mol) between the calculated and literature values for enthalpies of formation. The potential uncertainties in the calculations or the experimental/literature values should be discussed. Such a comparison is instructive in order both

to quantify the limitations of the BAC-MP4 values and to potentially point out experimental or calculated values that may be uncertain.

Of all the species, CF₂=O has the largest difference. Although the quoted uncertainty for this molecule is small, there is reason to believe that the experimental data may include contributions from side reactions complicating its determination. In addition, other recent calculations indicate that the enthalpy of formation of CF₂=O should be higher^{14,15} and well within the uncertainty of our calculations. It is instructive to note that many of the species with large differences between calculated and literature values are oxyfluoro-species: CF₂=O, CF₃O, CF₃OF, CF₃OH, CF₃OO, and CH₃OF. The enthalpies of formation for CF₃O and CF₃OF were determined from heats of reactions involving CF₂=O. Consequently, if the accepted value for the enthalpy of formation of CF₂=O was higher, the values for the other species would also be higher (and closer to the calculated values). Similarly, the enthalpies of formation of CF₃OH and CH₃OF were estimated using group additivity based on the other species. Consequently, their enthalpies of formation would also need to be adjusted. The enthalpy of formation of CF₃OO was determined by assuming that the CF₃-OO bond dissociation

TABLE 5: C₁ Fluorinated Hydrocarbons: Vibrational Frequencies (ν (cm⁻¹))

species	$\nu(1)$	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$	$\nu(6)$	$\nu(7)$	$\nu(8)$	$\nu(9)$	$\nu(10)$	$\nu(11)$	$\nu(12)$	$\nu(13)$	$\nu(14)$	$\nu(15)$
CH ₄	1329	1329	1329	1520	1520	2855	2948	2948	2948						
CH ₃ F	1059	1171	1171	1475	1476	1476	2887	2959	2959						
CH ₂ F ₂	510	1105	1123	1164	1258	1464	1529	2942	3007						
CHF ₃	492	492	681	1127	1186	1186	1414	1414	3037						
CF ₄	422	422	610	610	610	896	1315	1315	1315						
[•] CH ₃	275	1375	1375	2933	3090	3090									
[•] CH ₂ F	771	1134	1144	1444	2692	3088									
[•] CHF ₂	521	1041	1150	1181	1343	3005									
[•] CF ₃	491	491	677	1086	1286	1286									
:CH ₂ [sing]	1397	2794	2850												
:CHF	1189	1404	2733												
:CF ₂	651	1156	1241												
[•] CH	2731														
[•] CF	1260														
CH ₂ =O	1193	1235	1500	1811	2821	2885									
CHF=O	659	1051	1115	1374	1877	2997									
CF ₂ =O	563	610	779	977	1306	1953									
[•] CH=O	1117	1914	2608												
[•] CF=O	632	1081	1915												
CH ₃ O [•]	728	990	1082	1414	1423	1487	2842	2901	2918						
CH ₂ FO [•]	527	912	1047	1108	1198	1413	1440	2885	2938						
CHF ₂ O [•]	443	499	645	1015	1147	1155	1355	1391	2961						
CF ₃ O [•]	225	411	572	583	607	883	1275	1278	1309						
CH ₃ OH	311	1040	1061	1151	1346	1462	1475	1485	2844	2885	2952	3677			
CH ₂ FOH [fcoh gauche]	351	529	1019	1069	1133	1244	1363	1446	1522	2903	2991	3657			
CHF ₂ OH [hcoh trans]	301	499	532	641	1025	1119	1192	1310	1384	1438	3040	3630			
CF ₃ OH	233	428	441	583	608	617	889	1124	1235	1324	1414	3654			
CH ₃ OF	244	437	922	1090	1154	1206	1433	1445	1484	2891	2971	2976			
CH ₂ FOF	103	329	484	1030	1117	1152	1153	1222	1442	1531	2941	3009			
CHF ₂ OF	124	298	454	552	647	1052	1129	1167	1208	1391	1412	3037			
CF ₃ OF	133	262	424	430	572	597	676	887	1083	1284	1297	1337			
[•] CH ₂ OH	356	760	1032	1151	1325	1453	2943	3051	3686						
[•] CHFOH	323	526	966	1076	1175	1253	1376	3020	3647						
[•] CF ₂ OH [fcoh trans]	239	480	492	674	1042	1105	1284	1371	3667						
[•] CH ₂ OF	154	335	347	1190	1253	1461	1649	2771	2875						
[•] CHFOF	2	14	58	660	1051	1118	1374	1874	2999						
CF ₃ OOH	139	257	289	429	437	572	604	674	879	1068	1263	1294	1319	1438	3630
CF ₃ OO [•]	122	279	420	442	571	593	686	878	1124	1251	1288	1340			
HC(O)OH [trans]	618	639	1065	1139	1286	1386	1817	2964	3608						
FC(O)OH [trans]	545	557	607	791	965	1215	1398	1882	3642						
HC(O)O [•]	507	821	1058	1218	1689	2010									
FC(O)O [•]	486	585	761	961	1303	1901									
CF ₂ (OH) ₂	162	338	432	449	583	595	606	880	1101	1153	1158	1408	1451	3658	3658
[•] OCF ₂ (OH)	242	348	428	562	573	606	877	1105	1235	1286	1388	3648			

energy is identical to that known for CH₃-OO. However, it is reasonable to expect that the CF₃-OO bond would be somewhat stronger given the large positive charge on the carbon atom (due to electron withdrawal by the fluorine atoms). Indeed, our BAC-MP4 calculations indicate that the C-O bond in CF₃-OO is about 35 kJ/mol stronger than that in CH₃-OO.

There are a number of other species with significant differences between calculated and literature values that are only indirectly tied to experimental measurements. For references to the literature values see Tables 2 and 3. The enthalpy of formation of the HCOO radical is an estimate based on group additivity. The enthalpy of formation of the CF₂=CF radical is an estimate based on trends in C-F bond dissociation energies (from appearance potential measurements) as a function of bond lengths. The enthalpies of formation of the fluoroethyl radicals, CF₃-CHF and CH₂F-CF₂, were determined from estimated C-H bond dissociation energies based on correlations between rates of H atom abstraction by OH radicals, C-H bond frequencies, and known C-H bond strengths. A few of the fluoroethanes, CH₂F-CF₃, CHF₂-CF₃, and CF₃-CF₃, show calculated enthalpies of formation that are significantly lower than the experimentally derived values. Given that these are highly fluorinated species, any uncertainty in the C-F BAC correction (additive) will be amplified. The BAC parameters for C-F bonds are based on calibration with CF₄. Using C₂F₆ as the reference species would provide better agreement between calculated and experimental enthalpies of formation for the fluoroethanes and fluoroethyl radicals, although slightly worse

agreement for the fluoromethanes and fluoromethyl radicals. The small species CH, CHF, and CF₂ have experimental enthalpies of formation with small uncertainties, yet differ significantly from the calculated values. It is likely that for these small species that either are open shelled species (CH) or are closed shell species with UHF instabilities (CHF and CF₂) use of larger basis sets and higher order theories should yield better calculated values.

Geometries. We also make a comparison between literature values, where available, for bond distances, bond angles, vibrational frequencies, and moments of inertia. In brief, it is found that on the average the calculated bond distances are within about 1%, the calculated bond angles are within about 1°, the calculated vibrational frequencies are within about 2.5%, and the calculated moments of inertia are within approximately 2.5% of their respective literature values. In general, the precision of the calculations were better than these values, as discussed below, and comparable to that for most experimentally derived data.

Moments of inertia for C₁ and C₂ fluorinated hydrocarbons calculated using the geometries at the HF/6-31G(d) level are given in Table 4. A comparison (not shown) between calculated and literature values^{16,17} for the fluoromethanes and fluoroethanes (where available) indicates that the calculated moments of inertia are about 2.5% lower than the literature values on the average, with a standard deviation of about 0.7%.

Calculated HF/6-31G(d) vibrational frequencies (scaled by 0.89) for C₁ and C₂ fluorinated hydrocarbons are given in Tables

TABLE 6: C₂ Fluorinated Hydrocarbons: Vibrational Frequencies (ν (cm⁻¹))

species	$\nu(1)$	$\nu(2)$	$\nu(3)$	$\nu(4)$	$\nu(5)$	$\nu(6)$	$\nu(7)$	$\nu(8)$	$\nu(9)$	$\nu(10)$	$\nu(11)$	$\nu(12)$	$\nu(13)$	$\nu(14)$	$\nu(15)$	$\nu(16)$	$\nu(17)$	$\nu(18)$
C ₂ H ₆	291	794	794	947	1194	1194	1382	1410	1468	1468	1473	1473	2857	2862	2901	2901	2924	2924
CH ₃ -CH ₂ F	244	393	783	867	1043	1107	1169	1269	1381	1417	1453	1469	1503	2869	2896	2925	2929	2948
CH ₂ F-CH ₂ F	130	273	444	787	1045	1064	1067	1157	1121	1268	1338	1444	1500	1506	2915	2916	2952	2975
CH ₃ -CHF ₂	231	364	449	548	846	957	1119	1146	1159	1375	1391	1431	1455	1458	2883	2948	2951	2968
CH ₂ F-CHF ₂	114	235	413	466	559	896	1081	1111	1125	1153	1238	1332	1402	1457	1486	2923	2971	2986
CH ₃ -CF ₃	224	350	350	522	522	577	811	977	977	1263	1263	1277	1429	1453	1453	2898	2974	2974
CHF ₂ -CHF ₂	77	223	240	398	502	582	768	903	1120	1131	1157	1205	1337	1393	1417	1460	2975	2984
CH ₂ F-CF ₃	105	209	341	398	516	530	646	828	980	1101	1200	1216	1304	1315	1448	1485	2935	2990
CHF ₂ -CF ₃	72	201	235	351	406	505	559	569	706	859	1130	1169	1217	1256	1324	1385	1466	2995
CF ₃ -CF ₃	62	205	205	337	370	370	504	504	602	602	691	793	1110	1274	1274	1280	1280	1453
C ₂ H ₅ *	148	411	777	967	994	1169	1386	1436	1455	1460	2822	2883	2914	2960	3047			
CH ₂ F-CH ₂ *	159	383	440	831	956	1060	1100	1228	1388	1426	1486	2856	2907	2974	3071			
CF ₃ -CHF*	184	389	641	879	1023	1088	1153	1338	1405	1442	1458	2839	2903	2935	2999			
CH ₂ F-CHF*	103	306	451	684	879	1014	1083	1165	1245	1348	1417	1476	2917	2966	3023			
CHF ₂ -CH ₂ *	126	362	376	469	614	908	957	1142	1152	1369	1391	1427	2928	2993	3096			
CH ₃ -CF ₂ *	186	354	443	520	837	973	1081	1249	1250	1408	1446	1450	2862	2936	2966			
CH ₂ F-CH ₂ *	85	203	348	502	717	830	971	1048	1205	1290	1313	1418	1477	2933	2986			
CHF ₂ -CHF*	81	220	349	502	696	751	879	1094	1125	1201	1363	1384	1426	2971	3030			
CF ₃ -CH ₂ *	122	316	361	461	519	569	593	832	933	1182	1267	1283	1429	3000	3108			
CHF ₂ -CF ₂ *	61	209	222	396	516	583	749	874	1108	1148	1231	1317	1377	1440	2995			
CF ₃ -CHF*	80	204	339	403	507	537	653	714	844	1161	1192	1219	1289	1424	3048			
CF ₃ -CF ₂ *	57	197	216	350	408	500	571	582	697	830	1134	1238	1271	1286	1418			
C ₂ H ₄	801	978	982	1031	1208	1336	1438	1657	2965	2986	3031	3054						
CH ₂ =CHF	467	714	916	922	977	1149	1301	1393	1690	3003	3060	3086						
CHF=CHF [Z]	226	492	748	804	906	1004	1111	1255	1380	1760	3071	3094						
CHF=CHF [E]	309	338	538	846	932	1127	1143	1275	1275	1745	3078	3087						
CH ₂ =CF ₂	423	528	630	713	865	918	952	1332	1386	1749	3027	3114						
CHF=CF ₂	223	307	469	586	605	816	922	1145	1265	1368	1824	3105						
CF ₂ =CF ₂	199	200	382	431	530	540	563	777	1164	1341	1355	1915						
C ₂ H ₃ *	740	791	856	1068	1257	1460	2928	3012	3061									
CHF=CH* [Z]	481	644	756	810	1080	1247	1475	3018	3104									
CHF=CH* [E]	437	629	825	853	1053	1253	1453	3062	3100									
CH ₂ =CF*	427	614	797	905	1093	1367	1537	2975	3076									
CHF=CH* [Z]	204	401	719	728	946	1120	1326	1579	3098									
CHF=CF* [E]	296	298	518	685	1049	1163	1260	1568	3052									
CF ₂ =CH*	416	519	528	624	819	904	1278	1586	3129									
CF ₂ =CF*	204	279	414	459	588	864	1203	1318	1664									
HC:CH	709	709	788	788	2006	3221	3321											
HC:CF	442	442	685	685	1043	2263	3293											
FC:CF	291	291	407	407	771	1321	2502											
HC:C*	496	1654	3235															
FC:C*	218	1003	2072															
CH ₂ =CO	439	555	646	993	1131	1399	2124	3015	3105									
CHF=CO	252	480	615	681	1028	1207	1425	2108	3074									
CF ₂ =CO	207	273	378	442	673	793	1315	1450	2208									
*CH=CO	66	479	550	1246	1879	3253												
*CF=CO	251	279	497	765	1333	1712												
CH ₃ -CHO	135	488	764	861	1099	1129	1371	1398	1434	1443	1815	2813	2862	2911	2965			
CH ₂ F-CHO [fcc trans]	84	315	515	721	1020	1078	1106	1223	1328	1392	1461	1822	2858	2910	2959			
CHF ₂ -CHO [hcco cis]	76	316	369	416	592	978	1082	1128	1131	1312	1369	1395	1841	2875	3003			
CF ₃ -CHO [fcc cis]	73	252	309	423	515	515	688	835	982	1225	1226	1330	1383	1857	2894			
CH ₃ -CO*	87	454	826	938	1037	1356	1432	1433	1912	2871	2946	2950						
CH ₂ F-CO* [fcc trans]	138	312	496	842	895	1101	1215	1346	1451	1924	2907	2964						
CHF ₂ -CO* [hcco cis]	54	367	407	411	590	947	1134	1151	1320	1366	1941	2976						
CF ₃ -CO* [fcc cis]	58	234	389	412	524	531	667	795	1203	1240	1269	1960						

5 and 6, respectively. These frequencies are simply listed in increasing value; specific normal modes have not been assigned.

A comparison between calculated and literature values¹⁶⁻¹⁸ for the vibrational frequencies of the fluoromethanes and fluoroethanes (where available) is given in Table 7. The normal mode assignments are included (where available). It was determined that on average the calculated C-F stretching frequencies were about 3% higher, the calculated C-H stretching frequencies were about 2% lower, and all other normal modes were about 1-3% lower than their respective literature values. The standard deviations of the differences were about 0.5-1.0%. It is instructive to note that for a few frequencies the differences between calculated and literature values are large; for example, for CH₂F-CF₃ a calculated vibrational frequency at 1101 cm⁻¹ is compared to a literature value of 973 cm⁻¹, for a difference of 128 cm⁻¹. One could speculate that a vibrational band in the experimental spectrum was misassigned to a fundamental frequency when it may have been a combina-

tion band. A clear example of this is for the C-C stretch in CF₃-CF₃. The calculated value is 1453 cm⁻¹, while both review articles^{17,18} selected 1228 cm⁻¹ for the C-C stretch, a very large difference (225 cm⁻¹). We reviewed a number of the experimental sources of these data and found that Nielsen *et al.*¹⁹ assigned a vibrational band at 1420 cm⁻¹ as the C-C stretch. This is only 33 cm⁻¹ lower than the calculated value. This experimental value was included in Table 7. On the basis of the calculated vibrational frequencies reported here, it would be useful to review the recommended frequencies and make reassignments where necessary.

Calculated bond distances and bond angles for C₁ fluorinated hydrocarbons are presented in Table 8. Geometries for the C₂ fluorinated hydrocarbons are given in Tables 9 and 10. For each bond, the bond distance, bond angle, and dihedral angle are given. For example for CH₃-CH₂F, the C-C bond distance, the C-F bond distance, the two α C-H bond distances, and the three β C-H bond distances are 1.083, 1.373, 1.083,

TABLE 7: C₁ and C₂ Fluorinated Hydrocarbons: Calculated vs Experimental Vibrational Frequencies (ν (cm⁻¹))

SPECIES	v(1)	v(2)	v(3)	v(4)	v(5)	v(6)	v(7)	v(8)	v(9)	v(10)	v(11)	v(12)	v(13)	v(14)	v(15)	v(16)	v(17)	v(18)		
CH ₄ normal mode calculated experimental difference	v ₄ deg deform			v ₂ deg deform		v ₁ ss	v ₃ deg stretch													
	1329	1329	1329	1520	1520	2855	2948	2948	2948											
	1306	1306	1306	1534	1534	2917	3019	3019	3019											
	23	23	23	-14	-14	-62	-71	-71	-71											
CH ₃ F	v ₃ CF s		v ₆ rock		v ₂ sd	v ₅ dd		v ₁ CH ss	v ₄ CH d stretch											
	1059	1171	1171	1475	1476	1476	2887	2959	2959											
	1049	1182	1182	1464	1467	1467	2930	3006	3006											
	10	-11	-11	11	9	9	-43	-47	-47											
CH ₂ F ₂	v ₄	v ₉	v ₃	v ₇	v ₅	v ₈	v ₂	v ₁	v ₆											
	510	1105	1123	1164	1258	1464	1529	2942	3007											
	529	1090	1116	1176	1262	1435	1508	2949	3012											
	-19	15	7	-12	-4	29	21	-7	-5											
CHF ₃	v ₆ CF d deform		v ₃ CF sd	v ₂ CF s	v ₅ CF d stretch		v ₄ CH bend		v ₁ CH ss											
	492	492	681	1127	1186	1186	1414	1414	3037											
	507	507	700	1117	1152	1152	1372	1372	3036											
	-15	-15	-19	10	34	34	42	42	1											
CF ₄	v ₂ deg deform		v ₄ def deform			v ₁ ss	v ₃ deg stretch													
	422	422	610	610	610	896	1315	1315	1315											
	435	422	632	610	610	909	1281	1281	1281											
	-13	0	-22	0	0	-13	34	34	34											
CH ₃ -CH ₃	v ₄	v ₉	v ₃	v ₁₂ bend		v ₂	v ₆	v ₁₁		v ₈		v ₁	v ₅	v ₁₀		v ₇				
	tors	bend	CC s	bend		CH d	CH d	CH deform		CH deform		CH s	CH s	CH stretch		CH stretch				
	291	794	794	947	1194	1194	1382	1410	1468	1468	1473	1473	2857	2862	2901	2901	2924	2924		
	275	821	821	993	1155	1155	1375	1379	1460	1460	1486	1486	2899	2954	2963	2963	2994	2994		
16	-27	-27	-46	39	39	7	31	8	8	-13	-13	-42	-92	-62	-62	-70	-70			
CH ₃ -CH ₂ F	v ₁₈	v ₁₁	v ₁₇	v ₁₀	v ₉	v ₁₆	v ₈	v ₁₅	v ₇	v ₆	v ₅	v ₁₄	v ₄	v ₃	v ₂	v ₁	v ₁₂	v ₁₃		
	tors	CF d	rock	CF s	CC s	rock	rock	twist	wag	s def	d def	d def	sciss	ss	ss	CH s	as	ds		
	244	393	783	867	1043	1107	1169	1269	1381	1417	1453	1469	1503	2869	2896	2925	2929	2948		
	243	415	810	880	1048	1048	1108	1277	1365	1395	1449	1449	1479	2915	2941	3003	3003	3003		
1	-23	-27	-13	-5	59	61	-8	16	22	4	20	24	-46	-45	-79	-74	-55			
CH ₃ -CHF ₂	231	364	449	548	846	957	1119	1146	1159	1375	1391	1431	1455	1458	2883	2948	2951	2968		
	222	383	470	571	868	930	1129	1143	1171	1360	1372	1414	1460	1460	2960	2978	3001	3018		
	9	-19	-21	-23	-22	27	-10	3	-12	15	19	17	-5	-2	-77	-30	-50	-50		
CH ₃ -CF ₃	tors	CF rock		CF deform		CH d	CC s	CH rock		CF stretch		CF s	CH d	CH deform		CH s	CH stretch			
	224	350	350	522	522	577	811	977	977	1263	1263	1277	1429	1453	1453	2898	2974	2974		
	220	365	365	541	541	602	830	970	970	1233	1233	1280	1408	1443	1443	2975	3035	3035		
	4	-16	-15	-19	-19	-25	-19	7	7	30	30	-4	21	10	10	-77	-62	-62		
CH ₂ F-CF ₃	105	209	341	398	516	530	646	828	980	1101	1200	1216	1304	1315	1448	1485	2935	2990		
	120	225	352	408	539	549	665	842	885	973	1103	1182	1298	1374	1427	1464	2984	3013		
	-15	-17	-11	-10	-23	-19	-19	-14	95	128	97	34	6	-59	21	21	-49	-23		
CHF ₂ -CF ₃	72	201	235	351	406	505	559	569	706	859	1130	1169	1217	1256	1324	1385	1466	2995		
	82	216	246	361	413	508	523	577	725	867	1111	1145	1198	1218	1309	1359	1393	3008		
	-10	-15	-11	-10	-7	-3	36	-8	-19	-8	19	24	19	38	15	26	73	-13		
CF ₃ -CF ₃	v ₄ tors		v ₁₂ rock		v ₃ sd	v ₉ rock		v ₁₁ deg deform		v ₈ deg deform		v ₆ sd	v ₂ ss	v ₅ ss	v ₇ deg stretch		v ₁₀ deg stretch		v ₁ CC s	
	62	205	205	337	370	370	504	504	602	602	691	793	1110	1274	1274	1280	1280	1453		
	71	220	220	348	372	372	520	520	619	619	714	807	1117	1250	1250	1251	1251	1420		
	-9	-15	-15	-11	-2	-2	-16	-16	-17	-17	-23	-14	-7	24	24	29	29	33		

ss	symmetric stretch
ds	degenerate stretch
sd	symmetric deformation
dd	degenerate deformation
deg	degenerate
s	stretch
d	deformation
deform	deformation
tors	torsion

and 1.084–1.086 Å, respectively. The FCC bond angle, the two α HCC bond angles, and the three β HCC bond angles are 109.5°, 111.6°, and 110.3–110.5°, respectively. The dihedral angle is the angle between the bond and a reference plane. In this example, the reference plane is chosen to be defined by the two carbon atoms and the “first” hydrogen atom (C1–C2–H1). The other two beta C–H bonds are rotated 120° (on either side) from the reference plane. The two α C–H bonds are rotated 60° (on either side) from the reference plane, while the C–F bond is rotated 180° from the reference plane. The dihedral angles indicate that CH₃–CH₂F is a gauche form (the bonds to one carbon “bisect” the bonds to the adjacent carbon).

A comparison (not shown) was made between the calculated and literature values^{16,17} for the bond distances and angles for the fluoromethanes and fluoroethanes (where available). It was determined that the calculated bond lengths (C–C, C–H, and C–F) were on the average about 1.1% shorter than their literature values, with a standard deviation of about 0.6%. For bond angles, it was determined that the calculated values were on the average within about 1.2° of the literature values.

Conclusions

A bond additivity correction procedure has been applied to a large body (about 100 species) of *ab initio* molecular orbital

TABLE 9: Bond Distances (Å) and Angles (deg): C₂ Fluorinated Hydrocarbons

C ₂ H ₆				C ₂ H ₅				C ₂ H ₄				C ₂ H ₃								
R	θ	Ω		R	θ	Ω		R	θ	Ω		R	θ	Ω	R	θ				
C1-C2	1.528			C1-C2	1.498			C1-C2	1.317			C1-C2	1.328							
C2-H1	1.086	111.2	0.0	C2-H1	1.086	111.3	0.0	C1-H1	1.076	121.8		C1-H1	1.077	121.5						
C2-H2	1.086	111.2	120.0	C2-H2	1.086	111.3	120.5	C1-H2	1.076	121.8		C1-H2	1.080	121.8						
C2-H3	1.086	111.2	-120.0	C2-H3	1.091	111.7	-119.7	C2-H3	1.076	121.8		C2-H3	1.072	134.3						
C1-H4	1.086	111.2	60.0	C1-H4	1.075	120.4	38.0	C2-H4	1.076	121.8										
C1-H5	1.086	111.2	180.0	C1-H5	1.075	120.4	-158.4													
C1-H6	1.086	111.2	-60.0																	
CH ₃ -CH ₂ F				CH ₃ -CHF				CH ₂ F-CH ₂				CH=CHF				CH ₂ =CF				
C1-C2	1.512			C1-C2	1.489			C1-C2	1.489			C1-C2	1.309		C1-C2	1.324				
C2-H1	1.084	110.5	0.0	C1-H1	1.085	110.5	0.0	C1-F1	1.371	110.0	0.0	C1-F1	1.329	122.4	C1-H1	1.076	121.0			
C2-H2	1.084	110.5	119.9	C1-H2	1.084	110.2	-120.0	C1-H1	1.084	111.4	-119.8	C1-H1	1.072	125.7	C1-H2	1.072	119.8			
C2-H3	1.086	110.3	-120.0	C2-H3	1.076	121.8	165.2	C2-H2	1.074	119.7	164.0	C2-H2	1.073	119.8	C2-F1	1.306	128.3			
C1-H4	1.083	111.6	59.2	C2-F1	1.341	114.3	-55.0	C2-H3	1.074	119.2	-32.9	C2-H3	1.074	121.5						
C1-H5	1.083	111.6	-179.1	C1-H4	1.089	111.4	119.8	C1-H4	1.087	111.9	119.1									
C1-F1	1.373	109.5	-59.9																	
CH ₂ F-CH ₂ F				CH ₂ F-CHF									CHF=CHF[Z]				CHF=CF[Z]			
C1-C2	1.512			C1-C2	1.482							C1-C2	1.307		C1-C2	1.324				
C2-H1	1.081	110.9	0.0	C2-H1	1.081	110.0	0.0					C1-F1	1.324	122.6	C1-H1	1.068	123.5			
C2-H2	1.081	110.9	121.7	C2-H2	1.081	110.2	121.1					C1-H1	1.070	123.1	C1-F1	1.330	121.4			
C2-F1	1.369	107.9	-119.2	C2-F1	1.375	111.0	-119.2					C2-H2	1.070	123.1	C2-F2	1.300	128.6			
C1-H3	1.081	110.9	58.3	C1-H3	1.074	122.0	54.3					C2-F2	1.324	122.6						
C1-H4	1.081	110.9	180.0	C1-F2	1.332	115.4	-161.7													
C1-F2	1.369	107.9	-60.9																	
CH ₃ -CHF ₂				CH ₂ -CF ₂				CHF ₂ -CH ₂				CH ₂ =CF ₂				CF ₂ =CH				
C1-C2	1.502			C1-C2	1.491			C1-C2	1.485			C1-C2	1.304		C1-C2	1.311				
C2-H1	1.083	110.1	0.0	C2-H1	1.082	109.9	0.0	C2-F1	1.346	110.2	0.0	C1-F1	1.303	125.2	C1-F1	1.309	125.1			
C2-H2	1.083	109.3	119.8	C2-H2	1.082	109.9	120.3	C2-F2	1.345	110.2	118.8	C1-F2	1.303	125.2	C1-F2	1.304	124.8			
C2-H3	1.083	110.1	-120.3	C2-H3	1.087	110.0	-119.8	C2-H1	1.081	113.9	-120.6	C2-H1	1.071	119.9	C2-H1	1.066	133.9			
C1-H4	1.079	113.8	60.2	C1-F1	1.323	114.7	55.8	C1-H2	1.072	119.2	37.8	C2-H2	1.071	119.9						
C1-F1	1.346	110.0	-178.8	C1-F2	1.323	114.7	-176.2	C1-H3	1.072	119.2	-154.8									
C1-F2	1.346	110.0	-60.9																	
CH ₂ F-CHF ₂				CH ₂ F-CF ₂				CHF ₂ -CHF				CHF=CF ₂				CF ₂ =CF				
C1-C2	1.506			C1-C2	1.490			C1-C2	1.487			C1-C2	1.304		C1-C2	1.319				
C2-H1	1.081	110.0	0.0	C2-H1	1.080	109.6	0.0	C2-H1	1.079	111.4	0.0	C1-F1	1.299	125.4	C1-F1	1.304	124.8			
C2-H2	1.081	109.6	121.2	C2-H2	1.080	109.6	121.0	C2-F1	1.337	110.0	121.1	C1-F2	1.303	122.9	C1-F2	1.303	122.9			
C2-F1	1.362	108.5	-119.4	C2-F1	1.367	110.0	-119.5	C2-F2	1.346	110.8	-120.4	C2-H1	1.068	123.4	C2-F3	1.302	126.5			
C1-H3	1.078	113.0	65.1	C1-F2	1.315	115.2	54.3	C1-H2	1.074	120.6	45.0	C2-F3	1.327	120.6						
C1-F2	1.339	110.0	-173.4	C1-F3	1.315	115.2	-175.4	C1-F3	1.324	114.6	-172.3									
C1-F3	1.343	108.1	-55.8																	
CH ₃ -CF ₃				CF ₃ -CH ₂									CF ₂ =CF ₂				CHF=CH[Z]			
C1-C2	1.500			C1-C2	1.483							C1-C2	1.300		C1-C2	1.322				
C2-H1	1.082	109.4	0.0	C2-F1	1.323	111.5	0.0					C1-F1	1.302	123.4	C1-H1	1.074	125.4			
C2-H2	1.082	109.4	120.0	C2-F2	1.323	111.5	120.4					C1-F2	1.302	123.4	C1-F1	1.330	122.0			
C2-H3	1.082	109.4	-120.0	C2-F3	1.328	112.2	-119.8					C2-F3	1.302	123.4	C2-H2	1.068	132.9			
C1-F1	1.325	111.6	60.0	C1-H1	1.071	118.7	36.9					C2-F4	1.302	123.4						
C1-F2	1.325	111.6	180.0	C1-H2	1.071	118.7	-157.5													
C1-F3	1.325	111.6	-60.0																	
CHF ₂ -CHF ₂				CHF ₂ -CF ₂									CHF=CHF[E]				CHF=CH[E]			
C1-C2	1.512			C1-C2	1.500							C1-C2	1.307		C1-C2	1.321				
C2-H1	1.078	111.7	0.0	C2-H1	1.077	111.3	0.0					C1-F1	1.329	120.3	C1-H1	1.071	125.4			
C2-F1	1.332	109.7	121.2	C2-F1	1.333	108.8	121.1					C1-H1	1.070	125.3	C1-F1	1.336	122.0			
C2-F2	1.338	108.4	-120.3	C2-F2	1.339	109.8	-120.7					C2-H2	1.070	125.3	C2-H2	1.069	135.7			
C1-H2	1.078	111.7	65.8	C1-F3	1.314	113.2	50.3					C2-F2	1.329	120.3						
C1-F3	1.332	109.7	-173.0	C1-F4	1.308	114.6	179.5													
C1-F4	1.338	108.4	-54.5																	
CH ₂ F-CF ₃				CF ₃ -CHF									CHF=CF[E]							
C1-C2	1.508			C1-C2	1.491															
C2-H1	1.080	109.2	0.0	C2-F1	1.317	111.5	0.0													
C2-H2	1.080	109.2	120.8	C2-F2	1.320	109.2	120.1													
C2-F1	1.356	108.7	-119.6	C2-F3	1.323	112.1	-120.5													
C1-F2	1.317	111.7	59.0	C1-F4	1.321	113.6	55.7													
C1-F3	1.318	111.7	179.9	C1-H1	1.072	119.8	-162.3													
C1-F4	1.324	109.1	-60.4																	
CHF ₂ -CF ₃				CF ₃ -CF ₂																
C1-C2	1.517			C1-C2	1.507															
C2-H1	1.077	111.1	0.0	C2-F1	1.313	109.8	0.0													
C2-F1	1.330	108.5	120.9	C2-F2	1.313	109.8	119.9													
C2-F2	1.331	108.5	-120.8	C2-F3	1.318	111.3	-120.0													
C1-F3	1.317	109.7	59.5	C1-F4	1.306	113.3	55.6													
C1-F4	1.311	111.4	180.0	C1-F5	1.306	113.3	-175.6													
C1-F5	1.317	109.7	-59.5																	
CF ₃ -CF ₃												HCCH				HCC				
C1-C2	1.526											C1-C2	1.185		C1-C2	1.215				
C2-F1	1.311	109.8	0.0									C1-H1	1.057	180.0	C1-H1	1.058	179.7			
C2-F2	1.311	109.8	120.0									C2-H2	1.057	180.0						
C2-F3	1.311	109.8	-120.0																	
C1-F4	1.311	109.8	60.0									HCCF				FCC				
C1-F5	1.311	109.8	180.0									C1-C2	1.177		C1-C2	1.196				
C1-F6	1.311	109.8	-60.0									C1-F1	1.269	180.0	C1-F1	1.272	179.3			
												C2-H1	1.055	180.0						
												FCCF								
												C1-C2	1.166							
												C1-F1	1.275	180.0						
												C2-F2	1.275	180.0						

TABLE 10: Bond Distances (Å) and Angles (deg): C₂ Fluorinated (Oxy)Hydrocarbons

CH ₂ =CO	R	Θ	Ω	CH=CO	R	Θ	Ω
C1-C2	1.306			C1-C2	1.254		
C1-O1	1.145	180.0	0.0	C1-O1	1.168		
C2-H1	1.071	119.3	180.0	C2-H1	1.06		
C2-H2	1.071	119.3	180.0				
CHF=CO				CF=CO			
C1-C2	1.308			C1-C2	1.398		
C1-O1	1.147	92.1	0.0	C1-O1	1.163	128.4	0.0
C2-F1	1.339	120.1	180.0	C2-F1	1.296	125.0	180.0
C2-H1	1.067	122.4	180.0				
CF ₂ =CO							
C1-C2	1.300						
C1-O1	1.151	90.0	0.0				
C2-F1	1.312	123.0	180.0				
C2-F2	1.312	123.0	180.0				
CH ₃ -CHO				CH ₃ -CO			
C1-C2	1.504			C1-C2	1.513		
C2-O1	1.188	124.4	0.0	C2-O1	1.165	129	0.0
C2-H4	1.095	115.3	180.0	C1-H1	1.08	110.6	0.0
C1-H1	1.087	109.8	-121.1	C1-H2	1.084	109.0	121.3
C1-H2	1.087	109.9	121.2	C1-H3	1.084	109.0	-121.3
C1-H3	1.082	110.3	0.0				
CH ₂ F-CHO (fcc _o trans)				CH ₂ F-CO (fcc _o trans)			
C1-C2	1.511			C1-C2	1.518		
C2-O1	1.186	122.1	0.0	C2-O1	1.163	126.5	0.0
C2-H1	1.093	122.5	180.0	C1-F1	1.355	110.3	180.0
C1-F1	1.364	109.3	180.0	C1-H1	1.082	108.8	120.1
C1-H2	1.082	109.9	119.9	C1-H2	1.082	108.8	-120.1
C1-H3	1.082	109.9	-119.9				
CHF ₂ -CHO (hcco cis)				CHF ₂ -CO (hcco cis)			
C1-C2	1.516			C1-C2	1.539		
C2-O1	1.183	122.0	0.0	C2-O1	1.158	126.1	0.0
C2-H1	1.091	123.1	180.0	C1-H1	1.079	112.1	0.0
C1-H2	1.077	112.6	0.0	C1-F1	1.330	108.0	121.2
C1-F1	1.340	108.3	121.7	C1-F2	1.330	108.0	-121.2
C1-F2	1.340	108.3	-121.7				
CF ₃ -CHO (fcc _o cis)				CF ₃ -CO (fcc _o cis)			
C1-C2	1.524			C1-C2	1.541		
C2-O1	1.178	122.2	0.0	C2-O1	1.155	126.3	0.0
C2-H1	1.090	123.8	180.0	C1-F1	1.310	112.2	0.0
C1-F1	1.306	112.4	0.0	C1-F2	1.313	108.9	120.6
C1-F2	1.321	109.3	121.1	C1-F3	1.313	108.9	-120.6
C1-F3	1.321	109.3	-121.1				

computations on fluorocarbon molecules. Where available, the computations have been compared with literature values and show overall excellent agreement, consistent with the uncertainties in the literature values. This computational procedure, although not strictly an *ab initio* method, uses molecular orbital theory and applies additive bond corrections which enables the use of lower levels of correlation and basis set size while maintaining high accuracy. The substantially lower computational cost relative to other methods reporting the same potential accuracy enables this method to be applied to both larger molecules and large sets of species. The ultimate benefit is to the end user, who will have access to large bodies of thermochemical data from a single source, with some knowledge of the expected uncertainties in the values.

References and Notes

- Nyden, M. D.; Linteris, G. T.; Burgess, D. R., Jr.; Westmoreland, P. R.; Tsang, W.; Zachariah, M. R. Flame Inhibition Chemistry and the Search for Additional Fire Fighting Chemicals In *Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays*; Grosshandler, W., Gann, R., Pitts, W., Eds.; NIST Spec. Pub. 861; 1994; pp 467-641.
- Westmoreland, P. R.; Burgess, D. R. F., Jr.; Tsang, W.; Zachariah, M. R. *Symp. (Int.) Combust.* **1994**, *25*, 1505.
- (a) Burgess, D. R., Jr.; Zachariah, M. R.; Tsang, W.; Westmoreland, P. R. Key Species and Important Reactions in Fluorinated Hydrocarbon Flame Chemistry. In *Halon Replacements: Technology and Science*; Miziolek, A., Tsang, W., Eds.; ACS Symp. Ser.; ACS: Washington, DC, 1995; Vol. 611, chapter 25. (b) Zachariah, M. R.; Westmoreland, P. R.; Burgess, D. R. F., Jr.; Tsang, W.; Melius, C. F.; Theoretical Prediction of Thermochemical and Kinetic Properties of Fluorocarbons. In *Halon Replacements: Technology and Science*; Miziolek, A., Tsang, W., Eds.; ACS Symp. Ser.; ACS: Washington, DC, 1995; Vol. 611, chapter 27.

(4) (a) Burgess, D. R. F., Jr.; Zachariah, M. R.; Tsang, W.; Westmoreland, P. R.; Thermochemical and Chemical Kinetic Data for Fluorinated Hydrocarbons. *NIST Tech. Note 1412*; 1995; pp 1-174. (b) Burgess, D. R. F., Jr.; Zachariah, M. R.; Tsang, W.; Westmoreland, P. R. *Prog. Energy Combust. Sci.*, in press.

(5) (a) Melius, C. F.; Binkley, J. S. *Symp. (Int.) Combust.* **1986**, *21*, 1953. (b) Melius, C. F. Thermochemistry of Hydrocarbon Intermediates in Combustion: Application of the BAC-MP4 Method. In *Chemistry and Physics of Energetic Materials*; Bulusu, S. N., Ed.; Kluwer Academic Publishers: Dordrecht, 1990; Vol. 309, p 21. (c) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1995**, *99*, 2166.

(6) Frish, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J.; Topiol, S.; Pople, J. A. *Gaussian 90*; Gaussian Inc.: Pittsburgh, PA, 1990.

(7) Martell, J. M.; Boyd, R. J. *J. Phys. Chem.* **1992**, *96*, 6287.

(8) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Chem. Phys.* **1990**, *93*, 1187.

(9) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Chem. Phys.* **1990**, *93*, 6620.

(10) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Chem. Phys.* **1991**, *94*, 2774.

(11) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Chem. Phys.* **1991**, *95*, 7299.

(12) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530.

(13) Martin, J. P.; Paraskevopoulos, G. *Can. J. Chem.* **1983**, *61*, 861.

(14) Schnieder, W. F.; Wallington, T. J. *J. Phys. Chem.* **1994**, *98*, 7448.

(15) Montgomery, J. A., Jr.; Michels, H. H.; Francisco, J. S. *Chem. Phys. Lett.* **1994**, *220*, 391.

(16) Rodgers, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1974**, *3*, 117-140.

(17) Chen, S. S.; Rodger, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1975**, *4*, 441-456.

(18) Shimanouchi, T. Tables of Molecular Vibrational Frequencies. *NSRDS-NBS* **1972**, *39*, 1.

(19) Nielsen, J. R.; Richards, C. M.; McMurry, H. L. *J. Chem. Phys.* **1948**, *16*, 67.

(20) Stull, D. R.; Prophet, H. JANAF Thermochemical Tables. *NSRDS-NBS* **1971**, *37*, 1.

(21) Kolesov, V. P. *Russ. Chem. Rev.* **1978**, *47*, 1145.

(22) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(23) Kee, R. J.; Rupley, F. M.; Miller, J. A. The Chemkin Thermodynamic Database. Sandia National Laboratories Report SAND87-8215B, 1987.

(24) Pritchard, G. O.; Nilsson, W. B.; Kirtman, B. *Int. J. Chem. Kinet.* **1984**, *16*, 1637.

(25) Rodgers, A. S. *ACS Symp. Ser.* **1978**, *66*, 296.

(26) Gurvich, L.; Veyts, I. V.; Alcock, C. B., Eds. *Thermodynamic Properties of Individual Substances*; Hemisphere Pub. Corp.: New York, 1991.

(27) Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J.; Watson, R. T. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1259.

(28) Chen, S. S.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1977**, *6*, 105.

(29) Batt, L.; Walsh, R. *Int. J. Chem. Kinet.* **1982**, *14*, 933-944.

(30) Batt, L.; Burrows, J. P.; Robinson, G. N. *Chem. Phys. Lett.* **1981**, *78*, 467.

(31) Tsang, W. Heats of Formation of Organic Radicals by Kinetic Methods. In *Energetics of Free Radicals*; Greenberg, A., Liebman, J. F., Eds.; Chapman & Hall: New York, 1996.

(32) Benson, S. W. *Thermochemical Kinetics*; John Wiley: New York, NY, 1976.

(33) Tsang, W.; Hampson, R. F. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1087.

(34) Kerr, J. A.; Timlin, D. M. *Int. J. Chem. Kinet.* **1971**, *3*, 427.

(35) Lacher, J. R.; Skinner, H. A. *J. Chem. Soc. A* **1968**, 1034.

(36) Millward, G. E.; Hartig, R.; Tschuikow-Roux, E. *J. Phys. Chem.* **1971**, *75*, 3195.

(37) Tschuikow-Roux, E.; Salomon, D. R. *J. Phys. Chem.* **1987**, *91*, 699.

(38) Stadelmann, J. P.; Vogt, J. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *35*, 83.

(39) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(40) Bryant, W. M. D. *J. Polym. Sci.* **1962**, *56*, 277.

(41) Nuttall, R. L.; Laufer, A. H.; Kilday, M. V. *J. Chem. Thermodyn.* **1971**, *3*, 167.

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