Stabilities, Excitation Energies, and Dissociation Reactions of CF_2Cl_2 and CF_2Br_2: Quantum Chemical Computations of Heats of Formation of Fluorinated Methanes, Methyls, and Carbenes

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The heats of formation of a range of chlorofluoro-, bromofluoro-, and iodofluoromethanes, methyls, and carbenes were computed using the Gaussian-3 (G3) and Gaussian-2 (G2) methods. From a number of computed isodesmic reaction enthalpies, the heats of formation (at 298 K) of the key methyl species in the decomposition reactions of difluoromethanes, namely CF_2Cl, CF_2Br, and CF_2I, were determined as -64.7 ± 2.0, -52.3 ± 2.0, and -39.3 ± 2.0 kcal mol^{-1}, respectively, while our recommended heat of formation for CI_4 is 77.0 ± 3.0 kcal mol^{-1}. Using the available thermochemistry the energetics of the dissociation reactions of CF_2X_2 (X = Cl, Br, I) corresponding to the product channels $CF_2X + X$ and $CF_2 + X_2$ (as well as $CF_2 + 2X$) were thus computed and compared. The energetics favor the molecular channel but only by ∼10−12 kcal mol^{-1} in the case of CF_2Cl_2 and CF_2Br_2. However, no transition states were found in these systems for the molecular elimination of Cl_2 and Br_2. By contrast, H_2 elimination in CF_2H_2 was found to be favored by ∼ 40 kcal mol^{-1} (at the G2 level) with the corresponding transition state predicted to be 17.3 kcal mol^{-1} below the radical products $CHF_2 + H$. The vertical excitation energies of CF_2Cl_2 and CF_2Br_2 (to the lowest singlet and triplet B_1, A_2, B_2, and A_1 excited states) were computed using a range of methods including CASPT2 and EOM-CCSD in conjunction with the cc-pVTZ basis set. The results obtained for the lowest energy, viz., $\tilde{A}(^1B_1) \leftarrow \tilde{X}(^1A_1)$, transitions are consistent with the available experimental data. The excited state potential energy surfaces, as calculated at the CASPT2 level of theory, are found to be repulsive with respect to a single C−Cl or C−Br bond stretch, but have shallow local minima in C_{2v} symmetry, i.e., when *both* C−Cl or C−Br bonds are stretched to ∼2.3 Å, that suggest the existence of weakly bound metastable states.

Introduction

The photolytic reactions of halons, in particular chlorofluoro- and bromofluorocarbons, are of considerable current interest, especially because of the current need for the elucidation and quantification of the ozone depleting potential of these molecules.[1,2] Dibromodifluoromethane, CF_2Br_2, has been the subject of a number of studies. In particular, the mechanism and dynamics of its ultraviolet photodissociation have remained a contentious issue over the years as the different experiments appeared to support different models. The question still asked is whether CF_2Br_2 photodissociates (a) into CF_2 and Br_2 via a molecular channel, (b) into CF_2Br + Br radicals, or (c) into CF_2 + 2Br via a single or two successive radical channels. A concise summary of the experimental work to date is given by Cameron et al.[3]

Cameron et al.[3] have recently completed an extensive study of the photodissociation dynamics of CF_2Br_2 at a number of photolysis wavelengths between 223 and 260 nm. In these experiments the CF_2 vibrational state distribution and the rotational contour at each wavelength were measured, along with the translational recoil energy of CF_2, and the photofragment excitation spectrum of CF_2Br_2 near the threshold for CF_2 production. These experiments provided unambiguous evidence that CF_2 formation is accompanied by the production of two Br atoms. This conclusion was reached by consideration of the thermochemistry of the dissociation reactions in conjunction with the measured energies of the CF_2 fragments.

Concurrently with the experimental work discussed above, the authors of this paper carried out a quantum chemical study of the thermochemistry of CF_2Br_2 and its possible photofragments,[4] using the Gaussian-2 techniques G2 and G2(MP2).[5,6] To gauge the accuracy of the calculations, an analogous study was carried out on the CF_2Cl_2 system, while for CF_2I_2 the G2-[ECP(HW)],[7] another variant of G2, utilizing an effective core potential (ecp) for the iodine atom, was employed. After the publication of the Gaussian-3 (G3) method,[8] the thermochemistry relevant to the chlorofluorocarbons was recalculated using G3 as well. We also studied the decomposition of CF_2Cl_2 and CF_2Br_2 in the ground electronic state, as it may occur in a thermal (pyrolysis) reaction, using complete active space SCF (CASSCF)[9,10] and complete active space second-order perturbation theory (CASPT2)[11−13] methods along with G2 and G3. Our findings for these systems are contrasted with the results of analogous studies of CH_2F_2. Finally, we carried out a theoretical investigation of a number of electronically excited states of CF_2Cl_2 and CF_2Br_2 using a variety of methods, including CASPT2, equations of motion coupled cluster with single and double excitations (EOM-CCSD), and time-dependent density functional theory (TD-DFT).

Theory and Computational Methods

The theoretical prediction of thermochemistry to chemical accuracy, i.e., to within ∼1 kcal mol^{-1}, is now a realistic

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endeavor, resulting from recent advances in the area of ab initio quantum chemistry and the steady decrease of the cost-to-power ratio of computers. The starting point for the theoretical prediction of heats of formations is the quantum chemical calculation of heats of reactions that involve the species of interest, which then enables, through the use of Hess's law, the computation of the required heat of formation.

Given the availability of accurate experimentally derived heats of formation of atoms in the gas phase, the most obvious approach is to deduce the heat of formation of a molecule from its computed atomization energy. Such an approach requires the accurate and balanced energetic description of the molecule and its constituent atoms that places stringent requirements on the quantum chemical methods used, in particular the treatment of electron correlation, as well as large, near-complete basis sets. A practical way of satisfying these requirements is to extrapolate to a hypothetical complete basis limit a sequence of atomization energies computed at a high level of theory with systematically enlarged basis sets, as pioneered by Martin and co-workers[14,15] and Dixon and Feller[16,17] as well as others.[18,19]

An alternative approach, developed by Pople and co-workers and implemented in the Gaussian methods G1,[20] G2,[5] and more recently G3,[8] as well as variants of these,[21−24] achieve the objectives of producing accurate atomization energies by correcting the atomic and molecular energies obtained in a quadratic configuration interaction (QCISD(T)) calculation in a small split valence + polarization functions basis (6-311G-(d,p) or 6-31G(d)). The corrections comprise MP4 and MP2 estimates of the changes in energy with systematic enlargements of the basis sets and also include an empirical (higher level) correction. Using computed atomization energies at 0 K in conjunction with experimental heats of formation of the elements in their atomic states, the heats of formation of the molecules at 0 K and hence at 298 K are readily obtained, as discussed in detail by Curtiss et al.,[25] by calculating also the appropriate thermal contributions to the atomic and molecular enthalpies. The prediction of chemically accurate heats of formation (usually understood to be ∼1 kcal mol^{-1}) requires of course the same level of accuracy in the computed atomization energies. For small molecules this is achievable. For example, for the Gaussian data set of 299 molecules, on average, the G2 and G3 atomization energies have been found to be within 1.48 and 1.02 kcal mol^{-1} of experiment. More recently, Martin and Oliveira,[14] using a range of extrapolation schemes for CCSD-(T) energies, demonstrated an even higher level of accuracy of 0.24 kcal mol^{-1} in the computation of heats of formation of some 30 small first- and second-row molecules.

A useful alternative to the use of atomization energies is the computation of isodesmic or isogyric reaction energies, where the number of bond types in the former, and just the number of electron pairs in the latter, are conserved. It has long been appreciated that the calculation of isodesmic or isogyric reaction energy is much less demanding with respect to the resolution of electron correlation due to the cancellation of errors that occurs.[26−28] Thus reasonably accurate predictions of heats of formation are possible using relatively low levels of theory. However the success of such an approach depends crucially on the availability of accurate thermochemical data for molecules that are chemically similar to those under study, i.e., with the same type of bonds. In this work isodesmic reactions are used extensively in an effort to obtain the most accurate heats of formation for the species of interest as well as to check the consistency of the various methods used, viz. G3, G2 and G2(MP2).

The major part of the work reported in this paper was initially carried out using the G2 and G2(MP2) levels of theory. However, with the advent of G3 and its demonstrated success for halogenated hydrocarbons,[8,29] we recalculated most of the thermochemistry studied in this work. Unfortunately, thus far the G3 method has not been extended to molecules containing third- and fourth-row atoms. Therefore, in this work bromine-containing molecules are treated by G2 and G2(MP2), while for molecules with iodine the G2[ECP(HW)] scheme of Glukhovtsev et al.[7] is used which utilizes the Hay−Wadt effective core potentials (ecp)[30] for iodine. All G2, G3, and related calculations were carried out using the Gaussian94 and 98 programs.[31,32]

The ground state potential energy surfaces associated with the decomposition reactions of CF_2Br_2, CF_2Cl_2, and CH_2F_2 were explored using both SCF and MP2 methods as well by the complete active space (CASSCF) approach, in an effort to characterize both the atomic and molecular decomposition channels. The CASSCF geometry optimizations were carried out using the DALTON programs,[33] while single-point second-order complete active space perturbation theory (CASPT2) calculations were performed using MOLCAS4.[34]

The vertical electronic excitation energies of CF_2Cl_2 and CF_2Br_2 were computed by a number of techniques: configuration interaction with singles (CIS),[35] random phase approximation (RPA),[36] and time-dependent density functional method (TD-DFT),[37−39] (using Gaussian98), CASSCF, CASPT2 (by MOLCAS4), and the equations of motion method with a coupled cluster (with single and double excitations) reference (EOM-CCSD),[40] using the ACES II programs.[41]

All computations were performed on DEC alpha 600/5/333 and COMPAQ XP1000/500 workstations of the Theoretical Chemistry group at the University of Sydney.

Heats of Formation

The G3 energies (including zero-point vibrational contributions) for a number of chlorofluoromethanes and methyls are listed in Table 1 along with the heats of formation at 298 K ($\Delta_f H^0_{298}$) that were obtained from atomization energies (AE) computed at the G3 and G2 levels of theory, as well from isodesmic reaction enthalpies (ID). In the case of G3 the differences between the AE and ID results are fairly small, 1.2 kcal mol^{-1} at most. The analogous differences in the G2 AE and bond additivity corrected (BAC) results of Berry et al.[42] (which are equivalent to the application of isodesmic schemes) are considerably larger, being ∼4 kcal mol^{-1}. Much of this discrepancy can be traced to the neglect of spin−orbit coupling (SO) contributions to the atomic energies, which are quite large in the case of halogen atoms: −0.38 and −0.84 kcal mol^{-1} for F and Cl, respectively. Application of this correction to the G2/AE data reduces the discrepancy between the G3/AE and G2/AE results to ∼2 kcal mol^{-1} or less. As expected, the use of isodesmic reactions results in significant error cancellations, including the spin−orbit effects discussed above, so that the level of agreement between the G3/ID and G2/BAC results is generally quite good, the maximum difference being 2.0 kcal mol^{-1}. Moreover, these results agree reasonably well with the available experimental data.

The isodesmic reactions that were utilized in this work to obtain the heats of formation in Table 1 are summarized in Table 2. The heats of formation used in these calculations are given in Table A1 in the Appendix. The latter are mostly experimental data but in some cases, e.g., for CH_3F, CH_2F_2, and CHF_3, we used values that had been obtained by G3 isodesmic calcula-

TABLE 1: Chlorofluoromethanes and Chlorofluoromethyl Species: G3 Total Energy and Heats of Formation from G2 and G3 Atomization Energies (AE), Isodesmic Reactions (ID), G2 with Bond Additivity Corrections (BAC), and Experiments (in kcal mol^{-1} Unless Otherwise Specified)

		$\Delta_f H^0_{298}$				
	E_0[G3]/E_h	G3/AE	G3/ID	G2/AE (SO)[a]	G2/BAC[b]	expt
CHF_2Cl	−698.328 16	−116.0	−115.8	−119.0 (−117.3)	−115.3	−115.1[c]
						−115.4± 0.7[d]
CF_3Cl	−797.546 22	−170.7	−170.3	−174.9 (−172.8)	−169.6	−169.2[c]
CF_2Cl_2	−1157.787 91	−119.5	−119.8	−122.8 (−120.3)	−118.4	−117.5[c]
						−115.1 ± 2[e]
$CFCl_3$	−1518.033 33	−70.7	−71.4	−72.9 (−69.9)	−69.4	−69.0[c]
CHF_2	−238.201 32	−58.6	−57.4	−59.8 (−59.0)		−59.2 ± 2.0[f]
CF_2Cl	−697.666 79	−66.0	−64.7	−68.0 (−66.4)		

[a] With spin−orbit coupling correction. [b] Reference 42. [c] Reference 43. [d] Reference 44. [e] Reference 45. [f] Reference 46.

TABLE 2: Chlorofluoromethanes: Heats of Formation (at 298 K) of Italicized Species from Isodesmic Reactions (in kcal mol^{-1})[a]

reaction	G2	G2(MP2)	G3
$CH_2F_2 + CH_3Cl \rightarrow \mathit{CHF_2Cl} + CH_4$	−115.87	−115.56	−115.78
$CHF_3 + CH_2Cl_2 \rightarrow \mathit{CF_3Cl} + CH_3Cl$	−170.89	−170.52	−170.35
$CH_2F_2 + CH_2Cl_2 \rightarrow \mathit{CF_2Cl_2} + CH_4$	−119.88	−119.30	−119.70
$CHF_3 + 2CH_3Cl \rightarrow \mathit{CF_2Cl_2} + CH_4 + CH_3F$	−119.50	−119.24	−119.72
$CH_3Cl + CF_2Cl_2 \rightarrow \mathit{CFCl_3} + CH_3F$	−70.85	−71.06	−71.39
$CH_2Cl_2 + CHF_2 \rightarrow \mathit{CF_2Cl} + CH_3Cl$	−65.39	−65.07	−64.69
$CH_3Cl + CHF_2 \rightarrow \mathit{CF_2Cl} + CH_4$	−65.02	−64.67	−64.71
$CHF_2Cl + CH_3 \rightarrow \mathit{CF_2Cl} + CH_4$	−65.05	−64.95	−64.52

[a] The heats of formation used in these calculations are given in Table A1 in the Appendix.

TABLE 3: Bromofluoromethanes, Methyl, and Carbene Species: Total G2 Energies and Heats of Formation from G2 and G2(MP2) Atomization Energies (AE) and Isodesmic Reactions (ID) (in kcal mol^{-1}, Unless Indicated Otherwise)

		$\Delta_f H^0_{298}$			
	E_0[G2]/E_h	G2/AE[a]	G2/ID	G2(MP2)/AE[a]	literature[b]
CH_3Br	−2612.390 44	−8.1	−10.9	−8.1	−8.2 ± 0.2[c]
					−9.0 ± 0.32[d]
CF_2Br_2	−5382.682 66	−91.8	−92.4	−93.1	−90.9[e]
CF_3Br	−2909.872 33	−158.1	−156.5	−159.4	−154.7 ± 0.7[f]
					−155.2 ± 0.8[g]
CH_2Br	−2611.730 32	41.8	40.0	41.9	40.4[h]
CF_2Br	−2810.042 85	−52.8	−52.3	−53.8	
$CHBr$	−2611.073 71	89.3	89.1	89.0	89.1 ± 4.3[i]
$CFBr$	−2710.263 90	20.7	21.1	19.8	≥20.6[j]
$CClBr$	−3070.248 32	68.6	67.4	67.0	
CBr_2	−5183.081 62	82.1	80.9	81.2	80.6± 2.0[k]

[a] Including spin−orbit corrections to atomic energies (Br −3.51, Cl −0.84, F −0.38, C −0.09; all in kcal mol^{-1}). [b] Experimental value unless indicated otherwise. [c] Reference 47. [d] Reference 48. [e] Reference 45. [f] Reference 43. [g] References 49, 50. [h] Reference 51. [i] Reference 52. [j] Reference 53. [k] From CCSD(T)/cc-pVQZ calculations, ref 54.

TABLE 4: Bromofluoromethanes, Methyl, and Carbene Species: Heats of Formation (at 298 K) of Italicized Species from Isodesmic Reactions (in kcal mol^{-1})[a]

reaction			G2	G2(MP2)
$CH_3Cl + Br$	→	$\mathit{CH_3Br} + Cl$	−10.90	−10.21
$CH_2F_2 + 2CH_3Br$	→	$\mathit{CF_2Br_2} + 2CH_4$	−92.50	−92.16
$CHF_2Cl + 2CH_3Br$	→	$\mathit{CF_2Br_2} + CH_3Cl + CH_4$	−91.73	−91.71
$CHF_3 + CH_3Br$	→	$\mathit{CF_3Br} + CH_4$	−156.50	−156.30
$CH_3Br + CH_3$	→	$\mathit{CH_2Br} + CH_4$	39.98	39.99
$CH_2F_2 + CH_2Br$	→	$\mathit{CF_2Br} + CH_4$	−52.68	−52.42
$CHF_2Cl + CH_2Br$	→	$\mathit{CF_2Br} + CH_3Cl$	−51.91	−51.96
$CH_2Br + CHF_2$	→	$\mathit{CF_2Br} + CH_3$	−51.88	−51.70
$CCl_2 + 2CH_3Br$	→	$\mathit{CBr_2} + 2CH_3Cl$	80.92	81.05
$HCF + CH_3Br$	→	$\mathit{CFBr} + CH_4$	20.77	20.83
$CF_2 + CH_3Br$	→	$\mathit{CFBr} + CH_3F$	21.21	21.17
$CFCl + CH_3Br$	→	$\mathit{CFBr} + CH_3Cl$	21.17	21.21
$CF_2 + CBr_2$	→	$2\mathit{CFBr}$	21.33	21.45
$HCF + CFBr$	→	$\mathit{CHBr} + CF_2$	88.45	88.45
$CH_2 + CBr_2$	→	$2\mathit{CHBr}$	89.11	89.12
$CHCl + CFBr$	→	$\mathit{CClBr} + HCF$	67.72	67.49
$CFCl + CFBr$	→	$\mathit{CClBr} + CF_2$	67.10	66.83
$CCl_2 + CBr_2$	→	$2\mathit{CClBr}$	67.63	67.62

[a] The heats of formation used in these calculations are given in Table A1 in the Appendix.

tions.[29] Such data would then be based on other experimental data, such as CH_4 and CF_4 in the above example.

The level of consistency between the G2, G2(MP2), and G3 results in Table 1 is excellent, the largest deviation being ∼1.4 kcal mol^{-1}. The lower level of agreement between the G3/ID and G2/BAC results is due to the use of different reaction schemes.

The G2 energies and the calculated G2 and G2(MP2) heats of formation for the bromofluoromethanes, methyl and carbene species studies are listed in Table 3. The heats of formation obtained from a range of isodesmic reactions are given in Table 4. In the case of molecules containing third-row atoms, G2 theory, as formulated by Curtiss et al.,[55] includes spin−orbit corrections for both atomic and molecular species. The G2/AE and G2(MP2)/AE results in Table 3 were obtained using the appropriate spin−orbit-corrected atomic energies, as in G3. As the ground states of most molecules are spatially nondegenerate singlets, the spin−orbit corrections are expected to be very small. In the case of $CF_2Br(^2A')$ we obtained the value of just 3 cm^{-1} for the spin−orbit coupling correction, by application of the Pauli−Breit spin−orbit coupling operator in a basis of Russell−Saunders states,[56−58] as implemented in the GAMESS programs.[59] The same calculation for the $Br(^2P)$ atom yielded 3.16 kcal mol^{-1}, which is in reasonable agreement with the experimental value[60] of 3.51 kcal mol^{-1}, as well as the computed value of 3.63 kcal mol^{-1} reported by Curtiss et al.[55] The agreement between the (spin−orbit corrected) G2/AE and G2/ID heats of formation is quite good, with the maximum difference (in the case of CH_3Br) being 2.8 kcal mol^{-1}. The data in Tables 3 and 4 also demonstrate good agreement between the G2 and G2(MP2) results.

The agreement between the computed and the available experimental heats of formation of the chlorofluoro and bro-

TABLE 5: Iodofluoromethane and Methyl Species: Heats of Formation (at 298 K) of Italicized Species from Isodesmic Reactions (in kcal mol^{-1})[a]

reaction			G2[ECP(HW)]	expt
$2CH_3I$	→	$\mathit{CH_2I_2} + CH_4$	25.8	28.1 ± 1.0[b], 29.2 ± 1.0[c]
$3CH_3I$	→	$\mathit{CHI_3} + 2CH_4$	49.4	
$4CH_3I$	→	$\mathit{CI_4} + 3CH_4$	75.3	64.0[b]
$4CF_3I$	→	$\mathit{CI_4} + 3CF_4$	75.8	
$2CH_2I_2$	→	$\mathit{CI_4} + CH_4$	79.8	
$CH_3I + CHF_3$	→	$\mathit{CF_3I} + CH_4$	−141.0	−140.8,[d] −140.49 ± 0.76[e]
$2CH_3I + 2CH_3F$	→	$\mathit{CF_2I_2} + 3CH_4$	−62.9	
$2CH_3 + CF_4 + 2CH_3I$	→	$2\mathit{CF_2I} + 3CH_4$	−39.3	

[a] The heats of formation used in these calculations are given in Table A1 in the Appendix. [b] Reference 62. [c] Reference 63. [d] Reference 43. [e] References 50, 64.

mofluoro species is generally good: within ~2.0 kcal mol^{-1} for all but two molecules (CF_2Cl_2 and $CFCl_3$). Unfortunately, as often no confidence limits are available in the case of the recent recommended experimental values tabulated by NIST, it is not possible to arrive at a more realistic appraisal of the quality of the computed data. Nevertheless, as in previous work of ours,[29] we estimate the G3/ID and G2/ID values for the current sets of heats of formation to be accurate to within ±2 kcal mol^{-1}; that would imply uncertainties of at least ±0.3 and ±0.4 kcal mol^{-1} in the experimental values for CF_2Cl_2 and $CFCl_3$, respectively. Thus, our recommended values for the heats of formation of the chlorofluoro- and bromofluoromethyl radicals are $\Delta_f H^0_{298}(CF_2Cl) = -64.7 \pm 2$ and $\Delta_f H^0_{298}(CF_2Br) = -52.3 \pm 2$ (kcal mol^{-1}). In addition to the above halomethane and methyl molecules, we computed heats of formation of a number of bromocarbenes. These are found to agree closely with the results of recent computations by Schwartz and Marshall[61] using similar methods to ours.

The computed heats of formation of a number of iodofluoromethane and methyl species, obtained via isodesmic schemes, as indicated, are given in Table 5. The G2 enthalpies of all iodine-containing molecules were obtained using the G2[ECP(HW)] scheme of Glukhovtsev et al.,[7] which utilizes the Hay−Wadt[30] ecp's for iodine. The agreement between the computed and experimental heats of formation of CH_3I and CF_3I is comparable to what was achieved for the chloro- and bromofluoromethanes which suggests that, as concluded by Glukhovtsev et al.[7] too, this ecp-based approach has a reasonable degree of reliability. Thus, in the case of CI_4, where the calculated heats of formation are ~10 kcal mol^{-1} above the value derived from experiments, we expect the computed values to be more reliable. We therefore recommend $\Delta_f H^0_{298}(CI_4) = 77.0 \pm 3.0$ kcal mol^{-1}.

Decomposition Reactions of CF_2Br_2, CF_2Cl_2, CF_2I_2, and CH_2F_2

As outlined in the Introduction, the main focus of this work is the study of the decomposition reactions of CF_2Br_2, while those of CF_2Cl_2, CF_2I_2, and CH_2F_2 were studied largely for comparative purposes. The thermochemistry of the following reactions has thus been computed:

$$CF_2X_2 \rightarrow CF_2X + X \quad (1)$$

$$CF_2X \rightarrow CF_2 + X \quad (2)$$

$$CF_2X_2 \rightarrow CF_2 + 2X \quad (3)$$

$$CF_2X_2 \rightarrow CF_2 + X_2 \quad (4)$$

TABLE 6: Decomposition Reactions of CF_2X_2 (X = H, Cl, Br, I): Heats of Reactions (at 298 K, Unless Otherwise Indicated) Calculated from Computed (G3, G2, G2[ECP(HW)]) Heats of Formation of CF_2X_2, CF_2X, and CF_2 (Tables 1, 2, and 5) and Experimental Values for X and X_2 (in kcal mol^{-1})

	G3/ID		G2/ID (0K)	G2-ECP/ID
reaction	X = H	X = Cl	X = Br	X = I
$CF_2X_2 \rightarrow CF_2X + X$	102.5	84.1	66.8 (66.7)	49.1
$CF_2X \rightarrow CF_2 + X$	64.0	48.2	33.4 (33.1)	19.3
$CF_2X_2 \rightarrow CF_2 + 2X$	166.5	132.3	100.2 (99.9)	68.4
$CF_2X_2 \rightarrow CF_2 + X_2$	62.3	74.3	54.2	32.3

where X = H, Cl, Br, or I. The results are summarized in Table 6 and in Figure 1. Clearly, the strength of C−X bonds markedly diminishes across the series X = H, Cl, Br, and I, in both the halomethane and methyl molecules. The unusually high stability of CF_2 is clearly responsible for the much weaker C−X bonds in the halomethyls. What is also quite striking, however, is that while for CH_2F_2, the reaction enthalpy of the molecular dissociation channel (4) is ~40 kcal mol^{-1} lower than the enthalpy change associated with the C−H bond breaking reaction 1, for the chloro-, bromo-, and iodofluoromethanes the difference is much less, ranging from ~10 to 17 kcal mol^{-1}. For the latter series of molecules then the molecular dissociation channel may well be expected to be associated with a higher activation energy than for the radical decomposition reaction 1, since the barrier height for the former is likely to be in excess of 20 kcal mol^{-1} above the reaction enthalpy. These estimates conform to the multireference CI (MRCI) results of Lewerenz et al.[65] for CF_2Cl_2, according to which the barrier to molecular dissociation is ~38 kcal mol^{-1} above the energy of the radicals $CF_2Cl + Cl$.

In light of the above, it is not surprising that we were unable to find transition state structures, i.e., first-order saddle points on the ground state potential energy surfaces, for the molecular decomposition reactions of CF_2Cl_2 and CF_2Br_2. Both the MP2/6-31G(d) and CASSCF/cc-pVDZ geometry searches failed in this endeavor. Note that Lewerenz et al.[65] located the saddle point for CF_2Cl_2 by pointwise energy calculations in C_{2v} symmetry, varying only the C−Cl and Cl−Cl distances, but did not test the index of the stationary point that had been found. In our work the only first-order saddle points that were located by the CASSCF calculations were found to correspond to abstraction reactions, i.e.

$$CF_2X + X \rightarrow CF_2 + X_2 \quad (5)$$

A study of the CASSCF reaction energies showed that for CF_2Cl_2 the radical decomposition channel (1) would actually be predicted to be favored by 3 kcal mol^{-1} over the molecular channel (4), although for CF_2Br_2 the situation is reversed, with the molecular channel favored by ~8 kcal mol^{-1}. Given such a situation in the case of CF_2Cl_2, it is obvious that a CASSCF search for a barrier may well to lead to the radical decomposition

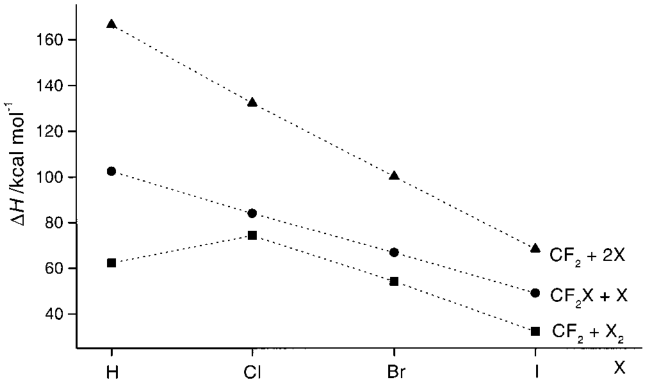

Figure 1. Decomposition reactions of CF_2X_2 (X = H, Cl, Br, I): Computed heats of reactions at 298 K from Table 6.

products $CF_2Cl + Cl$, since in trying to find the lowest energy saddle point the optimizer keeps increasing the C−Cl distance once the curvature of the potential energy with respect to R_{CCl} is negative, which it is as the bond breaks. The optimization process can thus effectively converge to the geometry of the near-dissociated system. This is exactly what we found for both CF_2Cl_2 and in CF_2Br_2 (in addition to the saddle points corresponding to the abstraction reactions (5)), irrespective of the choice of starting geometries. Thus, we conclude that on the CASSCF surface the transition states for the molecular dissociation channels are likely to have higher energies than the radical products.

However, for CF_2Br_2 the existence of a molecular dissociation channel appears well-established. Most recently, Abel et al.[66] reported threshold energies of 54.5 ± 1.4 and 59.2 ± 1.4 kcal mol^{-1} for the unimolecular Br_2 elimination and C−Br bond fission, respectively, on the basis of their infrared multiphoton excitation and decomposition experiments. The latter value is at considerable variance with our calculated bond energy of 66.7 kcal mol^{-1}, although if we allow for a maximum error of ±4 kcal mol^{-1} (given that we estimate the error in the computed heats of formation of CF_2Br_2 and CF_2Br as ±2 kcal mol^{-1}), the discrepancy between theory and experiment could be as low as ~2.2 kcal mol^{-1}. However, as we may expect some error cancellation when taking the difference of the above heats of formation, i.e., a higher accuracy in our computed bond energy than ± 4 kcal mol^{-1}, the discrepancy between theory and experiment is of some concern. We note, however, that other published experimental values[66] for the C−Br bond energy in CF_2Br_2 range from 59.8 to 68.6 kcal mol^{-1}. With regard to the demonstrated existence of the molecular channel with a barrier that is 4.7 kcal mol^{-1} below the bond fission energy, we conclude that a higher level of theory than CASSCF would be needed to locate the transition state, such as CASPT2 or MR-CI. While we are unaware of experimental verification of an analogous molecular channel for CF_2Cl_2, on the basis of the CF_2Br_2 results we would expect that the barrier in the former would be considerably less than the 38 kcal mol^{-1} suggested by the calculations of Lewerenz et al.[65]

For CH_2F_2 the transition state corresponding to molecular dissociation was readily found at all levels of theory, viz., SCF, MP2, and CASSCF. The structure of the transition state at the MP2/6-31G(d) level, along with those of the CASSCF/cc-pVDZ transition states of the abstraction reactions of CF_2Cl_2 and CF_2Br_2, are given in Figure 2. The computed vibrational frequencies of these transition states are available in Table S1 of the Supporting Information. In the case of CF_2Cl_2 it was explicitly verified, by intrinsic reaction coordinate (IRC) calculations, that the above transition state does connect the reactants and products of the abstraction reaction (5). We expect the same to be true for CF_2Br_2 as well. The barrier height (at 0 K) for the CH_2F_2 system, computed at the G2 level, is 34.1 kcal mol^{-1} above the products $CF_2 + H_2$, which is 17.3 kcal mol^{-1} below the radical products $CHF_2 + H$. Clearly, in this system the molecular dissociation channel is expected to dominate over radical dissociation.

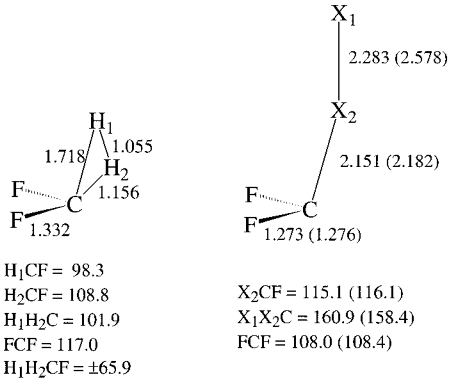

Figure 2. Transition state geometries (bond distances in Å and bond angles in degrees) for H_2 elimination in CF_2H_2 at MP2/6-31G(d)level and Cl (or Br) abstraction in CF_2Cl_2 and CF_2Br_2 (latter in parentheses) at CASSCF/cc-pVDZ level of theory (X_1, X_2 = Cl or Br). All systems are of C_s symmetry.

TABLE 7: CF_2Cl_2 Vertical Excitation Energies (eV) Computed at Various Levels of Theory, As Indicated, Using cc-pVTZ Basis at B3LYP/cc-pVTZ Geometry

state	CIS	RPA	TD-DFT	CASSCF	CASPT2	EOM-CCSD[a]	expt
$^3B_1$	6.73	6.38	5.89	7.04	6.13	6.52 (6.45)	
$^3A_2$	7.07	6.76	6.23	7.43	6.48	6.86 (6.78)	7.2[b]
$^3B_2$	7.28	6.98	6.57	7.68	6.79	7.13 (7.06)	
2 $^3A_1$	7.40	7.10	6.78	7.77	6.92	7.28 (7.21)	
$^1B_1$	8.01	7.89	6.73	8.01	6.83	7.13 (7.23)	7.0[c]
$^1A_2$	8.30	7.90	6.95	8.31	7.13	7.59 (7.51)	
$^1B_2$	8.57	8.18	7.38	8.57	7.50	7.96 (7.88)	8.11[c]
2 $^1A_1$		8.38	7.76	8.83	7.69	8.16 (8.08)	8.61[c]

[a] Values in parentheses calculated with the cc-pVTZ + Rydberg functions basis as discussed in text. [b] From electron impact measurements, ref 67. [c] Reference 68.

Electronic Excitation Energies of CF_2Cl_2 and CF_2Br_2

The electronic excitation energies of CF_2Cl_2 and CF_2Br_2 were computed at a number of different levels of theory, ranging from the popular configuration interaction with singles (CIS) method to CASSCF, CASPT2, and EOM-CCSD. Given the current level of interest in density functional theory (DFT) and its application to the computation of excitation energies via the time-dependent Hartree−Fock method (TD-DFT), the latter method along with RPA within the Hartree−Fock approximation was also used, enabling a comparison of these six methodologies to be made. The calculations on the two molecules were performed using the cc-pVTZ basis set at the DFT, viz., B3LYP/cc-pVTZ, ground state equilibrium geometries. For CF_2Cl_2 the EOM-CCSD calculations were repeated using the cc-pVTZ basis enlarged by the addition of Rydberg type s (exponents: 0.0143, 0.0048) and p functions (exponents: 0.0403, 0.0134) on the carbon atom.

The resulting vertical excitation energies are summarized in Tables7 and 8. In general, the results from the two highest level ab initio calculations, viz., EOM-CCSD and CASPT2, are in reasonable agreement. CIS and RPA seem to perform well for the triplet states, but in the case of singlet excitations these two methods tend to systematically overestimate the excitation

TABLE 8: CF_2Br_2 Vertical Excitation Energies (eV) Computed at Various Levels of Theory, As Indicated, Using cc-pVTZ Basis at B3LYP/cc-pVTZ Geometry

state	CIS	RPA	TD-DFT	CASSCF	CASPT2	EOM-CCSD	expt
$^3B_1$	5.11	4.76	4.35	5.45	4.52	4.92	
$^3A_2$	5.45	5.19	4.66	5.82	4.85	5.25	
$^3B_2$	5.68	5.42	5.01	6.08	5.13	5.54	
2 $^3A_1$	5.79	5.51	5.21	6.18	5.27	5.68	
$^1B_1$	6.20	5.83	5.03	6.23	5.08	5.58	5.46[a]
$^1A_2$	6.50	6.10	5.25	6.52	5.41	5.86	
$^1B_2$	6.80		5.67	6.87	5.74	6.23	
2 $^1A_1$		6.47	5.98	7.06	5.91	6.42	

[a] Reference 3.

energies. Overall, the performance of the TD-DFT method is quite good, when compared with EOM-CCSD and CASPT2. As the addition of Rydberg type functions to the basis appears to have quite a small effect on the excitation energies of CF_2Cl_2, the analogous computations for CF_2Br_2 were not carried out.

The EOM-CCSD and CASPT2 predictions for the $\tilde{A}(^1B_1) \leftarrow \tilde{X}(^1A_1)$ excitation in both CF_2Cl_2 and CF_2Br_2 bracket the experimental values, with the EOM-CCSD values being within ~0.2 eV of experiment. In the case of other excitations, especially to the 2 $^1A_1$ state in CF_2Cl_2, the agreement with experiment is less satisfactory.

The energies of the $^3B_1$, $^3B_2$, $^3A_2$, $^3A_1$, $^1B_1$, $^1B_2$, and $^1A_2$ states of CF_2Cl_2 and CF_2Br_2 were also computed as a function of one of the CCl and CBr bond stretches respectively at the CASPT2/cc-pVDZ level of theory. The potential energy curves obtained are all repulsive,[4] as expected, and correlate with the CF_2X-($^2A'$) + $X(^2P)$ dissociation products (X = Cl, Br), as does the ground state. (When distorted by a C−X stretch, CF_2X_2 assumes C_s symmetry and the A_1, B_1 states become A', while the B_2, A_2 states become A''.) Qualitatively, the potential energy curves are effectively the same as those published by Lewerenz et al.[65] for CF_2Cl_2 (obtained by multireference CI calculations) and therefore not shown in this paper.

On stretching both C−X bonds, such that the C_{2v} symmetry of the molecule was retained, the energies of all states were found to decrease more rapidly, as one may expect, but recross the surfaces associated with a single C−X stretch as the asymptotic limit $CF_2X + X$ lies at a lower energy than $CF_2 + 2X$. In the case of the $^3B_1$, $^3A_2$, and $^1B_1$ states, the potential energy curves also displayed a minimum at CX distances of ~2.3 Å. The computed CASPT2/cc-pVTZ potential energy curve for the $^1B_1$ state of CF_2Cl_2 is shown in Figure 3, along with the corresponding curve for the $^1A_1$ ground state. This behavior suggests the possible existence of weakly bound excited states of CF_2Cl_2 and CF_2Br_2 and consequently more detailed CASPT2 calculations were carried out for the $^3B_1$ and $^1B_1$ states of these two molecules, where the CX and XX distances were optimized via single-point energy calculations in C_{2v} symmetry, with the CF_2 fragment geometry kept fixed at its ground-state equilibrium (CASSCF/cc-pVDZ) values. The results are summarized in Table 9. The optimized CX and XX distances are ~2.3 and 2.8 Å while the corresponding dissociation energies relative to CF_2 ($^1A_1$) + 2X (^2P) are ~20 and 29 kcal mol^{-1} for the singlet and triplet states, respectively. (These energies are also shown on the potential energy diagram as $^1B_1$(opt) and $^3B_1$(opt) in Figure 3.) As the computed data in Table 6 indicate, the $CF_2X + X$ products are ~48 and 33 kcal mol^{-1} more stable than $CF_2 + 2X$, for CF_2Cl_2 and CF_2Br_2 respectively. As these are in excess of the dissociation energies of the above excited states, it is clear that the latter correspond to metastable states or possibly saddle points. From a CASPT2/cc-pVTZ computation of the harmonic force field of CF_2Cl_2 in its $^1B_1$ state with respect to the C−Cl stretches and Cl−C−Cl bend (i.e., treating the molecule as a pseudotriatomic system), it was verified that the optimized geometry is indeed a true local minimum on the potential energy surface, i.e., a metastable state. Thus there is a barrier to distortion to C_s symmetry and thus transfer to the lower energy dissociative A' potential energy surface, although that barrier is likely to be quite small. We expect therefore that the $^3B_1$ and $^1B_1$ states of both CF_2Cl_2 and CF_2Br_2, as characterized in Table 9, are all metastable.

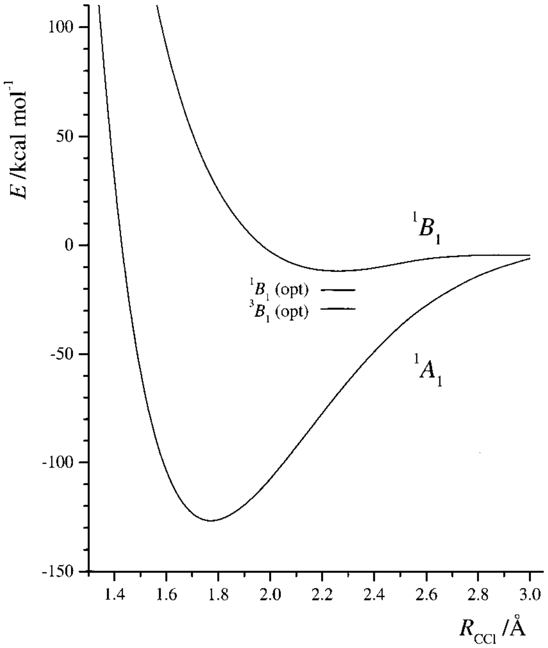

Figure 3. CASPT2/cc-pVTZ potential energy curves of $^1A_1$ ground state and $^1B_1$ excited state in C_{2v} symmetry with respect to symmetric CCl stretch with all other geometric parameters fixed at ground state equilibrium values (CASSCF/cc-pVDZ). The $^1B_1$(opt) and $^3B_1$(opt) energies were obtained by optimizing the CCl and ClCl distances (see Table 9).

TABLE 9: Equilibrium Geometric Parameters[a] and Dissociation Energies[b] of $^1B_1$ and $^3B_1$ CF_2Cl_2 and CF_2Br_2 Computed by CASPT2 Method Using cc-pVTZ Basis Set

		R_{CX}/Å	R_{XX}/Å	θ_{XCX}/deg	D_e/kcal mol^{-1}
CF_2Cl_2 (X = Cl)	$^1B_1$	2.3	2.7	72	20.0
	$^3B_1$	2.2	2.7	73	28.9
CF_2Br_2 (X = Br)	$^1B_1$	2.4	2.9	74	21.1
	$^3B_1$	2.3	2.9	75	29.5

[a] CF bond lengths and FCF bond angles frozen at $^1A_1$ ground state equilibrium values (1.31 Å, 108.7 deg). [b] Dissociation reaction: $CF_2X_2(^1B_1,^3B_1) \rightarrow CF_2(^1A_1) + 2X(^2P)$.

It is worth noting that Lewerenz et al.[65] also explored excited states of CF_2Cl_2 in C_{2v} symmetry, but in their work the electronic states were correlated with those of the CF_2 and Cl_2 molecules. While in the case of the $^1A_1$ ground state the molecular dissociation limit would lie ~58 kcal mol^{-1} below the CF_2 + 2Cl limit (i.e., the zero energy in Figure 3), the corresponding $CF_2(^1A_1) + Cl_2(^1\Pi_u)$ limit in case of the $^1B_1$ state (as calculated at the CASPT2/cc-pVTZ level) would be only ~4 kcal mol^{-1} below the CF_2 ($^1A_1$) + 2Cl (^2P) asymptote. Indeed the small barrier in the vicinity of 2.7 Å that the $^1B_1$ curve appears to have is consistent with such molecular dissociation. The resulting crossing of the $^1B_1$ and $^1A_1$ surfaces, along with an avoided crossing between the ground and excited $^1A_1$ surfaces

TABLE A1: Heats of Formation[a] Used in Isodesmic Calculations of Tables 1−6

molecule	$\Delta_f H^0_{298}$/kcal mol^{-1}	method	reference
CH_4	−17.90	expt (review)	43
CH_3F	−56.5 (±2.0)	G3/ID	29
CH_2F_2	−107.8 (±2.0)	G3/ID	29
CHF_3	−166.8 (±2.0)	G3/ID	29
CF_4	−223.0	expt (review)	43
CH_3Cl	−20.0	expt (review)	43
CH_2Cl_2	−22.8	expt (review)	43
CHF_2Cl	−115.1	expt (review)	43
CF_2Cl_2	−119.7 (±2.0)	G3/ID	this work
CH_3Br	−9.0 (±0.3)	expt	48
CH_3I	3.5 (±0.2)	expt	50, 69
CH_2I_2	28.1 (±1.0)	expt	62
CF_3I	−140.8 (±0.7)	expt (review)	45
CH_3	34.8	expt (review)	43
CHF_2	−57.0 (±2.0)	G3/ID	29
CH_2Br	40.4 (±2.0)	G3/ID	this work
CH_2	102.6 (±1.0)	CCSD(T)/CBS calc	54
CHF	35.1 (±1.0)	CCSD(T)/CBS calc	54
CF_2	−45.9 (±1.0)	CCSD(T)/CBS calc	16, 17, 54
CHCl	76.4 (±1.0)	CCSD(T)/CBS calc	54
CFCl	7.0 (±1.0)	CCSD(T)/CBS calc	54
CCl_2	54.7 (±1.0)	CCSD(T)/CBS calc	54
CFBr	21.1 (±2.0)	G3/ID	this work
CBr_2	80.6 (±2.0)	CCSD(T)/cc-pVQZ calc	54

[a] Experimental or estimated errors shown in parentheses where available.

would then provide a mechanism for the presence of molecular photodissociation products on $^1B_1 \leftarrow {}^1A_1$ excitation in CF_2Cl_2, as noted by Lewerenz et al.[65]

Using qualitative MO arguments, the existence of apparently stable excited state molecules can be understood as being generated by the promotion of a nonbonding a_1, b_1, or b_2 electron from the Cl_2 moiety into a CCl_2 antibonding MO of b_1 symmetry. In reality, however, dynamical electron correlation is essential for the stabilization of the resulting molecules, since no minima are evident at the CASSCF level of theory.

Conclusion

The heats of formation of a number of chlorofluoro-, bromofluoro-, and iodofluoromethanes, methyls, and carbenes were computed using the G3 and G2 methodologies, with effective core potentials for iodine, from both atomization and isodesmic reaction enthalpies. In particular, the standard heats of formation at 298 K of CF_2Cl, CF_2Br, and CF_2I, were determined as −64.7 ± 2, −52.3 ± 2, and −39.3 ± 2 kcal mol^{-1}, respectively. These data then predict the enthalpy changes for the bond fission reactions ($CF_2X_2 \rightarrow CF_2X + X$) as 84.1, 66.8, and 49.1 kcal mol^{-1} for X = Cl, Br, and I, respectively, while the corresponding enthalpies for molecular dissociation ($CF_2X_2 \rightarrow CF_2 + X_2$) are 74.3, 54.2, and 32.3 kcal mol^{-1}. Thus, molecular elimination is favored by only ∼10−12 kcal mol^{-1} in the case of CF_2Cl_2 and CF_2Br_2, but no transition states were found for such molecular eliminations on the ground state surfaces. By contrast, H_2 elimination in CF_2H_2 was found to be favored by ∼40 kcal mol^{-1} with the corresponding transition state located at 17.3 kcal mol^{-1} below the radical products CHF_2 + H.

Using a range of methods, including CASPT2 and EOM-CCSD, and the cc-pVTZ basis set, the vertical electronic excitation energies of CF_2Cl_2 and CF_2Br_2 (to the lowest singlet and triplet B_1, A_2, B_2, and A_1 excited states) were computed. The computed excitation energies for the lowest energy, viz., $B_1 \leftarrow A_1$ transition, as computed by the CASPT2 or EOM-CCSD methods, are consistent with the available experimental data. The excited state potential energy surfaces (calculated by CASPT2) are repulsive with respect to a single C−Cl or C−Br bond stretch, but have shallow minima in C_{2v} symmetry, i.e., when *both* C−Cl or C−Br bonds are stretched to ∼2.3 Å, which we believe to correspond to metastable states.

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Appendix

The heats of formation used in the isodesmic calculations of Tables 1−6 are given in Table A1.

Supporting Information Available: Table S1 containing computed vibrational frequencies of transition states of the reactions $CF_2H_2 \rightarrow CF_2 + H_2$ and $CF_2X + X \rightarrow CF_2 + X_2$ (X = Cl, Br). This material is available free of charge via the Internet at http://pubs.acs.org.

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