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Thermochemistry of the Fluoroformyloxyl Radical: A Computational Study Based on Coupled Cluster Theory[†]

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The standard enthalpy of formation of FCO_2 (X $^2B_2$) was determined by a computational approach based on coupled cluster theory [CCSD(T)] with energies extrapolated to the basis-set limit, with additional corrections accounting for core−valence correlation, scalar relativity, spin−orbit coupling, and zero-point vibrational motions. Utilizing a variety of independent reaction schemes, our best estimate is $\Delta_f H^\circ_0(FCO_2) = -86.0 \pm 0.6$ kcal mol^{-1} [$\Delta_f H^\circ_{298}(FCO_2) = -86.7 \pm 0.6$ kcal mol^{-1}], which is shown to be more accurate than previous theoretical and experimental values. The chosen computational procedure was also applied to HCO (X $^2A'$), where we find excellent agreement with experiment, and to FCO (X $^2A'$), where we recommend an improved value of $\Delta_f H^\circ_0(FCO) = -42.1 \pm 0.5$ kcal mol^{-1} [$\Delta_f H^\circ_{298}(FCO) = -42.0 \pm 0.5$ kcal mol^{-1}]. Further theoretical results concern the C−F bond dissociation energy, electron affinity, ionization energy, first and second excitation energies in FCO_2, fluoride ion affinity of CO_2, and equilibrium geometries of the molecules treated presently. For FCO (X $^2A'$) we propose an improved equilibrium structure: $r_e(CF) = 132.5(2)$ pm, $r_e(CO) = 116.7(2)$ pm, and $\theta_e(FCO) = 127.8(2)°$.

1. Introduction

The fluoroformyloxyl (fluorocarboxyl) radical FCO_2 is one of the key intermediate species formed in the atmospheric degradation of hydrofluorocarbons, hydrochlorofluorocarbons, and chlorofluorocarbons, and there is evidence to assume that FCO_2 is long-lived enough to react with other atmospheric species.[1,2] The existence of covalently bound FCO_2 is remarkable since analogous species are not stable: the formyloxyl radical HCO_2 has a negative C−H bond dissociation energy,[3−6] and XCO_2 (X = Cl, Br, I) radicals are very weakly bound van der Waals complexes.[7] However, compared with other halocarbon molecules (e.g., H_3C−F, F_3C−F, and Cl_3C−F), the FCO_2 radical has a quite weak C−F bond: by use of the measured[7] electron affinity of FCO_2, the known[8] fluoride ion affinity of carbon dioxide, and the electron affinity of the F atom,[9] the C−F bond dissociation energy in FCO_2 was derived[7] to be as small as $D_0(F-CO_2) = 11.5 \pm 3$ kcal mol^{-1}. In the same study,[7] the enthalpy of formation for FCO_2 was determined to be $\Delta_f H^\circ_{298}(FCO_2) = -85.2 \pm 2.8$ kcal mol^{-1}.

Early ab initio calculations[10] at the Gaussian-2 (G2) level of theory[11] predicted $\Delta_f H^\circ_{298}(FCO_2) = -86.0$ kcal mol^{-1}. However, it was noted subsequently[12] that at the G2 level the zero-point vibrational energy in this radical is grossly overestimated, and the previously[10] calculated G2 value of $\Delta_f H^\circ_{298}(FCO_2)$ was corrected for this error to obtain $\Delta_f H^\circ_{298}(FCO_2) = -90.9$ kcal mol^{-1}. Later, $\Delta_f H^\circ_{298}(FCO_2)$ was calculated[13] to be −86.5 kcal mol^{-1} at the superior Gaussian-3 (G3) level of theory.[14] When isodesmic reaction schemes with total energies from hybrid density functional theory (B3LYP[15,16]) were employed, $\Delta_f H^\circ_{298}(FCO_2)$ was estimated to be -90.5 ± 3 kcal mol^{-1}.[17] G3//B3LYP/6-311++G(3df, 3pd) isodesmic reaction energies were used to derive a $\Delta_f H^\circ_{298}(FCO_2)$ value of -87.9 ± 2 kcal mol^{-1}.[18] In our previous paper[19] on FCO_2 we focused on its gas-phase detection by spectroscopic methods, and we computed $\Delta_f H^\circ_{298}(FCO_2) = -87.4$ kcal mol^{-1} at the coupled cluster level.[20]

In summary, theoretical estimates of the enthalpy of formation for FCO_2 at $T = 298$ K span a range of almost 5 kcal mol^{-1} (from −86.0 to −90.9 kcal mol^{-1}), while the experimental[7] value carries a rather large uncertainty (±2.8 kcal mol^{-1}). In view of this situation, we have decided to perform large-scale quantum-chemical calculations aiming at an accurate and reliable result for the standard enthalpy of formation of FCO_2. For this purpose, total energies were computed according to a protocol that closely resembles that of Weizmann-2 (W2) theory.[21,22] We derive the enthalpy of formation both from the atomization energy and from various reaction energies in which the enthalpy of formation of all species apart from the target species is known accurately and precisely from experiment.[23] Our best theoretical estimate of $\Delta_f H^\circ_{298}(FCO_2)$ is compared with its experimental[7] counterpart, which leads to a critical reconsideration and correction of the latter.

In analogy to FCO_2, the enthalpies of formation of the formyl (HCO) and fluoroformyl (FCO) radicals were studied, mainly in order to validate the accuracy that may be achieved by our computational procedure.

Furthermore, the first (A $^2A_2$) and second (B $^2A_1$) electronically excited states of FCO_2 and the ground states of FCO_2^- and FCO_2^+ were treated at the same level to determine the adiabatic excitation energies, the electron affinity, and the ionization energy of FCO_2, which are compared with respective data available from the literature.[7,8,24−26]

2. Theoretical Methods

The adopted approach consists of several steps that are outlined in the following.

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2.1. Molecular Geometries. The structure of FCO_2 in its ground electronic state (X $^2B_2$) was optimized within the constraint of C_{2v} point group symmetry[7,19,27] at the level of partially spin-adapted open-shell coupled cluster theory with single and double excitations[28,29] augmented by a perturbational estimate of the effects of connected triple excitations.[30] This variant of open-shell coupled cluster theory denoted as RCCSD(T) is based on a high-spin restricted open-shell Hartree−Fock (ROHF) determinant.[31]

Two basis sets are involved: the first one is the augmented correlation-consistent polarized valence quadruple-ζ basis (aug-cc-pVQZ),[32] which was employed to optimize the molecular geometry within the frozen core approximation (i.e., the carbon, fluorine, and oxygen 1s-like core molecular orbitals were constrained to be doubly occupied). The second basis is the correlation-consistent polarized core−valence quadruple-ζ basis (cc-pCVQZ),[33] which was used to optimize the geometry with and without correlating the core electrons. The differential effects on the structural parameters resulting from the latter two optimizations were used to correct the RCCSD(T)/aug-cc-pVQZ geometry for inner-shell correlation effects in order to arrive at a "best estimated" theoretical equilibrium structure for FCO_2 (X $^2B_2$).[19]

The geometries of all other species studied presently were optimized in complete analogy to FCO_2 (X $^2B_2$). This includes the first (A $^2A_2$, C_{2v})[7] and second (B $^2A_1$, C_{2v})[25,27] excited states of FCO_2 and the following molecules, radicals, and ions: FCO_2^- (X $^1A_1$, C_{2v}), FCO_2^+ (X $^1A_1$, C_{2v}), FCO_2^+ (a $^3B_1$, C_{2v}), HCO (X $^2A'$, C_s), FCO (X $^2A'$, C_s), CH_4 (X $^1A_1$, T_d), CO_2 (X $^1\Sigma_g^+$, $D_{\infty h}$), H_2O (X $^1A_1$, C_{2v}), CO (X $^1\Sigma^+$, $C_{\infty v}$), HF (X $^1\Sigma^+$, $C_{\infty v}$), OH (X $^2\Pi$, $C_{\infty v}$), and H_2 (X $^1\Sigma_g^+$, $D_{\infty h}$). Of course, in the case of systems without open shells, the corresponding closed-shell coupled cluster approach was used [CCSD(T)],[34−37] which is based on a restricted closed-shell Hartree−Fock (RHF) wave function.[31] All geometry optimizations were carried out employing numerical gradients as implemented in the MOLPRO program package.[38] The largest internal gradient components at the stationary points were typically less than 2×10^{-5} au.

Unless noted otherwise, all contributions to the total energy of a given molecular species were calculated at these theoretical equilibrium geometries ("best estimates").

2.2. Self-Consistent-Field Energies. Depending on the variant of coupled cluster theory applied (see below), the Hartree−Fock self-consistent field (SCF) contribution to the total energy was calculated at the level of either restricted open-shell Hartree−Fock (ROHF) theory, unrestricted Hartree−Fock (UHF) theory, or restricted closed-shell Hartree−Fock (RHF) theory.[31] SCF energies were computed by employing two basis sets of the augmented correlation-consistent family (aug-cc-pVXZ),[32] viz., $X = Q$ (quadruple-ζ) and $X = 5$ (quintuple-ζ). As recommended previously for W2 theory,[22] these SCF energies were extrapolated to the complete basis-set (CBS) limit by use of the formula

$$E_{\mathrm{SCF}}(X) = E_{\mathrm{HF}}(\mathrm{CBS}) + AX^{-5} \qquad (1)$$

where $E_{\mathrm{SCF}}(X)$ is the SCF energy obtained with the aug-cc-pVXZ bases [$X = 4$ (Q) and 5], $E_{\mathrm{HF}}(\mathrm{CBS})$ denotes the estimated Hartree−Fock limit, and A is a fitting constant.

2.3. Valence Correlation Energies. The valence correlation contribution from single and double excitations to the total energy of a given open-shell species was calculated by use of three variants of open-shell coupled cluster theory, RCCSD,[28,29] UCCSD,[28,29,39] and UHF-CCSD.[34] The first one has already been specified in section 2.1. The second one is also based on ROHF orbitals but the spin constraint is relaxed in the coupled-cluster part of the wave function. The third approach, which uses a UHF reference determinant, is a completely unrestricted method. We emphasize that UCCSD must not be confused with UHF-CCSD: these two approaches employ different reference determinants (ROHF and UHF, see above). For closed-shell species, the appropriate standard CCSD approach[34,36] was applied, which is based on RHF orbitals. Following the practice of W2 theory,[22] the (R, U, UHF-)CCSD energies of a given atom or molecule were calculated by employing the aug-cc-pVXZ basis sets with $X = Q$ and $X = 5$. The associated CBS limits were then estimated[22] by use of[40]

$$\Delta E_{\mathrm{CCSD}}(X) = \Delta E_{\mathrm{CCSD}}(\mathrm{CBS}) + BX^{-3} \qquad (2)$$

where $\Delta E_{\mathrm{CCSD}}(X)$ is the (R, U, UHF-)CCSD correlation energy obtained with the aug-cc-pVXZ bases, $\Delta E_{\mathrm{CCSD}}(\mathrm{CBS})$ is the respective CBS limit, and B is a fitting constant.

The correction for the effects of connected triple excitations to the valence correlation energy was computed perturbatively at the (R, U, UHF-)CCSD(T) level of theory[30,35] by employing the aug-cc-pVXZ basis sets[32] with $X = T$ (triple-ζ) and $X = Q$. As in W2 theory,[22] these smaller basis sets are considered to be sufficient for that purpose because the energy contribution from connected triple excitations is known to converge faster with basis-set size than that from singles and doubles.[41] The CBS limit $\Delta E_{(\mathrm{T})}(\mathrm{CBS})$ of the triples energy contributions $\Delta E_{(\mathrm{T})}(X)$ [$X = 3$ (T) and 4 (Q)] was estimated by the same two-parameter extrapolation scheme[40] as for the singles and doubles part of the valence correlation energy:[22]

$$\Delta E_{(\mathrm{T})}(X) = \Delta E_{(\mathrm{T})}(\mathrm{CBS}) + CX^{-3} \qquad (3)$$

where C is a fitting parameter.

The RCCSD/RCCSD(T),[28−30,37] UCCSD/UCCSD(T),[28−30,37,39] and CCSD/CCSD(T)[34−37] single-point energies were calculated with MOLPRO,[38] whereas the corresponding UHF-CCSD/UHF-CCSD(T) [34,35] computations were performed with the ACESII program.[42]

2.4. Core−Valence Correlation. Similar to W2 theory,[22] the core−valence contribution ΔE_{CV} to the correlation energy was evaluated as the difference between (R, U, UHF-)CCSD(T)/cc-pCVQZ correlation energies without and with constraint of the core orbitals to be doubly occupied.

2.5. Scalar Relativistic Corrections. Scalar relativistic contributions[43,44] ΔE_{SR} to the total energy of a given species were included, in close analogy to the HEAT model chemistry.[45] To be more specific, ΔE_{SR} was evaluated by contracting the one-particle density matrix obtained at the all-electron (U, UHF-)CCSD(T)/aug-cc-pCVTZ level with the one-electron Darwin and mass-velocity operators (aug-cc-pCVTZ is the augmented correlation-consistent polarized core−valence triple-ζ basis[32,33]). ΔE_{SR} was calculated from UCCSD(T)[30,39] when ROHF orbitals were used and from UHF-CCSD(T)[34,35] when UHF orbitals were used, for the sake of formal consistency; the difference between the ΔE_{SR} values is negligibly small for the open-shell species presently under study. The scalar relativistic corrections were calculated with ACESII.[42]

2.6. Spin−Orbit Corrections. The total energies of C(^{3}P), F(^{2}P), O(^{3}P), and OH (X $^2\Pi$) were corrected for effects due to spin−orbit coupling. The respective corrections ΔE_{SO} were taken from experiment as given in ref 46 (all values in millihartrees): C −0.14, F −0.61, O −0.36, OH −0.32. For all other species involved in this study, the first-order spin−orbit coupling contributions vanish. Second-order spin−orbit effects, which are expected to be insignificant for the thermochemistry of FCO_2, were not included.

2.7. Zero-Point Vibrational Energies. Following the practice in W2 theory,[22] zero-point vibrational energies (ZPVEs) were calculated at the correlated level of Kohn−Sham density functional theory[47] by use of the Becke three-parameter hybrid exchange functional[15] and the Lee−Yang−Parr correlation functional[16] (B3LYP). These calculations (namely, the corresponding geometry optimizations and the subsequent harmonic force field evaluations) were performed with the GAUSSIAN 03 and GAUSSIAN 98 programs[48,49] employing the correlation-consistent polarized valence triple-ζ basis (cc-pVTZ).[50] The harmonic ZPVEs ΔE_{ZPVE} were scaled by 0.985, primarily to correct them for anharmonicity.[22]

For the sake of comparison, the harmonic vibrational wavenumbers in FCO_2 (X $^2B_2$, A $^2A_2$, and B $^2A_1$) were also calculated at the UHF-CCSD(T) level[34,35] by use of analytic second derivatives[51] of the energy and at the level of EOMIP-CCSD (equation-of-motion CCSD method for ionized states[52]) by use of analytic gradients. These calculations also employed the cc-pVTZ basis set and were carried out with the ACESII program.[42]

2.8. Total Energies and Standard Enthalpies of Formation. In the present work, the total energy E_0 of a given chemical species is a sum of seven terms that have been detailed above:

$$E_0 = E_{\mathrm{HF}}(\mathrm{CBS}) + \Delta E_{\mathrm{CCSD}}(\mathrm{CBS}) + \Delta E_{\mathrm{(T)}}(\mathrm{CBS}) + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{SO}} + \Delta E_{\mathrm{ZPVE}} \quad (4)$$

Similar to a recent theoretical evaluation of the enthalpy of formation $\Delta_f H_0^\circ(\mathrm{HO_2})$ of the hydroperoxyl radical,[53] $\Delta_f H_0^\circ(\mathrm{FCO_2})$ was determined by employing a number of chemical reactions in which the $\Delta_f H_0^\circ$ values for all reactants and products apart from FCO_2 are known accurately and precisely from experiment.[23,45] The reaction energies ΔE_0 for the chosen pathways to FCO_2 were calculated from the relevant total energies E_0. For a given reaction, $\Delta_f H_0^\circ(\mathrm{FCO_2})$ was deduced from ΔE_0 by utilizing the experimental[23,45] $\Delta_f H_0^\circ$ values for the other species involved in the formation of FCO_2. The enthalpy of formation of FCO_2 at $T = 298.15$ K, $\Delta_f H_{298}^\circ(\mathrm{FCO_2})$, was derived from $\Delta_f H_0^\circ(\mathrm{FCO_2})$ by use of the integrated heat capacities $H^\circ(298.15\ \mathrm{K}) - H^\circ(0\ \mathrm{K})$ of FCO_2 in the gas phase and those of the elements (carbon, fluorine, and oxygen) in their reference states. While the integrated heat capacity of FCO_2 was calculated statistically[31] from the unscaled B3LYP/cc-pVTZ harmonic vibrational wavenumbers,[22] the corresponding enthalpy increments for the elemental reference states were taken from CODATA.[54]

Although the focus of this paper is on the enthalpy of formation of FCO_2, several other quantities were also calculated with appropriate total energies E_0 as defined in eq 4: these are the adiabatic excitation energies T_0(A $^2A_2$) and T_0(B $^2A_1$) in FCO_2, the electron affinity $EA_0(\mathrm{FCO_2})$, the ionization energy $IE_0(\mathrm{FCO_2})$, the C−F bond dissociation energy $D_0(\mathrm{F{-}CO_2})$, and the fluoride ion affinity of CO_2, $D_0(\mathrm{F^-{-}CO_2})$.

By analogous procedures, the enthalpies of formation of the HCO and FCO radicals were also computed, mainly to validate the accuracy that may be achieved by the present computational protocol.

3. Results and Discussion

3.1. Molecular Geometries. Table 1 shows our best estimated theoretical equilibrium structures of FCO_2 in its ground electronic state (X $^2B_2$) and in the first two excited doublet states (A $^2A_2$ and B $^2A_1$). The structures of the anion FCO_2^- (X $^1A_1$) and the cation FCO_2^+ (X $^1A_1$ and a $^3B_1$) are also reported. The predicted[19] equilibrium geometry of FCO_2 (X $^2B_2$) should be very close to the true (experimental) equilibrium structure since it leads to rotational constants that agree with experiment[19] to within 0.17% (after accounting for the relatively small effects of rovibrational interaction). Such an accuracy of the predicted[19] rotational constants in FCO_2 (X $^2B_2$) corresponds to an accuracy of the geometrical parameters of about 0.1 pm for bond lengths and 0.1° for bond angles. Turning to the excited states of FCO_2 (A $^2A_2$ and B $^2A_1$), we cannot exclude somewhat larger errors of the best estimated structures, but we expect them to be sufficiently accurate to allow for a realistic calculation of the associated excitation energies. With regard to the best estimated equilibrium structures in FCO_2^- (X $^1A_1$) and FCO_2^+ (X $^1A_1$), we assume similar errors as generally found for closed-shell molecules when treated at the CCSD(T) level of theory in conjunction with large basis sets,[55] that is, 0.2−0.3 pm for bond distances and up to 0.3° for bond angles.

TABLE 1: Computed Equilibrium Geometries of FCO_2, FCO_2^-, and FCO_2^+

species	parameter[a]	best estimate[b]	B3LYP/cc-pVTZ
FCO_2 (X $^2B_2$)	r_e(CF)	131.02[c]	131.94
	r_e(CO)	123.44[c]	123.41
	θ_e(OCO)	118.80[c]	119.87
FCO_2 (A $^2A_2$)	r_e(CF)	132.69	133.48
	r_e(CO)	124.91	125.00
	θ_e(OCO)	125.32	125.61
FCO_2 (B $^2A_1$)	r_e(CF)	136.03	137.54
	r_e(CO)	124.61	124.08
	θ_e(OCO)	137.34	138.19
FCO_2^- (X $^1A_1$)	r_e(CF)	146.16	149.25
	r_e(CO)	122.28	122.11
	θ_e(OCO)	136.50	137.06
FCO_2^+ (X $^1A_1$)	r_e(CF)	122.50	122.56
	r_e(CO)	126.05	126.02
	θ_e(OCO)	88.44	83.01
FCO_2^+ (a $^3B_1$)	r_e(CF)	124.27	124.83
	r_e(CO)	127.02	127.11
	θ_e(OCO)	104.97	105.29

[a] Bond lengths r_e are given in picometers, and bond angles θ_e are given in degrees. [b] See text. [c] Reference 19.

Electron detachment from FCO_2^- shortens the C−F bond considerably, and the extent of this shortening depends clearly on the electronic state of FCO_2 that is formed: X $^2B_2$, 15.14 pm; A $^2A_2$, 13.47 pm; or B $^2A_1$, 10.13 pm. The corresponding lengthening of the C−O bonds is much smaller (1.16−2.63 pm). The OCO bond angle is predicted to decrease by about 17.7° and 11.2° when FCO_2 is formed in its X $^2B_2$ and A $^2A_2$ states, respectively, whereas formation of the B $^2A_1$ state changes the OCO bond angle by less than 1° (see Table 1). Upon ionization of FCO_2 (X $^2B_2$) to the most stable cationic species FCO_2^+ (X $^1A_1$), it is again the C−F bond that becomes much shorter (by 8.52 pm), while the C−O bond distances increase somewhat (2.61 pm). The OCO bond angle is predicted to decrease dramatically, by as much as 30.4°. The pronounced decrease of this angle in the sequence FCO_2^- (X $^1A_1$) $\rightarrow$ FCO_2 (X $^2B_2$) $\rightarrow$ FCO_2^+ (X $^1A_1$) may qualitatively be explained by the character of the $5b_2$ molecular orbital (MO), which loses one electron in each step: this MO is strongly antibonding in the region between the two oxygen atoms (for a figure of the highest-lying MOs occupied in FCO_2^-, see for example refs 7 and 12). In FCO_2^+ (X $^1A_1$) this orbital is no longer occupied. Therefore, its antibonding effect is no longer present, resulting in the smallest OCO bond angle encountered. When FCO_2 (X $^2B_2$) is ionized such that the cation is formed in its triplet state (a $^3B_1$), the $5b_2$ MO is still occupied by one electron, and

TABLE 2: Computed and Experimental Equilibrium Geometries of Chemical Species Other Than FCO_2 Treated in This Study

species	parameter[a]	best estimate[b]	CCSD(T)/aug-cc-pCVQZ	B3LYP/cc-pVTZ	experiment	ref
HCO (X $^2A'$)	r_e(CH)	111.76	111.77	112.43	111.91(50)	57
	r_e(CO)	117.64	117.60	117.30	117.54(15)	57
	θ_e(HCO)	124.63	124.63	124.29	124.43(25)	57
FCO (X $^2A'$)	r_e(CF)	132.52	132.50	133.18	133.4(60)	58
	r_e(CO)	116.75	116.72	116.72	116.9(60)	58
	θ_e(FCO)	127.80	127.79	127.60	127.3(6)	58
CH_4 (X $^1A_1$)	r_e(CH)	108.68	108.67	108.83	108.57(10)	59
CO_2 (X $^1\Sigma_g^+$)	r_e(CO)	116.10	116.09	116.04	115.997 92(22)	60
H_2O (X $^1A_1$)	r_e(OH)	95.82	95.81	96.13	95.784(5)	61[c]
	θ_e(HOH)	104.49	104.48	104.53	104.508(5)	61[c]
CO (X $^1\Sigma^+$)	r_e(CO)	112.96	112.93	112.62	112.832	62
HF (X $^1\Sigma^+$)	r_e(HF)	91.71	91.73	92.23	91.681	62
OH (X $^2\Pi$)	r_e(OH)	96.98	96.98	97.46	96.966	62
H_2 (X $^1\Sigma_g^+$)	r_e(HH)	74.20[d]	74.20[d]	74.29	74.144	62

[a] Bond lengths r_e are given in picometers, and bond angles θ_e are given in degrees. [b] See text. [c] See also ref 63. [d] Identical with the bond length optimized at the CCSD/aug-cc-pVQZ level.

the $1a_2$ MO becomes singly occupied, too. The latter is also antibonding in the region between the two oxygen atoms,[7,12] but less so than the $5b_2$ MO. Consequently, the OCO bond angle in FCO_2^+ (a $^3B_1$) is indeed significantly smaller than in FCO_2 (X $^2B_2$), but still clearly larger than in FCO_2^+ (X $^1A_1$) (see Table 1). Of course, similar MO arguments can be used to rationalize the size of the OCO bond angle in FCO_2 (X $^2B_2$) compared with the first excited state (A $^2A_2$) and the anion.[7,12]

At the best estimated geometries, the expectation values of the spin-squared operator S^2 calculated with the UHF wave function (aug-cc-pVTZ basis) are 0.7983 (X $^2B_2$), 0.9939 (A $^2A_2$), and 0.7854 (B $^2A_1$) in FCO_2. Obviously, spin contamination is small in the electronic ground and second excited state, whereas in the A $^2A_2$ state there is a modest deviation between $\langle S^2\rangle$ and the S^2 eigenvalue of 0.75 for a pure doublet state. Small to modest spin contamination found in the UHF reference wave function is not expected to cause major problems in a corresponding coupled-cluster calculation.[56] Nevertheless, we have checked explicitly whether optimizations of the FCO_2 geometry in the three states of interest (X $^2B_2$, A $^2A_2$, and B $^2A_1$) show some dependence on the specific open-shell coupled-cluster treatment [RCCSD(T), UCCSD(T), or UHF-CCSD(T)]. Using the economical cc-pVTZ basis and applying the frozen-core approximation, we find only very small differences in the calculated geometrical parameters: for a given electronic state and a given pair of coupled-cluster wave functions (see above), the C−F and C−O bond lengths differ at most by 0.13 and 0.07 pm, respectively, and the deviations in the OCO bond angles do not exceed 0.10°. Hence, our best estimated state-specific structures of FCO_2 (see Table 1) should not depend significantly on the chosen open-shell coupled-cluster approach.

For the sake of completeness, Table 1 lists also the corresponding B3LYP/cc-pVTZ structures where the harmonic force fields were evaluated in order to calculate zero-point vibrational energies. The B3LYP/cc-pVTZ structures are reasonably close to the respective best estimated geometries, which may also be compared with theoretical structures available in the literature, especially those from QCISD/6-31G* calculations,[7,25] UHF-CCSD(T)/DZP[12] and QRHF-CCSD(T)/DZP,[12] as well as CCSD(T)/6-311G(2df).[26]

Table 2 contains theoretical and experimental equilibrium geometries of molecules other than neutral or charged FCO_2 that are also involved in this study. These molecules mostly serve as auxiliary species in the reaction schemes, which are utilized to derive a theoretical value for the enthalpy of formation of FCO_2 (X $^2B_2$). Theoretical r_e structures shown in Table 2 comprise best estimated geometries as defined in section 2.1 and corresponding B3LYP/cc-pVTZ structures. In the case of HCO, FCO, and some other small molecules (CH_4, CO_2, H_2O, CO, HF, OH, and H_2), it is still practical to optimize their structures at the (R) CCSD(T) level of theory employing the complete aug-cc-pCVQZ basis[32,33] where diffuse and core-correlating functions are present simultaneously (resulting in 109 Gaussian-type orbitals per first-row atom). Our procedure to obtain best estimated geometries aims at structures that reproduce those calculated directly in one step at the (R) CCSD(T)/aug-cc-pCVQZ level correlating all electrons. Geometries optimized at this level of theory are also collected in Table 2 and are indeed virtually identical to the corresponding best estimated structures: bond lengths and bond angles differ at most by 0.04 pm and 0.01°, respectively. By comparison with experiment,[57−63] the currently best estimated structures appear to be as accurate as can be expected:[55] errors in bond distances do not exceed 0.15 pm, and the bond angles in HCO and H_2O are in error by 0.20° and 0.02°, respectively. These comparisons with experiment do not include FCO, whose geometrical parameters could only be determined with very large uncertainties (±6 pm) in the bond lengths.[58] Since our best estimated equilibrium structure of FCO is almost indistinguishable from the RCCSD(T)/aug-cc-pCVQZ geometry (see Table 2), the best present theoretical equilibrium structure is expected to be more reliable than its experimental[58] counterpart. We recommend the following structural parameters in FCO (X $^2A'$): r_e(CF) = 132.5(2) pm, r_e(CO) = 116.7(2) pm, and θ_e(FCO) = 127.8(2)°.

3.2. Enthalpies of Formation of HCO and FCO. To check the accuracy that may be achieved by the present approach for the enthalpy of formation of an open-shell species, we calculated $\Delta_f H_0^\circ$(HCO) and $\Delta_f H_0^\circ$(FCO) in addition to the target quantity $\Delta_f H_0^\circ$(FCO_2). HCO and especially FCO were selected as test cases because they bear some structural relationship to FCO_2, and there is an accurate experimental $\Delta_f H_0^\circ$(HCO) value available in the literature:[23,45] 10.06 ± 0.09 kcal mol^{-1}. This value from so-called Active Thermochemical Tables (ATcT)[23] is close to the corresponding JANAF[64] value of 10.3 ± 1.9 kcal mol^{-1} but considerably more precise. Unfortunately, the experimental[64] value for $\Delta_f H_0^\circ$(FCO) carries a large uncertainty (−41 ± 15 kcal mol^{-1}), making it less suited for a stringent comparison with our theoretical data. On the other hand, there seems to exist a reliable theoretical[65] $\Delta_f H_0^\circ$(FCO) value that has been derived from extrapolated CCSD(T) energies including core−valence and spin−orbit corrections: −44.1 ± 0.5 kcal mol^{-1}.

Table 3 shows the results for HCO (X $^2A'$). Five reactions have been chosen: use of the first reaction is completely

TABLE 3: Enthalpy of Formation at $T = 0$ K Calculated for the Ground State of the Formyl Radical by Various Reaction Schemes

	$\Delta_f H^\circ_0$(HCO), kcal mol^{-1}			
reaction	RCCSD(T)[a]	UCCSD(T)[a]	UHF-CCSD(T)[a]	HEAT[b]
(1) H + C + O → HCO	10.22	10.15	10.20	10.17
(2) H + CO → HCO	10.13	9.85	9.91	10.02
(3) C + OH → HCO	10.32	10.23	10.27	10.25
(4) CO_2 + 3H → HCO + H_2O	10.01	9.72	9.78	9.95
(5) 2CO + H_2O → 2HCO + O	10.24	9.89	9.96	10.07
mean value	10.19	9.97	10.02	10.09
scatter[c]	0.31	0.51	0.49	0.30

[a] Variant of open-shell coupled cluster theory chosen to calculate the total energy of open-shell species involved. For further details see text. [b] HEAT total energies from ref 45. [c] Difference between the corresponding largest and smallest $\Delta_f H^\circ_0$(HCO) values.

TABLE 4: Enthalpy of Formation at $T = 0$ K Calculated for the Ground State of the Fluoroformyl Radical by Various Reaction Schemes

	$\Delta_f H^\circ_0$(FCO), kcal mol^{-1}		
reaction	RCCSD(T)[a]	UCCSD(T)[a]	UHF-CCSD(T)[a]
(1) F + C + O → FCO	−41.89	−41.98	−41.93
(2) F + CO → FCO	−41.97	−42.29	−42.22
(3) CO + HF → FCO + H	−41.79	−42.19	−42.12
(4) CO_2 + F → FCO + O	−41.88	−42.32	−42.25
(5) CO_2 + CO + 2HF → 2FCO + H_2O	−41.86	−42.26	−42.18
mean value (reactions 1−5)	−41.88	−42.21	−42.14
scatter[b] (reactions 1−5)	0.18	0.34	0.32
(6) HCO + F → FCO + H	−42.05	−42.08	−42.07

[a] Variant of open-shell coupled cluster theory chosen to calculate the total energy of open-shell species involved. For further details see text. [b] Difference between the corresponding largest and smallest $\Delta_f H^\circ_0$(FCO) values.

equivalent to the atomization energy approach,[22,45,46] whereas the second, fourth, and fifth reactions feature reactants and products with C−O multiple bonds (however, they are not isodesmic and should thus show only limited error cancellation). The third reaction has been selected due to its formal simplicity. The three columns headed by RCCSD(T), UCCSD(T), and UHF-CCSD(T) list the corresponding enthalpies of formation of HCO at $T = 0$ K as extracted from the calculated reaction enthalpies (see section 2 for a description of these different variants of open-shell coupled cluster theory). In addition, $\Delta_f H^\circ_0$(HCO) values were derived on the basis of total energies from the HEAT model chemistry.[45] The HEAT protocol includes a treatment of electron correlation at the coupled cluster CCSDTQ level (full treatment of all excitations up to quadruples) and is designed to achieve high accuracy for enthalpies of formation of atoms and small molecules.[45]

In the remaining text of this discussion we use the shorthand notations RCC, UCC, and UHF-CC instead of the more complete designations RCCSD(T), UCCSD(T), and UHF-CCSD(T), respectively.

The individual RCC values for $\Delta_f H^\circ_0$(HCO) are always somewhat larger than the UCC and UHF-CC counterparts, the differences being quite small, however: 0.07−0.35 and 0.02−0.28 kcal mol^{-1}, respectively. The individual UCC and UHF-CC data are even closer, the latter being slightly larger than their UCC counterparts (0.04−0.07 kcal mol^{-1}). The HEAT values are best compared with those from UHF-CC since the HEAT total energies are based on UHF orbitals in the case of open-shell species:[45] the corresponding differences amount to 0.02−0.17 kcal mol^{-1} in absolute value.

The scatter of the $\Delta_f H^\circ_0$(HCO) values resulting from the different reactions ranges from 0.31 to 0.51 kcal mol^{-1} for RCC, UCC, and UHF-CC, similar to the scatter of the HEAT results (0.30 kcal mol^{-1}). The present individual RCC, UCC, and UHF-CC results for $\Delta_f H^\circ_0$(HCO) vary from 9.72 to 10.32 kcal mol^{-1}, and their overall mean value is equal to 10.06 kcal mol^{-1} which differs from the average of the HEAT values by only 0.03 kcal mol^{-1}. Both average values are in excellent agreement with the most precise value from experiment,[23,45] which is $\Delta_f H^\circ_0$(HCO) = 10.06 ± 0.09 kcal mol^{-1}.

For the sake of the subsequent discussion concerning FCO and FCO_2, we point out that if the HEAT values are disregarded, the present best theoretical estimate $\Delta_f H^\circ_0$(HCO) = 10.1 kcal mol^{-1} is defined by the overall mean value of the individual RCC, UCC, and UHF-CC results for this quantity. Judging from the performance of W2 theory[22] (which always employs restricted open-shell wave functions for open-shell species) this estimate is expected to carry an uncertainty of ±0.5 kcal mol^{-1}.

Table 4 contains the results for the second test case: FCO (X $^2A'$). As for HCO, five reactions were chosen to derive values for $\Delta_f H^\circ_0$(FCO) from theoretical reaction enthalpies. Use of the first reaction is again equivalent to the atomization energy approach. [22,45,46] The sixth reaction involving HCO as a reactant was not used to predict a $\Delta_f H^\circ_0$(FCO) value but serves merely as a check whether the present best estimate for this quantity (see below) is consistent with the $\Delta_f H^\circ_0$(HCO) value from experiment.[23,45] The HEAT[45] total energy of FCO has not yet been reported, and therefore Table 4 does not contain any HEAT data.

Except for the sixth reaction, individual RCC values for $\Delta_f H^\circ_0$(FCO) are always somewhat larger (more positive) than the UCC and UHF-CC counterparts, the differences being about as small as found for HCO (see above): 0.09−0.44 and 0.04−0.37 kcal mol^{-1}, respectively. The individual UHF-CC data for $\Delta_f H^\circ_0$(FCO) are nearly identical to their UCC analogues, with differences of 0.05−0.08 kcal mol^{-1} (0.01 kcal mol^{-1} for reaction 6). The $\Delta_f H^\circ_0$(FCO) values resulting from the five selected reactions (1−5) scatter by 0.18−0.34 kcal mol^{-1} depending on the type of open-shell coupled cluster theory (RCC, UCC, or UHF-CC). Considering all 15 individual data

TABLE 5: Enthalpy of Formation at $T = 0$ K Calculated for the Ground State of the Fluoroformyloxyl Radical by Various Reaction Schemes

	$\Delta_f H_0^\circ(FCO_2)$, kcal mol^{-1}		
reaction	RCCSD(T)[a]	UCCSD(T)[a]	UHF-CCSD(T)[a]
(1) $C + F + 2O \rightarrow FCO_2$	−85.90	−85.89	−85.84
(2) $C + F + 2OH \rightarrow FCO_2 + 2H$	−85.69	−85.74	−85.70
(3) $C + HF + 2O \rightarrow FCO_2 + H$	−85.72	−85.80	−85.73
(4) $CO + F + O \rightarrow FCO_2$	−85.98	−86.20	−86.13
(5) $CO + F + 2OH \rightarrow FCO_2 + H_2O$	−85.99	−86.13	−86.09
(6) $2CO + F + 4H \rightarrow FCO_2 + CH_4$	−86.20	−86.55	−86.47
(7) $CO_2 + F \rightarrow FCO_2$	−85.88	−86.23	−86.16
(8) $CO_2 + CO + 2HF + H_2O \rightarrow 2FCO_2 + 2H_2$	−85.68	−86.11	−86.03
mean value (reactions 1−8)	−85.88	−86.08	−86.02
scatter[b] (reactions 1−8)	0.52	0.81	0.77
(9) $FCO + O \rightarrow FCO_2$	−86.09	−85.99	−85.99
(10) $HCO + F + O \rightarrow FCO_2 + H$	−86.05	−85.98	−85.98

[a] Variant of open-shell coupled cluster theory chosen to calculate the total energy of open-shell species involved. For further details see text. [b] Difference between the corresponding largest and smallest $\Delta_f H_0^\circ(FCO_2)$ value.

for $\Delta_f H_0^\circ$(FCO) resulting from reactions 1−5, these values range from −42.32 to −41.79 kcal mol^{-1}. The associated overall mean value is $\Delta_f H_0^\circ$(FCO) = −42.1 kcal mol^{-1}, about 1 kcal mol^{-1} more negative than the JANAF[64] value (−41 ± 15 kcal mol^{-1}), which, however, carries a large uncertainty. On the basis of photoionization energy measurements,[66] there is an experimental $\Delta_f H_0^\circ$(FCO) value of −36.5 ± 2.9 kcal mol^{-1}. It is more precise than the JANAF[64] value but it appears to be significantly too small in absolute value when compared to the present best estimate (−42.1 kcal mol^{-1}), which should be accurate to 0.5 kcal mol^{-1} (i.e., the mean absolute error found for W2 theory[22]). It is satisfying that the present best estimate for $\Delta_f H_0^\circ$(FCO) is in almost perfect accordance with the $\Delta_f H_0^\circ$(FCO) values obtained from the sixth reaction. In this reaction, the experimental value for $\Delta_f H_0^\circ$(HCO) from Active Thermochemical Tables (ATcT)[23] as communicated in ref 45 was used to extract $\Delta_f H_0^\circ$(FCO) values from the theoretical (RCC, UCC, and UHF-CC) reaction enthalpies. Hence, the present value $\Delta_f H_0^\circ$(FCO) = −42.1 ± 0.5 kcal mol^{-1} is consistent with the experimental[23,45] value $\Delta_f H_0^\circ$(HCO) = +10.06 ± 0.09 kcal mol^{-1}.

We now compare our result with another theoretical value available in the literature:[65] $\Delta_f H_0^\circ$(FCO) = −44.1 ± 0.5 kcal mol^{-1}. This value based on the atomization energy approach was obtained from extrapolated CCSD(T) energies that were corrected for the effects of core−valence correlation, zero-point vibrational motions, and spin−orbit coupling. In comparison to the best value from this work, there is an unexpectedly large discrepancy of 2.0 kcal mol^{-1}. Looking for a possible explanation of this difference, we find that Table 12 of ref 65 gives the computed [CBS(aDTQ/mix)/CVQZ] vibrationless total atomization energy ΣD_e(FCO) as 295.9 kcal mol^{-1}. Footnotes *c* and *d* in Table 12 of ref 65 suggest that this ΣD_e(FCO) value does not yet include the spin−orbit correction. By subtraction of the contributions from spin−orbit coupling (0.68 kcal mol^{-1})[65] and zero-point vibrations (5.02 kcal mol^{-1})[65] from this value of ΣD_e(FCO),[65] we obtain ΣD_0(FCO) = 290.2 kcal mol^{-1}. On the contrary, ΣD_0(FCO) = 291.5 kcal mol^{-1} is reported in ref 65. If the value ΣD_0(FCO) = 290.2 kcal mol^{-1} is adopted, $\Delta_f H_0^\circ$(FCO) = −42.8 kcal mol^{-1} is derived when atomic (C, F, and O) enthalpies of formation at $T = 0$ K from the CODATA[54] or JANAF[64] compilation are used, and $\Delta_f H_0^\circ$(FCO) = −42.6 kcal mol^{-1} is obtained when the atomic enthalpies of formation from ATcT[23,45] are used. Obviously, the latter $\Delta_f H_0^\circ$(FCO) values are in much better agreement with the present one (−42.1 kcal mol^{-1}) than the original value (−44.1 kcal mol^{-1}) from ref 65. $\Delta_f H_{298}^\circ$(FCO) values derived from W1U[6,21] and G3[14] total atomization energies are −42.5 and −42.7 kcal mol^{-1}, respectively.[5,13] When thermal corrections from JANAF[64] are used, the corresponding values at $T = 0$ K are −42.6 and −42.8 kcal mol^{-1}, respectively, in reasonable agreement with our best estimate.

3.3. Enthalpy of Formation of FCO_2. Turning to the principal goal of this study, Table 5 lists our computed results for the enthalpy of formation of the fluoroformyloxyl radical in its ground electronic state at $T = 0$ K. Eight separate formation reactions of FCO_2 (1−8) were selected in order to derive $\Delta_f H_0^\circ(FCO_2)$ values in analogy to the procedure already applied for HCO and FCO (see above). The last two reactions (9 and 10 in Table 5) involving FCO and HCO were not used to predict $\Delta_f H_0^\circ(FCO_2)$ but serve as checks of the internal consistency of $\Delta_f H_0^\circ$(FCO), $\Delta_f H_0^\circ$(HCO), and $\Delta_f H_0^\circ(FCO_2)$ and will be discussed later. Before the numerical results are discussed in detail, a few preliminary remarks seem to be in order.

(i) Reactants and products other than the target or atomic species were chosen on the basis that their enthalpies of formation should be known from experiment[23,45] with high accuracy and precision. Furthermore, these auxiliary species should not have a complicated molecular or electronic structure in order to allow for a reasonable CCSD(T) treatment with regard to both computer time and methodological limitations of CCSD(T). For example, molecular oxygen (O_2) and fluorine (F_2) would have been ideal reactants from the point of view that both species represent reference states of the respective elements whose enthalpy of formation vanishes exactly by definition, that is, the values for $\Delta_f H_0^\circ(O_2)$ and $\Delta_f H_0^\circ(F_2)$ are indeed known with the largest possible accuracy and precision. On the other hand, the net post-CCSD(T) contribution to the bond dissociation energy of O_2 and F_2 is known[45] to be relatively large: 0.57 and 0.51 kcal mol^{-1}, respectively. Therefore, O_2 and F_2 were not used as reactants or products.[67] By contrast, the net post-CCSD(T) contributions to the binding energies are very small in many cases,[45] for example, less than 0.1 kcal mol^{-1} for OH, HF, CO, H_2O, CO_2, and HCO. Methane, which is also used as an auxiliary species in our reaction schemes, was not treated in ref 45, but the net post-CCSD(T) contribution to the total atomization energy in CH_4 is expected to be small, judging from the related CH_3 radical where the corresponding contribution was computed[45] to be about 0.02 kcal mol^{-1}.

(ii) We made sure that the actual reactions chosen to derive $\Delta_f H_0^\circ$ values are linearly independent from each other so that redundancies among these data are avoided (Tables 3−5). Of course, one can easily find other linearly dependent reactions forming the target molecules, using the same auxiliary species. With FCO_2 as an example, the reaction $CO_2 + HF \rightarrow FCO_2 + H$ is a linear combination of the first, third, and seventh reactions in Table 5.

(iii) The data shown in Table 5 were evaluated with the calculated (B3LYP/cc-pVTZ) zero-point vibrational energies (ZPVEs) of the relevant molecular species. The quantum-chemical treatment of FCO_2 is known[12] to be complicated by symmetry-breaking effects[56,68] that are due to second-order Jahn–Teller interactions between the ground state (X $^2B_2$) and nearby excited electronic states (A $^2A_2$ and B $^2A_1$). These interactions can severely complicate the calculation of frequencies for the nontotally symmetric vibrations.[12] Thus one may wonder how well such frequencies are described at the B3LYP/cc-pVTZ level and whether a realistic ZPVE value for FCO_2 (X $^2B_2$) is obtained. The B3LYP/cc-pVTZ results for the harmonic vibrational wavenumbers ω_i in FCO_2 (X $^2B_2$), (in reciprocal centimeters), are as follows: $\omega_1(a_1)$, 1518 (1475); $\omega_2(a_1)$, 988 (960); $\omega_3(a_1)$, 538 (519); $\omega_4(b_2)$, 1177 (1098); $\omega_5(b_2)$, 505 (474); $\omega_6(b_1)$, 757 (735). The numbers in parentheses refer to the fundamental wavenumbers ν_i that were observed in a neon matrix.[27] Of course, the comparison of harmonic and fundamental wavenumbers is not straightforward without explicit consideration of the effects of anharmonicity, and additional problems may arise here because the fundamentals of FCO_2 (X $^2B_2$) were not measured in the gas phase. Nevertheless, the computed harmonic wavenumbers seem realistic because they are reasonably close to the experimental[27] fundamentals: the corresponding deviations are 19–43 cm^{-1}, except for the antisymmetric C–O stretching mode ν_4, where the deviation (79 cm^{-1}) is almost twice as large as that (43 cm^{-1}) for the associated symmetric C–O stretching mode ν_1. This differential effect may indicate some minor problems due to symmetry-breaking.[12] The B3LYP/cc-pVTZ harmonic wavenumbers in FCO_2 (X $^2B_2$) yield a ZPVE of 7.840 kcal mol^{-1}, which is scaled to 7.722 kcal mol^{-1}. It has been pointed out[69] that by averaging the ZPVEs based on calculated harmonic wavenumbers ($^1/_2 hc\Sigma\omega_i$) and experimental fundamental ones ($^1/_2 hc\Sigma\nu_i$), a better approximation to the true anharmonic ZPVE can be obtained than with either set of wavenumbers alone. This procedure is capable of predicting anharmonic ZPVEs with an uncertainty of 0.1–0.2 kcal mol^{-1},[70] provided sufficiently accurate theoretical harmonic and experimental fundamental wavenumbers are available. In the case of FCO_2 (X $^2B_2$), this approach yields 7.680 kcal mol^{-1} when the harmonic wavenumbers from B3LYP/cc-pVTZ (see above) and the fundamentals observed in a neon matrix[27] are used. The very close agreement between this value and the scaled one from B3LYP/cc-pVTZ (7.722 kcal mol^{-1}) suggests that the latter is indeed realistic and sufficiently accurate for the present purpose.

(iv) Our current procedure to calculate the total energy of a given species (see section 2) is most appropriate for molecules without significant nondynamical electron correlation. As a diagnostic tool, the percentage of the vibrationless total atomization energy ΣD_e recovered at the SCF level has been reported[71] to be useful. In FCO_2 (X $^2B_2$), this percentage amounts to 57% (no matter which variant of open-shell coupled-cluster theory is used), whereas in HCO (X $^2A'$) and FCO (X $^2A'$) somewhat larger values are found: 66–67% and 61–64%, respectively, depending slightly on the details of the open-shell coupled-cluster approach. For the sake of comparison, in H_2O (a molecule essentially devoid of nondynamical electron correlation at its equilibrium geometry) the SCF component of the total binding energy amounts to 69%, and in OH (X $^2\Pi$) the SCF contribution to ΣD_e is 64–65%. On the contrary, these percentages are considerably smaller in species such as HO_2 (41%), NO (35%), or O_2 (28%).[45] According to this criterion,[71] we conclude that nondynamical electron correlation is not overly important in FCO_2 (X $^2B_2$) at its equilibrium geometry. A similar conclusion follows from the T_1 diagnostic[55,72] redefined for open-shell coupled-cluster theory.[73] T_1 values calculated with the MOLPRO program[38] at the UCCSD/aug-cc-pVTZ level applying the frozen-core approximation are as follows: FCO_2 (X $^2B_2$) 0.0194, FCO_2 (A $^2A_2$) 0.0142, FCO_2 (B $^2A_1$) 0.0207, FCO (X $^2A'$) 0.0240, HCO (X $^2A'$) 0.0257, and OH (X $^2\Pi$) 0.0091. According to the T_1 values, nondynamical electron correlation seems to be more important in HCO and FCO than in FCO_2. While this finding is perhaps somewhat counterintuitive, the T_1 values indicate nondynamical electron correlation not to be overly important in HCO, FCO, and FCO_2, in accordance with the conclusion drawn above.

(v) The electronic structure of molecules consisting of several strongly electronegative atoms such as oxygen and fluorine is known to be potentially more challenging for quantum-chemical methods than that of comparable molecules containing no such atoms. This concern is particularly true for species containing multiple O and F atoms that are directly bonded to each other, for example, FO_2 and FOOF. To achieve quantitative descriptions of such molecules, highly correlated wave functions in conjunction with sufficiently large basis sets are needed. The present theoretical treatment fulfils these requirements and has been shown[19] to yield accurate results for those properties of FCO_2 that are not affected by symmetry-breaking problems (see above).

Turning to the numerical results of $\Delta_f H^\circ_0(FCO_2)$, Table 5 shows the individual RCC values to be somewhat larger (more positive) than the UCC and UHF-CC counterparts (0.05–0.43 and 0.01–0.35 kcal mol^{-1}, respectively), except for the first and last two reactions (9 and 10), where the RCC values are slightly smaller (more negative) than the corresponding UCC and UHF-CC values (0.01–0.10 kcal mol^{-1}). The individual UCC data for $\Delta_f H^\circ_0(FCO_2)$ are always very close to their UHF-CC analogues; the differences do not exceed 0.08 kcal mol^{-1}. The alterations of $\Delta_f H^\circ_0(FCO_2)$ data between RCC, UCC, and UHF-CC are similar to those of $\Delta_f H^\circ_0(HCO)$ and $\Delta_f H^\circ_0(FCO)$ found previously (see above). Depending on the variant of open-shell coupled-cluster theory, the $\Delta_f H^\circ_0(FCO_2)$ values resulting from the different reactions scatter by 0.52–0.81 kcal mol^{-1}. The present best estimate $\Delta_f H^\circ_0(FCO_2) = -86.0 \pm 0.6$ kcal mol^{-1} is obtained from the overall mean value of all 24 individual results from reactions 1–8. The uncertainty attributed to this estimate is chosen such that all individual data ranging from −86.55 to −85.68 kcal mol^{-1} (see Table 5) are covered. It is reassuring that the $\Delta_f H^\circ_0(FCO_2)$ values resulting from reactions 9 and 10 are in almost perfect agreement with the current best estimate for this quantity. In the ninth reaction, the theoretical $\Delta_f H^\circ_0(FCO)$ value recommended above (−42.1 kcal mol^{-1}) was used to extract $\Delta_f H^\circ_0(FCO_2)$, while in the last reaction the experimental value for $\Delta_f H^\circ_0(HCO)$ from the Active Thermochemical Tables (ATcT)[23] quoted in ref 45 was employed. Thus, the values for the zero-point enthalpies of formation of FCO_2 (−86.0 kcal mol^{-1}), FCO (−42.1 kcal mol^{-1}), and HCO (+10.06 kcal mol^{-1})[23,45] appear to be consistent with each other. This further supports the reliability of the present best estimate of $\Delta_f H^\circ_0(FCO) = -42.1 \pm 0.5$ kcal mol^{-1}.

TABLE 6: Computed and Experimental Values for Various Parameters of FCO_2[a]

constant	RCCSD(T)[b]	UCCSD(T)[b]	UHF-CCSD(T)[b]	experiment	ref
$D_0(F-CO_2)$, kcal mol^{-1}	10.4	10.7	10.7	10.5 ± 2.1[c]	7
$D_0(F^--CO_2)$,[d] kcal mol^{-1}	31.3			30.7 ± 2;[e] 31.3[e]	8, 24
$EA_0(FCO_2)$, eV	4.316	4.297	4.301	4.277 ± 0.030	7
$IE_0(FCO_2)$, eV	12.590	12.609	12.605		
$T_0(A\ ^2A_2)$,[f] eV	0.586	0.574	0.587	0.579	7
$T_0(B\ ^2A_1)$,[g] eV	1.686	1.687	1.687	1.630	25

[a] $D_0(F-CO_2)$, C−F bond dissociation energy; $D_0(F^--CO_2)$, fluoride ion affinity of CO_2; EA_0, electron affinity; IE_0, ionization energy; T_0, adiabatic excitation energy. [b] Variant of open-shell coupled cluster theory chosen to calculate the total energy of open-shell species involved. For further details see text. [c] Reevaluated in this work (see text). [d] The calculation of this quantity involved total energies only of closed-shell species (FCO_2^-, CO_2, F^-). Accordingly, only one theoretical value is given. [e] The original values from refs 8 and 24 refer to $T = 298$ K; they were corrected for temperature effects in this work (see text). [f] The corresponding vibrationless T_e values (in electronvolts) are RCCSD(T) 0.604, UCCSD(T) 0.592, and UHF-CCSD(T) 0.606. [g] The corresponding vibrationless T_e values (in electronvolts) are RCCSD(T) 1.619, UCCSD(T) 1.621, and UHF-CCSD(T) 1.621.

The integrated heat capacity $H°(298.15\ K) - H°(0\ K)$ of FCO_2 was calculated to be 2.728 kcal mol^{-1} by use of the expression from rigid rotor−harmonic oscillator approximation[31] in conjunction with the unscaled B3LYP/cc-pVTZ harmonic vibrational frequencies of FCO_2 in its ground electronic state (see above). With the analogous enthalpy increments for the reference states of the elements (carbon, fluorine, and oxygen) taken from the CODATA compilation,[54] a thermal correction $\Delta_f H°_{298}(FCO_2) - \Delta_f H°_0(FCO_2) = -0.652$ kcal mol^{-1} is obtained. Hence, the present best estimate for the standard enthalpy of formation of FCO_2 ($X\ ^2B_2$) at room temperature ($T = 298.15$ K) is $\Delta_f H°_{298}(FCO_2) = -86.7 \pm 0.6$ kcal mol^{-1}.

Experimentally,[7] from electron affinity measurements and the known[8] enthalpy of formation of the anion FCO_2^-, $\Delta_f H°_{298}(FCO_2)$ was determined to be -85.2 ± 2.8 kcal mol^{-1}. Our currently recommended value for $\Delta_f H°_{298}(FCO_2)$ is well inside the experimental[7] error bars.

We have reconsidered the experimental[7] determination of $\Delta_f H°_{298}(FCO_2)$, which is based on eq 13 of ref 7. In our notation, this equation reads

$$\Delta_f H°_{298}(FCO_2) = \Delta_f H°_{298}(FCO_2^-) + EA_0(FCO_2) + {}^5/_2RT + [H°(298.15\ K) - H°(0\ K)]\ (FCO_2) - [H°(298.15\ K) - H°(0\ K)](FCO_2^-)$$

To make use of this equation, one needs the enthalpy of formation of the anion FCO_2^- at $T = 298.15$ K [$\Delta_f H°_{298}(FCO_2^-)$], the electron affinity of FCO_2 at $T = 0$ K [$EA_0(FCO_2)$], and the integrated heat capacities $H°(298.15\ K) - H°(0\ K)$ of FCO_2 and FCO_2^-. Additionally, the integrated heat capacity of the free electron calculated from classical statistical mechanics (${}^5/_2RT$) is taken into account in eq 13 of ref 7; that is, this equation refers explicitly to the so-called thermal electron convention.[23] $EA_0(FCO_2)$ has been measured,[7] and the integrated heat capacities of FCO_2 and FCO_2^- were calculated from their vibrational frequencies (for details see ref 7). The crucial point here is $\Delta_f H°_{298}(FCO_2^-)$, which was taken[7] from ref 8 to be -185 ± 2.6 kcal mol^{-1}. In ref 8, the fluoride ion affinity of carbon dioxide at $T = 298$ K has been determined (see eq 10 of ref 8) to be $D_{298}(F^--CO_2) = 31.7 \pm 2$ kcal mol^{-1}, which has then be used to evaluate the enthalpy of formation of FCO_2^- to be -185.6 ± 2 kcal mol^{-1}.[8] Assuming that this value refers to $T = 298$ K (which is not stated explicitly but seems likely as judged from the context[8]), one may wonder whether $\Delta_f H°_{298}(FCO_2^-) = -185.6 \pm 2$ kcal mol^{-1} corresponds to the thermal or to the stationary electron convention (the latter being also known as the ion convention[23]). The answer to this question depends on the value adopted for the enthalpy of formation of the fluoride ion in the gas phase, which was taken[8] from ref 74 to convert $D_{298}(F^--CO_2)$ to $\Delta_f H°_{298}(FCO_2^-)$. Unfortunately, ref 74 does not explicitly define the chosen convention, but footnote *e* of Table 1 in ref 74 suggests that the ion convention was adopted (since the electron affinity of the F atom at $T = 298$ K is approximated by its value at $T = 0$ K, which is reasonable only in the ion convention). In view of this rather unclear situation, we have decided to rederive the experimental $\Delta_f H°_{298}(FCO_2^-)$ value from

$$\Delta_f H°_{298}(FCO_2^-) = \Delta_f H°_{298}(CO_2) + \Delta_f H°_{298}(F^-) - D_{298}(F^--CO_2) \quad (5)$$

By inserting in eq 5 the ATcT values[23] for $\Delta_f H°_{298}(CO_2)$ and $\Delta_f H°_{298}(F^-)$, which refer explicitly[23] to the stationary electron convention, as well as the measured value[8] of $D_{298}(F^--CO_2)$, we obtain $\Delta_f H°_{298}(FCO_2^-) = -185.3 \pm 2$ kcal mol^{-1} in the stationary electron convention and accordingly -186.8 ± 2 kcal mol^{-1} in the thermal electron convention. The latter value was inserted in eq 13 of ref 7 (see above) while all other terms on the right-hand side of this equation were kept at the values from ref 7. In this manner, we calculate $\Delta_f H°_{298}(FCO_2)$ to be -86.6 ± 2.1 kcal mol^{-1}.[75] This corrected experimental[7] $\Delta_f H°_{298}(FCO_2)$ value is in excellent agreement with our current best theoretical estimate (-86.7 ± 0.6 kcal mol^{-1}).

Our best theoretical estimate for $\Delta_f H°_{298}(FCO_2)$ may also be compared with other theoretical values available in the literature.[10,12,13,17−20] These data were already quoted in section 1 and therefore need not be repeated here. Here we stress only that the $\Delta_f H°_{298}(FCO_2)$ value[13] from G3 theory[14] is in excellent agreement with the current best estimate. In addition, we note that a $\Delta_f H°_{298}(FCO_2)$ value of -80.5 ± 2.5 kcal mol^{-1} has been calculated from bond additivity-corrected Møller−Plesset fourth-order perturbation theory (BAC-MP4).[76] However, this value belongs to a geometry of FCO_2 with clearly different C−O bond lengths (116.3 and 131.8 pm).[76] Such a low-symmetry structure results from symmetry-breaking effects in the Hartree−Fock wave function of the FCO_2 radical[12] and does not correspond to the C_{2v} equilibrium geometry in its ground electronic state ($X\ ^2B_2$).[7,19,27]

3.4. Related Thermochemical Data. Table 6 lists our theoretical results for the C−F bond dissociation energy $D_0(F-CO_2)$ in FCO_2 ($X\ ^2B_2$), the fluoride ion affinity of carbon dioxide $D_0(F^--CO_2)$, the electron affinity $EA_0(FCO_2)$, and the ionization energy $IE_0(FCO_2)$, as well as the adiabatic excitation energies $T_0(A\ ^2A_2)$ and $T_0(B\ ^2A_1)$ in FCO_2. Corresponding experimental values are shown whenever available in the literature.[7,8,24,25]

TABLE 7: Computed[a] Structural and Vibrational Parameters of FCO_2 in Its Low-Lying Electronic States

	X $^2B_2$			A $^2A_2$			B $^2A_1$		
parameter[b]	B3LYP	UHF-CCSD(T)	EOMIP-CCSD	B3LYP	UHF-CCSD(T)	EOMIP-CCSD	B3LYP	UHF-CCSD(T)	EOMIP-CCSD
r_e(CF), pm	131.94	131.02	129.97	133.48	132.52	131.50	137.54	135.88	134.92
r_e(CO), pm	123.41	123.55	122.92	125.00	125.03	124.35	124.08	124.75	123.90
θ_e(OCO), deg	119.87	118.97	118.59	125.61	125.23	124.92	138.19	137.03	137.09
$\omega_1(a_1)$, cm^{-1}	1518	1565	1616	1416	1462	1513	1155	1161	1204
$\omega_2(a_1)$, cm^{-1}	988	1007	1048	984	1007	1045	829	917	956
$\omega_3(a_1)$, cm^{-1}	538	548	560	623	632	647	630	624	643
$\omega_4(b_2)$, cm^{-1}	1177	1223	1087	847	669	731	2618	2463	2471
$\omega_5(b_2)$, cm^{-1}	505	524	498	561	384	514	584	584	599
$\omega_6(b_1)$, cm^{-1}	757	767	784	746	733	789	762	757	789
ZPVE,[c] kcal mol^{-1}	7.840	8.055	7.997	7.400	6.988	7.489	9.402	9.301	9.522

[a] Employing the cc-pVTZ basis. All electrons were correlated. [b] r_e, bond lengths; θ_e, bond angles; ω_i, harmonic vibrational wavenumbers; ZPVE, associated zero-point vibrational energies. [c] Unscaled values.

The experimental[7] value for $D_0(F{-}CO_2)$ was presently redetermined from the experimental[8] $D_{298}(F^-{-}CO_2)$ value after conversion to $T = 0$ K (see below) and the experimental[7,9] electron affinities of F and FCO_2:

$$D_0(F{-}CO_2) = D_0(F^-{-}CO_2) + EA_0(F) - EA_0(FCO_2) \quad (6)$$

This redetermination followed the procedure specified in ref 7, where $D_0(F{-}CO_2)$ was evaluated to be 11.5 ± 3 kcal mol^{-1} by use of $D_{298}(F^-{-}CO_2)$ instead of $D_0(F^-{-}CO_2)$. The experimental uncertainty of ±2.1 kcal mol^{-1} in $D_0(F{-}CO_2)$ was calculated by propagating the experimental uncertainties in $D_0(F^-{-}CO_2)$ and $EA_0(FCO_2)$, which are ±2 and ±0.69 kcal mol^{-1}, respectively;[7,8] the uncertainty of the experimental[9] EA_0(F) value is negligibly small, 4×10^{-6} eV or less than 1×10^{-4} kcal mol^{-1}. In view of the excellent agreement with theory (see Table 6), the error bars in the experimental $D_0(F{-}CO_2)$ value appear to be too conservative and we recommend $D_0(F{-}CO_2) = 10.5 \pm 1$ kcal mol^{-1}. As pointed out previously,[7] the C−F bond in FCO_2 is very weak: $D_0(F{-}CO_2)$ is about 1 order of magnitude smaller than $D_0(H_3C{-}F)$, $D_0(F_3C{-}F)$, and $D_0(Cl_3C{-}F)$.[7]

As a check for consistency, the experimental value for $D_0(F{-}CO_2)$ may be used to evaluate an experimental value for $\Delta_f H_0^\circ(FCO_2)$:

$$\Delta_f H_0^\circ(FCO_2) = \Delta_f H_0^\circ(F) + \Delta_f H_0^\circ(CO_2) - D_0(F{-}CO_2) \quad (7)$$

It can easily be shown that such a procedure is entirely equivalent to the previous[7] determination of $\Delta_f H_{298}^\circ(FCO_2)$ when the corresponding thermal corrections needed to convert $EA_0(FCO_2)$ to $EA_{298}(FCO_2)$ are introduced. By use of the ATcT values[23] for $\Delta_f H_0^\circ$(F) and $\Delta_f H_0^\circ(CO_2)$, as well as $D_0(F{-}CO_2) = 10.5 \pm 1$ kcal mol^{-1} (see above), eq 7 leads to $\Delta_f H_0^\circ(FCO_2) = -86.0 \pm 1$ kcal mol^{-1}. Except for the claimed uncertainty, this result is in perfect agreement with the best theoretical estimate (see discussion above).

The fluoride ion affinity of CO_2 at $T = 0$ K [$D_0(F^-{-}CO_2)$] is trivially obtained from its value[8] at $T = 298$ K by use of the integrated heat capacities of F^- and CO_2 from JANAF;[64] the integrated heat capacity $H°(298.15\text{ K}) - H°(0\text{ K})$ of FCO_2^-, which is also needed, was calculated statistically from its B3LYP/cc-pVTZ harmonic vibrational wavenumbers to be 2.720 kcal mol^{-1}. Proceeding as described, we get $D_0(F^-\text{-}CO_2) = 30.7 \pm 2$ kcal mol^{-1} [compared to $D_{298}(F^-{-}CO_2) = 31.7 \pm 2$ kcal mol^{-1} as determined in ref 8]. The present theoretical value for $D_0(F^-{-}CO_2)$ is identical with the experimental value from ref 24 (31.3 kcal mol^{-1}) and exceeds its counterpart from ion cyclotron resonance techniques[8] by 0.6 kcal mol^{-1} (see Table 6). This deviation is close to the estimated error bar (±0.5 kcal mol^{-1}) of the theoretical value. The quoted uncertainty of the experimental[8] $D_0(F^-{-}CO_2)$ value appears to be somewhat too large. Error bars of ±1 kcal mol^{-1} seem more realistic. We recommend $D_0(F^-{-}CO_2) = 31 \pm 1$ kcal mol^{-1}.

The UCCSD(T) and UHF-CCSD(T) results for $EA_0(FCO_2)$ are well within the error bars (±0.030 eV) of the experimental value,[7] the deviations being 0.020 and 0.024 eV, respectively, whereas the analogous RCCSD(T) value falls just outside the experimental[7] uncertainty by 0.009 eV.

The ionization energy of FCO_2 has not yet been determined experimentally. The present theoretical $IE_0(FCO_2)$ values are in the range 12.59−12.61 eV, the average being 12.60 eV (290.6 kcal mol^{-1}). Previously,[26] at the CCSD(T)/6-311+G(3df)//CCSD(T)/6-311G(2df) level of theory, $IE_0(FCO_2)$ has been predicted to be 287.4 kcal mol^{-1}. Due to the use of larger basis sets and extrapolated total energies, the $IE_0(FCO_2)$ estimate from this work (12.60 eV or 290.6 kcal mol^{-1}) is expected to be more reliable than the previous one.[26] $IE_0(FCO_2)$ is defined as the energy difference between the cation FCO_2^+ in its most stable form and the neutral ground electronic state. The most stable form of FCO_2^+ is a closed-shell singlet state (X $^1A_1$). Ionization of FCO_2 (X $^2B_2$) may also remove one of the electrons in the doubly occupied $1a_2$ MO such that a triplet-state FCO_2^+ (a $^3B_1$) is formed. The RCCSD(T)-based energy E_0 of the latter is larger by 10.74 kcal mol^{-1} (0.466 eV) than its singlet counterpart (X $^1A_1$). Neglecting the effect of zero-point nuclear motions (B3LYP/cc-pVTZ, scaled ZPVEs), this energy separation amounts to 11.91 kcal mol^{-1} (0.517 eV).

The first excited electronic state (A $^2A_2$) of FCO_2 was measured to lie 0.579 eV above the ground state.[7] The theoretical adiabatic excitation energies T_0(A $^2A_2$) are in excellent agreement with experiment,[7] the absolute errors being as small as 0.005−0.008 eV. The RCCSD(T) and UHF-CCSD(T) results for T_0(A $^2A_2$) are almost identical, whereas the UCCSD(T) value is slightly smaller (0.012−0.013 eV).

The adiabatic excitation energy T_0(B $^2A_1$) of the second excited state of FCO_2 is presently overestimated by 0.056−0.057 eV; that is, the errors are significantly larger than those found for T_0(A $^2A_2$). When any ZPVE contributions to the relative energy of the B $^2A_1$ state are omitted, its energy is calculated to be close to 1.62 eV (see footnote *g* in Table 6); that is, only about 0.01 eV smaller than the experimental[25] value for T_0(B $^2A_1$) (1.630 eV). This suggests that the energetic separation of the second excited state from the electronic ground state may be described correctly as far as the electronic contributions are concerned and that the main source of error may be the computed (B3LYP/cc-pVTZ) ZPVE difference (unscaled, 1.562 kcal mol^{-1}; scaled, 1.538 kcal mol^{-1}) between the B $^2A_1$ and X $^2B_2$ states. If this is true, this error might be recognizable in the calculated vibrational spectra. Table 7 contains the computed harmonic wavenumbers ω_i of FCO_2 in the three lowest doublet states. The most striking difference between the computed harmonic wavenumbers for the X $^2B_2$ and B $^2A_1$ state appears for the antisymmetric C−O stretching mode ω_4, which is predicted (B3LYP/cc-pVTZ) to be larger by 1441 cm^{-1} in the upper state. Moreover, Table 7 shows that such a pronounced difference between the ω_4 values is by no means peculiar to B3LYP/cc-pVTZ since UHF-CCSD(T)/cc-pVTZ and EOMIP-CCSD/cc-pVTZ predict similarly large differences (1240 and 1384 cm^{-1}, respectively). It is known[12] that distortion of the FCO_2 radical along the antisymmetric C−O stretching normal coordinate gives rise to a second-order Jahn−Teller (SOJT) interaction between the X $^2B_2$ and B $^2A_1$ states. Due to this coupling of states, ω_4 is indeed expected to be larger in the upper state than in the lower state,[77] but the computed magnitude of this increase seems dubious,[12] and we consider it likely that it is overestimated by the present calculations. If so, the ZPVE value for the B $^2A_1$ state would be too large. This could well explain the overestimate of T_0(B $^2A_1$) in our calculations by 0.056−0.057 eV (ca. 450−460 cm^{-1}).

4. Conclusions

Total energies were calculated by a composite approach based on coupled cluster theory with single and double excitations including a perturbational estimate of the effects of connected triple excitations [CCSD(T)]. The error arising from the use of large (up to aug-cc-pV5Z) but nevertheless finite correlation-consistent basis sets was minimized by extrapolating to the complete basis-set limit. Corrections were also applied for core−valence correlation, scalar relativity (one-electron Darwin and mass-velocity terms), first-order spin−orbit coupling, and zero-point vibrational motions. No corrections were made for deficiencies in the treatment of triple excitations in CCSD(T) or for higher-order excitations. The current computational procedure is very similar to Weizmann-2 (W2) theory.[21,22]

The focus of this work was the evaluation of an accurate and reliable value for the standard enthalpy of formation of FCO_2 (X $^2B_2$). Using a variety of independent reaction schemes, we first treated HCO (X $^2A'$) and FCO (X $^2A'$) in order to check the performance of the present procedure. Our best theoretical estimate for the enthalpy of formation of HCO at $T = 0$ K is $\Delta_f H^\circ_0(HCO) = 10.1 \pm 0.5$ kcal mol^{-1}, in excellent agreement with the accurate and most precise value from experiment (10.06 ± 0.09 kcal mol^{-1}). In the case of FCO, the experimental value of the enthalpy of formation from the JANAF compilation (−41 ± 15 kcal mol^{-1}) carries a large uncertainty. Here we recommend the use of our best theoretical estimate, which is $\Delta_f H^\circ_0(FCO) = -42.1 \pm 0.5$ kcal mol^{-1} [$\Delta_f H^\circ_{298}(FCO) = -42.0 \pm 0.5$ kcal mol^{-1}]. Published values from other models of computational thermochemistry differ by up to 0.7 kcal mol^{-1} and should be somewhat less reliable. Finally, for the target species FCO_2 (X $^2B_2$), our recommendation is $\Delta_f H^\circ_0(FCO_2) = -86.0 \pm 0.6$ kcal mol^{-1} [$\Delta_f H^\circ_{298}(FCO_2) = -86.7 \pm 0.6$ kcal mol^{-1}]. The present best theoretical estimate for $\Delta_f H^\circ_{298}(FCO_2)$ is in reasonable agreement with the published experimental value (−85.2 ± 2.8 kcal mol^{-1})[7] derived from the measured electron affinity of FCO_2. We have argued that this experimental value needs to be corrected for an inconsistent use of the auxiliary $\Delta_f H^\circ_{298}(FCO_2^-)$ data that had been adopted from a different study. After this correction is applied, excellent agreement between theory and experiment is found for $\Delta_f H^\circ_{298}(FCO_2)$.

The C−F bond dissociation energy in FCO_2 (X $^2B_2$), its electron affinity, ionization energy, and the relative energies of the first (A $^2A_2$) and second (B $^2A_1$) electronically excited states in FCO_2, as well as the fluoride ion affinity of CO_2, have been computed at the same level. These additional theoretical results were compared with the available experimental data in detail.

As a byproduct of this investigation, accurate minimum-energy structures of the involved molecular species were calculated. In this context, we have become aware of the fact that experimentally the molecular structure of FCO (X $^2A'$) has been determined with rather large uncertainties (±6 pm) in the bond lengths. On the basis of our all-electron RCCSD(T)/aug-cc-pCVQZ geometry optimization for FCO, we recommend the following equilibrium structural parameters for the electronic ground state: $r_e(CF) = 132.5(2)$ pm, $r_e(CO) = 116.7(2)$ pm, and $\theta_e(FCO) = 127.8(2)^\circ$.

References and Notes

(1) Francisco, J. S.; Maricq, M. M. *Acc. Chem. Res.* **1996**, *29*, 391.

(2) Von Ahsen, S.; Willner, H.; Argüello, G. A. *J. Fluorine Chem.* **2004**, *125*, 1057.

(3) Kim, E. H.; Bradforth, S. E.; Arnold, D. W.; Metz, R. B.; Neumark, D. M. *J. Chem. Phys.* **1995**, *103*, 7801.

(4) Feller, D.; Dixon, D. A.; Francisco, J. S. *J. Phys. Chem. A* **2003**, *107*, 1604.

(5) Janoschek, R.; Rossi, M. J. *Int. J. Chem. Kinet.* **2004**, *36*, 661.

(6) Fabian, W. M. F.; Janoschek, R. *J. Mol. Struct. (THEOCHEM)* **2005**, *713*, 227.

(7) Arnold, D. W.; Bradforth, S. E.; Kim, E. H.; Neumark, D. M. *J. Chem. Phys.* **1995**, *102*, 3493.

(8) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.

(9) Blondel, C.; Cacciani, P.; Delsart, C.; Trainham, R. *Phys. Rev. A* **1989**, *40*, 3698.

(10) Dibble, T. S.; Francisco, J. S. *J. Phys. Chem.* **1994**, *98*, 11694.

(11) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(12) Schneider, W. F.; Maricq, M. M.; Francisco, J. S. *J. Chem. Phys.* **1995**, *103*, 6601.

(13) Haworth, N. L.; Smith, M. H.; Bacskay, G. B.; Mackie, J. C. *J. Phys. Chem. A* **2000**, *104*, 7600.

(14) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(16) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(17) Tucceri, M. E.; Badenes, M. P.; Croce, A. E.; Cobos, C. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1832.

(18) Badenes, M. P.; Croce, A. E.; Cobos, C. J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 747.

(19) Zelinger, Z.; Dréan, P.; Walters, A.; Avilès Moreno, J. R.; Bogey, M.; Pernice, H.; von Ahsen, S.; Willner, H.; Breidung, J.; Thiel, W.; Bürger, H. *J. Chem. Phys.* **2003**, *118*, 1214.

(20) In ref 19 we computed the $\Delta_f H^\circ_{298}(FCO_2)$ value according to eq 13 in ref 7, that is, from $\Delta_f H^\circ_{298}(FCO_2^-)$ and $EA_{298}(FCO_2)$. As given, this equation refers to the so-called thermal electron convention because the integrated heat capacity of the electron ($^5/_2RT = 1.481$ kcal mol^{-1} at $T = 298.15$ K) is explicitly taken into account to correct $EA_0(FCO_2)$ for temperature effects. To be consistent with this choice, $\Delta_f H^\circ_{298}(FCO_2^-)$ in this equation must also correspond to the thermal electron convention. However, in ref 19 we erroneously used a $\Delta_f H^\circ_{298}(FCO_2^-)$ value that was calculated by adoption of the so-called stationary electron convention (ion convention); that is, the enthalpy of the electron was excluded. Thereby we arrived at a $\Delta_f H^\circ_{298}(FCO_2)$ value of −85.87 kcal mol^{-1}. Due to this inconsistency, the latter value is too large by 1.481 kcal mol^{-1}, and the corrected value from ref 19 must read −87.35 kcal mol^{-1}.

(21) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.

(22) Parthiban, S.; Martin, J. M. L. *J. Chem. Phys.* **2001**, *114*, 6014.

(23) Ruscic, B.; Pinzon, R. E.; Morton, M. L.; von Laszevski, G.; Bittner, S. J.; Nijsure, S. G.; Amin, K. A.; Minkoff, M.; Wagner, A. F. *J. Phys. Chem. A* **2004**, *108*, 9979.

(24) Hiraoka, K.; Mizuse, S.; Yamabe, S. *J. Chem. Phys.* **1987**, *87*, 3647.

(25) Maricq, M. M.; Szente, J. J.; Li, Z.; Francisco, J. S. *J. Chem. Phys.* **1993**, *98*, 784.

(26) Francisco, J. S. *Chem. Phys. Lett.* **1997**, *265*, 521.

(27) Argüello, G. A.; Grothe, H.; Kronberg, M.; Willner, H.; Mack, H.-G. *J. Phys. Chem.* **1995**, *99*, 17525.

(28) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.

(29) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **2000**, *112*, 3106.

(30) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(31) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(32) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(33) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(34) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(35) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(36) Hampel, C.; Peterson, K. A.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1 and references therein.

(37) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(38) Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J. *MOLPRO*, versions 2002.3, 2002.6, and 2000.1, a package of ab initio programs designed by H.-J.Werner and P. J. Knowles; University of Birmingham, Birmingham, U.K., and Universität Stuttgart, Stuttgart, Germany, 2002.

(39) Rittby, M.; Bartlett, R. J. *J. Phys. Chem.* **1988**, *92*, 3033.

(40) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639.

(41) Klopper, W.; Noga, J.; Koch, H.; Helgaker, T. *Theor. Chem. Acc.* **1997**, *97*, 164.

(42) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int. J. Quantum Chem. Symp.* **1992**, *26*, 879.

(43) Cowan, R. D.; Griffin, M. *J. Opt. Soc. Am.* **1976**, *66*, 1010.

(44) Martin, R. L. *J. Phys. Chem.* **1983**, *87*, 750.

(45) Tajti, A.; Szalay, P. G.; Császár, A. G.; Kállay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vázquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, *121*, 11599.

(46) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(47) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 03*, Revisions B.01 and C.01; Gaussian, Inc.: Pittsburgh, PA, 2003, and Wallingford, CT, 2004, respectively.

(49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J. W.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, Revision A.11.1; Gaussian, Inc.: Pittsburgh, PA, 2001.

(50) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(51) Szalay, P. G.; Gauss, J.; Stanton, J. F. *Theor. Chem. Acc.* **1998**, *100*, 5.

(52) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1994**, *101*, 8938 and references therein.

(53) Flowers, B. A.; Szalay, P. G.; Stanton, J. F.; Kállay, M.; Gauss, J.; Császár, A. G. *J. Phys. Chem.* A **2004**, *108*, 3195.

(54) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(55) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, The Netherlands, 1995; p 47.

(56) Stanton, J. F.; Gauss, J. *Adv. Chem. Phys.* **2003**, *125*, 101.

(57) Hirota, E. *J. Mol. Struct.* **1986**, *146*, 237.

(58) Nagai, K.; Yamada, C.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc.* **1981**, *90*, 249.

(59) Gray, D. L.; Robiette, A. G. *Mol. Phys.* **1979**, *37*, 1901.

(60) Teffo, J.-L.; Ogilvie, J. F. *Mol. Phys.* **1993**, *80*, 1507.

(61) Partridge, H.; Schwenke, D. W. *J. Chem. Phys.* **1997**, *106*, 4618.

(62) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(63) Császár, A. G.; Czakó, G.; Furtenbacher, T.; Tennyson, J.; Szalay, V.; Shirin, S. V.; Zobov, N. F.; Polyansky, O. L. *J. Chem. Phys.* **2005**, *122*, 214305.

(64) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1).

(65) Dixon, D. A.; Feller, D. *J. Phys. Chem. A* **1998**, *102*, 8209.

(66) Buckley, T. J.; Johnson, R. D., III; Huie, R. E.; Zhang, Z.; Kuo, S. C.; Klemm, R. B. *J. Phys. Chem.* **1995**, *99*, 4879.

(67) The net post-CCSD(T) contributions to the C−F and C−O binding energies in FCO_2 have not yet been calculated. If these contributions were similarly large as for O_2 and F_2, they could be compensated to a certain extent when O_2 and/or F_2 are used as reactants.

(68) Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

(69) Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128.

(70) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484.

(71) De Oliveira, G.; Martin, J. M. L.; Silwal, I. K. C.; Liebman, J. F. *J. Comput. Chem.* **2001**, *22*, 1297.

(72) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.

(73) Jayatilaka, D.; Lee, T. J. *J. Chem. Phys.* **1993**, *98*, 9734.

(74) Woolf, A. A. *Adv. Inorg. Chem. Radiochem.* **1981**, 24, 1.

(75) Inserting $\Delta_f H^\circ_{298}(FCO_2^-) = -186.8$ kcal mol^{-1} instead of -185 kcal mol^{-1} in eq 13 of ref 7 while keeping all other terms unchanged yields $\Delta_f H^\circ_{298}(FCO_2) = -87.0$ kcal mol^{-1} instead of -85.2 kcal mol^{-1}. However, when repeating the original calculation of ref 7, we find $\Delta_f H^\circ_{298}(FCO_2) = -84.8$ kcal mol^{-1} rather than -85.2 kcal mol^{-1}. This small discrepancy for which we have no explanation causes the presently corrected experimental value for $\Delta_f H^\circ_{298}(FCO_2)$ to be more positive by 0.4 kcal mol^{-1} than expected. We employed the numerical values for $\Delta_f H^\circ_{298}(FCO_2^-)$, EA_0-(FCO_2), and $^5/_2RT$ given explicitly in ref 7 and recalculated the integrated heat capacities of FCO_2 (2.76 kcal mol^{-1}) and FCO_2^- (2.67 kcal mol^{-1}) following the prescription in ref 7.

(76) Zachariah, M. R.; Westmoreland, P. R.; Burgess, D. R., Jr.; Tsang, W.; Melius, C. F. *J. Phys. Chem.* **1996**, *100*, 8737.

(77) Russ, N. J.; Crawford, T. D.; Tschumper, G. S. *J. Chem. Phys.* **2004**, *120*, 7298 and references therein.