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Heat of formation of the CF_2^{++} dication: a theoretical estimate

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Abstract

Relative energies and ionization potentials of neutral and ionic fragments of CF_4 were calculated using the coupled cluster single double (triple)/correlation consistent triple zeta basis set ab initio method. The individual values were compared with available experimental and theoretical data to assess the accuracy of this approach for these particular systems. In addition, reaction enthalpies for possible fragmentation reactions were calculated. Maximum errors found were in the order of 5 kcal/mol (0.2 eV). The estimation of the heat of formation of the CF_2^{++} dication, derived from the calculations based on four different reactions, is 687 ± 5 kcal/mol (29.8 ± 0.2 eV). This value is considerably smaller than the one which follows from the appearance potential measurements (732 ± 7 kcal/mol). (Int J Mass Spectrom 201 (2000) 269–275) © 2000 Elsevier Science B.V.

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1. Introduction

Long-lived polyatomic dications have attracted considerable attention of both experimentalists [1,2] and theoreticians [3,4] during the past two decades. These dications sometimes exhibit unusual structures and reactivities and in this context they represent a challenging topic in gas phase ion chemistry. The CF_n^+ and CF_n^{++} series of cations and dications are of particular interest, e.g. due to their importance in plasma etching processes [5,6]. Furthermore, it is believed that CF_n^{x+} ions play a key role in the depletion of ozone in the outer atmosphere [7].

The thermochemistry of various decomposition products of CF_4 is of importance in evaluating and modeling the reactions that involve these species. Unfortunately, thermochemical values of some species show a large scatter [8] and, in particular, limited information is available on dications. The first measurements of appearance energies (AE) of doubly charged fragment ions of CF_4 led to 42.7 ± 0.3 eV for CF_3^{++} and 44.3 ± 0.3 eV for CF_2^{++} [9]. More recent measurements [10] gave 41.8 ± 0.3 eV for CF_3^{++}, 42.9 ± 0.3 eV for CF_2^{++}, and, in addition, 52.1 ± 0.3 eV for CF^{++}. Beynon and co-workers [11] determined the ionization energies (IEs) of the singly charged ions, 26.0 ± 0.4 eV for CF^+ and 26.3 ± 0.4 eV for CF_3^+, by a direct Q_{min} measurement using the charge stripping technique, and they also observed the presence of long lived excited states of the cations. Unfortunately, due to the low instru-

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ment resolution and interference of the $C_4H_2^{++}$ ion (*m/z* 50), the corresponding measurements to identify the IE(CF_2^+) failed. Later on, the reactivity of CF_2^{++} and CF_3^{++} dications was studied by Leone and co-workers [12–14] in collision experiments with a series of gases. From studies of charge transfer reactions with rare gases and skillful application of the reaction window concept, the double ionization energy $\mathrm{IE}^{\mathrm{I}\text{-}\mathrm{I}}(\mathrm{CF}_2)$ was estimated to be between 32.0 and 33.0 eV [13]. Using these values and the most recent IE of difluorocarbene (CF_2), 11.445 eV [8], IE(CF_2^+) should be between 20.5 and 21.5 eV. From their subsequent article [14] an IE for CF_2^+ of 21.1 eV can be derived. In these calculations we use IE(O_2) = 12.07 eV and IE(D_2) = 15.47 eV [8] as well as the reported exothermicities of the reactions

$$CF_2^{++} + D_2 \rightarrow CF_2^+ + D_2^+, \qquad \Delta H_R = 5.6\ \mathrm{eV} \tag{1}$$

$$CF_2^{++} + O_2 \rightarrow CF_2^+ + O_2^+, \qquad \Delta H_R = 9.1\ \mathrm{eV} \tag{2}$$

The occurrence of an excited state of CF_2^{++} lying ~4.0 eV above the lower state is also mentioned in that article. Similarly, a value of 26.4 eV for IE(CF^+) can be obtained from the exothermicities of the following reactions:

$$CF^{++} + D_2 \rightarrow CF^+ + D_2^+, \qquad \Delta H_R = 10.9\ \mathrm{eV} \tag{3}$$

$$CF^{++} + O_2 \rightarrow CF^+ + O_2^+, \qquad \Delta H_R = 14.3\ \mathrm{eV} \tag{4}$$

These data are in perfect agreement with the value given by Beynon and co-workers already in 1982 [11].

Recently, dynamics of reaction (1) have been reinvestigated by Herman and co-workers [15] in a crossed-beam scattering experiment. In addition to the charge transfer reaction (1) listed above, chemical reaction (5) leading to CF_2D^+ formation reported earlier [14], was also examined

$$CF_2^{++} + D_2 \rightarrow CF_2D^+ + D^+ \tag{5}$$

In their evaluation of reaction heats the authors used a value of IE(CF_2^{++}) derived from the appearance potential (AP) measurements [10] and noted the discrepancy between this value and that reported by Price et al. [14], 21.1 eV (486.6 kcal/mol).

In the past two decades only a few theoretical calculations have appeared on the CF_n^{++} dications. Koch and Frenking [16] performed MP2/6-31G* calculations for a series of CF_n ions including CF^{++} and CF_2^{++}. They found that the potential energy surface of CF_2^{++} exhibits a minimum for the linear structure, which is, considering the spin conservation rule, very stable toward fragmentation

$$CF_2^{++} \rightarrow CF^+ + F^+(^1S), \qquad \Delta H_R = 76.5\ \mathrm{kcal/mol} \tag{6}$$

The spin forbidden dissociation leading to the ground state $F^+(^3P)$ was found to be exothermic by 12.0 kcal/mol. The MP2/6-31G* calculated adiabatic ionization energies were 8.6 eV for CF, 25.5 eV for CF^+, 10.8 eV for CF_2, and 20.5 eV for CF_2^+.

Multireference configuration interaction (MRCI) calculations have been performed by Senekowitsch et al. for the ground ($^1\Sigma$ and $^2\Sigma$) and first excited states ($^3\Pi$ and $^2\Pi$) of CF^+ [17] and CF^{++} [18]. The singlet–triplet separation for CF^+ was found to be 4.77 eV at the MRCI/cc-pVTZ level. The $^2\Sigma \rightarrow {}^2\Pi$ excitation energy was theoretically predicted as 2.81 eV. The calculated values of the adiabatic IE were 9.17 eV for CF and 26.29 eV for CF^+. In addition, HF/6-31G* calculations [19] and MP2/6-31G* [20] of CF_4^+ and CF_3^+ were carried out by De La Vega and San Fabian. The CF_3^{++} dication was also investigated. However, only D_{3h} symmetric geometries were considered in these studies and no vibrational frequencies were given.

The discrepancy in the heat of formation of CF_2^{++} obtained from charge transfer measurements [8,14] and from AP [10] motivated us to consider a closer examination of this problem by theoretical methods. In this communication we report on a theoretical investigation of the CF_n^{x+} systems using a highly correlated and uniform level of theory. We employed the coupled cluster single double (triple) [CCSD(T)] method with a reasonably large and flexible basis set. This method is expected to deliver relative energies with absolute errors in the order of only few kcal/mol

[21–23]. To crosscheck the results of our calculations, we compared the estimates for individual singly charged fragments with energetics derived from experimental results.

2. Computational details

For energy calculations the coupled cluster method CCSD(T) [24–27] was used in conjunction with Dunning's correlation consistent triple zeta basis set (cc-pVTZ) with two *d* and one *f* polarization functions [28–30] as implemented in the MOLPRO97 program. The geometry was preoptimized at the density functional level (DFT) using the same basis set. The parametrized hybrid method, due to Becke [31,32], which involves a semiempirical combination of an "exact" (i.e. Hartree-Fock-like, but based on Kohn-Sham orbitals) exchange, and the gradient-corrected Becke exchange [33] and Lee-Yang-Parr correlation [34] functionals. DFT calculations were performed with the GAUSSIAN94 [35] program. In analogy with the GAUSSIAN keywords, this approximate DFT method will be referred to as B3LYP. From our previous studies we expect that the geometries and energies calculated with the B3LYP method will be at least of MP2/DZP quality [36–38] and should serve as good initial estimates for CCSD(T) calculations.

The CCSD(T) calculations were performed with the MOLPRO97 [39] program package using the restricted (open shell) coupled cluster code [40] based on restricted Hartree-Fock (RHF) orbitals. The 1*s* electrons at the carbon and fluorine atoms were kept frozen in the energy calculation. The geometry was also optimized at this level, using numerical first and second derivatives of the energy starting from the structures obtained at B3LYP. The following point group symmetries were kept during the optimization (for the nonabelian point groups, the calculations were actually performed exploiting the corresponding highest abelian subgroup): C_{2v} ($D_{\infty h}$) for CF_2 (CF_2^{++}), C_{3v} (D_{3h}) for CF_3 (CF_3^+), and T_d for CF_4. For the CF_3^{++} we used both the C_{2v} and D_{3h} symmetries and found a sizable Jahn-Teller distortion [41].

3. Results and discussion

The B3LYP and CCSD(T) geometries, total energies and harmonic vibrational frequencies of neutral, singly and doubly charged CF_n ($n = 1$, 2, and 3) are listed in Table 1. Their ionization energies, electron affinities and reaction enthalpies from our calculations are summarized in Table 2 together with the experimental reference data. The CCSD(T) calculated ionization energies compare well with the experiment. The largest deviation was found for the fluorine atom, where the CCSD(T) calculation yields 17.13 eV, compared with recent experimental values of 17.20 eV [42] and 17.423 eV [43]. Since the latter value is more reliable, we are left with an error of $\Delta E = 0.29$ eV. It can be shown [44] that the role of the one-electron basis is essential in the calculations of the IE(F) [CCSD(T)/aug-cc-pVQZ; IE(F) = 17.34 eV]. On the other hand, the CCSD(T)/cc-pVTZ calculated electron affinity of fluorine (3.32 eV) compares well with the experimental value of 3.40 eV.

Probably the best experimental IE value for CF($^2\Pi$), 9.11 ± 0.01 eV, was obtained from photoelectron spectroscopy measurements by Dyke et al. [45]. The value is very close ($\Delta E = 0.16$ eV) to our calculated adiabatic ionization energy of 8.95 eV. A further indication of the quality of our calculated results is the $^1\Sigma \rightarrow {}^3\Pi$ separation for CF^+; our calculations give 4.79 eV, in excellent agreement with other theoretical MRCI value of 4.77 eV [18]. Our calculated value of IE(CF^+) is 25.84 eV, again in agreement with both the MRCI calculations (26.29 eV) and the experimental charge stripping value of 26.0 ± 0.4 eV [11]. Similarly, our calculated adiabatic IE(CF_2), 11.20 eV, is only 0.24 eV lower than the very recent photoionization value of 11.445 ± 0.025 eV [46]. The ionization energy of CF_3, calculated by us, 8.77 eV, agrees well with the recent experimental result of 8.76 eV obtained from mass spectrometric equilibrium measurements [47]. Finally, CCSD(T) calculations gave 26.80 eV for the IE(CF_3^+); that is in agreement with the experimental value of 26.30 ± 0.3 eV [11]. In general, it appears that these directly calculated ionization energies of the CF_n^+ fragments are reliable within ±0.2 eV.

Table 1
Calculated energies, geometries, and frequencies for CF_4 and its fragments

		E_{tot} (Hartree)	R_{CF} (A)	α_{FCF}	Frequencies (cm^{-1})
$F(^2P)$	B3LYP	−99.762 866			
	CCSD(T)	−99.620 361			
$F^+(^3P)$	B3LYP	−99.113 922			
	CCSD(T)	−98.990 795			
$F^+(^1S)$	B3LYP	−98.980 429			
	CCSD(T)	−98.898 512			
$F^-(^1S)$	B3LYP	−99.850 170			
	CCSD(T)	−99.742 359			
$CF(^2\Pi)$	B3LYP	−137.835 253	1.276		σ 1304.8
	CCSD(T)	−137.604 560	1.278		σ 1321.3
$CF(^4\Sigma)$	B3LYP	−137.699 438	1.328		σ 1228.3
	CCSD(T)	−137.475 738	1.330		σ 1245.5
$CF^+(^3\Pi)$	B3LYP	−137.321 870	1.214		σ 1613.7
	CCSD(T)	−137.099 269	1.127		σ 1614.4
$CF^+(^1\Sigma)$	B3LYP	−137.488 873	1.157		σ 1792.0
	CCSD(T)	−137.275 569	1.161		σ 1787.3
$CF^{++}(^2\Sigma)$	B3LYP	−136.536 513	1.126		σ 1990.2
	CCSD(T)	−136.325 952	1.132		σ 1949.7
$CF_2(^1A_1)$	B3LYP	−237.792 855	1.305	104.6	a_1 670.2 b_2 1113.5 a_1 1231.5
	CCSD(T)	−237.419 132	1.302	104.9	a_1 672.9 b_2 1162.7 a_1 1256.8
$CF_2(^3B_1)$	B3LYP	−237.708 680	1.318	119.7	a_1 510.8 a_1 1136.9 b_2 1303.5
	CCSD(T)	−237.329 188	1.317	119.4	a_1 516.9 a_1 1162.6 b_2 1346.4
$CF_2^+(^2A_1)$	B3LYP	−237.379 819	1.220	124.6	a_1 643.2 a_1 1364.7 b_2 1678.4
	CCSD(T)	−237.007 645	1.220	124.8	a_1 647.3 a_1 1373.9 b_2 1708.4
$CF_2^{++}(^1\Sigma_g)$	B3LYP	−236.612 817	1.150	180.0	π_u 559.6 σ_g 1211.9 σ_u 2341.9
	CCSD(T)	−236.251 070	1.153	180.0	π_u 557.7 σ_g 1199.3 σ_u 2330.5
$CF_3(^2A_1)$	B3LYP	−337.696 293	1.321	111.3	e 504.7 a_1 697.5 a_1 1082.2 e 1243.5
	CCSD(T)	−337.172 609	1.317	111.4	Not calculated
$CF_3^+(^1A_1)$	B3LYP	−337.363 972	1.236	120.0	e' 588.3 a_2'' 798.9 a_1' 1051.3 e' 1665.6
	CCSD(T)	−336.850 236	1.233	120.0	e' 588.3 a_2'' 798.9 a_1' 1051.3 e' 1665.7
$CF_3^{++}(^2A_1)$	B3LYP	−336.447 183	1.564	109.9	b_2 321.4 a_1 371.3 a_1 606.4
			1.186		b_1 653.6 a_1 1260.0 b_2 1951.4
	CCSD(T)	−335.899 050	1.655	110.0	b_2 355.9 a_1 455.0 a_1 656.9
			1.186		b_1 669.6 a_1 1285.5 b_2 1995.2
$CF_4(^1A_{1g})$	B3LYP	−437.661 627	1.326	109.5	e 429.2 t 622.6 a_1 903.9 t 1256.9
	CCSD(T)	−437.001 103	1.319	109.5	Not calculated

To assess further the quality of the CCSD(T) calculations, we computed reaction enthalpies (ΔH_R) for several arbitrarily chosen reactions (some listed in Table 2) and compared them with the thermochemical values, determined from experimental heats of formation [8]. The results were encouraging: for the entire series, deviations between theory and experiment never exceeded 5 kcal/mol. Finally, it should be noted that deviancies between theory and experiment for the B3LYP method follow the same trend as the strict ab initio calculations. The absolute errors are, however, larger, being around ±0.5 eV (11 kcal/mol). One notable exception is the disappointing failure of the B3LYP functional to describe the ionization energy of CF_3^+. The B3LYP results deviate here by more than 1.5 eV from the CCSD(T) as well as from the experimental value. It is known that, contrary to the methods based on wave function, the effect of the incomplete basis is much smaller for DFT approaches [48–50] and thus we cannot expect any further improvement when using larger basis sets.

We have chosen three different reactions to esti-

Table 2
Calculated IE and ΔH_R of several dissociation reactions

	B3LYP cc-pVTZ (eV)	CCSD(T) cc-pVTZ(spdf) (eV)	Expt. IE (eV)	Error CCSD(T) (eV)
F(EA)	2.38	3.32	3.40	0.08
F(IE)	17.66	17.13	17.42	0.29
CF(IE)	9.43	8.95	9.11	0.16
CF^+(IE)	25.92	25.84	26.0	0.16
CF_2(IE)	11.24	11.20	11.44	0.24
CF_2^+(IE)	20.87	20.59		
CF_3(IE)	9.04	8.77	8.76	−0.01
CF_3^+(IE)	25.12	26.80	26.6	−0.20

Reactions	B3LYP (kcal/mol)	CCSD(T) (kcal/mol)	ΔH_R expt. (kcal/mol)	Error CCSD(T) (kcal/mol)
$CF_4 \rightarrow CF_3 + F$	127.05	130.61	129.64	−0.97
$CF_4 \rightarrow CF_3^+ + F + e^-$	335.59	332.90	337.00	4.10
$CF_4 \rightarrow CF_3^+ + F^-$	280.80	256.34	253.14	−3.20
$CF_3 \rightarrow CF_2 + F$	88.21	83.53	87.90	4.37
$CF_3 \rightarrow CF_2^+ + F^-$	292.61	265.19	267.60	2.41
$CF_3^+ \rightarrow CF_2^+ + F$	138.86	139.45	144.10	4.65

mate of the heat of formation of CF_2^{++} dication (Table 3). (1) A direct calculation based on the heat of formation of CF_2^+ (214.6 kcal/mol [8]) and theoretically calculated value of its IE; this leads to $\Delta H_f(CF_2^{++}) = 689.4$ kcal/mol. (2) The dissociation reaction

$$CF_3^+ \rightarrow CF_2^{++} + F^-(^1S) \tag{7}$$

using $\Delta H_f(CF_3^+) = 89.5$ kcal/mol and $\Delta H_f(F^-) = 59.4$ kcal/mol [8], together with the CCSD(T) calculated bond energy; this gives $\Delta H_f(CF_2^{++}) = 686.6$ kcal/mol. (3) Calculations based on two isodesmic reactions

$$2\,CF_3^+ \rightarrow CF_2^{++} + CF_4 + \Delta H_R \tag{8}$$

$$CF_3^+ + CF_2^+ \rightarrow CF_2^{++} + CF_3 + \Delta H_R \tag{9}$$

using $\Delta H_f(CF_3) = -112.4$ kcal/mol and $\Delta H_f(CF_4) = 223.0$ kcal/mol [8], and the reaction enthalpies calculated with the use of the CCSD(T) method (281.3 and 272.5 kcal/mol); this yields values for $\Delta H_f(CF_2^{++})$ of 683.4 kcal/mol [reaction (8)] and 689.0 kcal/mol [reaction (9)].

Thus, there is a satisfying consistence in the results for all model reactions. In summary we conclude that, based on our calibration study described previously, the heat of formation of the difluorocarbene dication (CF_2^{++}) is of 687 ± 5 kcal/mol (29.8 ± 0.2 eV). This is in good agreement with the value derived earlier by Leone et al [12,13] from studies of charge transfer between CF_2^{++} and rare gas ions. However, it is considerably smaller than the value derived from electron impact appearance potential measurement of CF_2^{++} from CF_4 (42.9 ± 0.3 eV [10]), $\Delta H_f(CF_2^{++}) = 732 \pm 7$ kcal/mol (31.7 ± 0.3 eV), and which was used earlier [15]. The latter value is so high that the difference (~2 eV) cannot be accounted

Table 3
Estimation of $\Delta H_f(CF_2^{++})$ and the reactions used

	Estimated $\Delta H_f(CF_2^{++})$	
Reaction	B3LYP (kcal/mol)	CCSD(T) (kcal/mol)
$CF_2^+ \rightarrow CF_2^{++} + IE(CF_2^+)$	695.89	689.35
$CF_3^+ \rightarrow CF_2^{++} + F^- + BDE$	714.28	686.56
$2CF_3^+ \rightarrow CF_2^{++} + CF_4 + \Delta H_R$	686.62	683.35
$CF_3^+ + CF_2^+ \rightarrow CF_2^{++} + CF_3 + \Delta H_R$	689.27	688.97

for by unfavorable Franck-Condon factors and suggests that electron impact ionization of CF_4 does not initially produce ground state CF_2^{++}.

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