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# Complete basis set ab initio computational study of ionization potential, electron affinity and the C-F bond dissociation energy for perfluorinated methane derivatives

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**Abstract.** A computational study of perfluorinated methane derivatives was performed with complete basis set ab initio methods. The total energies for their neutral, cation, and anionic states were computed. From these values, the energy gaps between different electronic states, ionization potentials, electron affinities, and C-F bond dissociation energies were calculated. The computed values are compared with experimental data and the reliability of complete basis set ab initio methods is discussed. New values for C-F bond dissociation energies are suggested.

**Key words:** Complete basis set – Ionization potential – Electron affinity – Perfluorinated methane

## 1 Introduction

There are many chemical and physical studies that require an accurate knowledge of ionization potential (IP), electron affinity (EA), bond dissociation energies, and excitation states of carbon-fluorine (CF) cations. These values are needed in the fields of combustion chemistry [1], mass spectroscopy [2], and atmospheric chemistry [3]. Some important processes that benefit from accurately computed physical properties of CF cations are plasma processes in fusion reactions, etching reactions in the semiconductor industry, and chemical reactions in mass spectroscopy. We demonstrated in previous computational studies the extraordinary accuracy of the complete basis set (CBS) ab initio method for computing energetic properties of small chemical systems. Here we use this method for an accurate evaluation of the excitation energies, IP, EA, and bond dissociation energies for fluorine, carbon, and their single-carbon derivatives.

## 2 Computational methods

All computational studies were performed with the Gaussian 94 program [4] with ab initio methods as implemented in the package. The Complete Basis Set Quadratic (CBSQ) method was developed by Petersson and coworkers [5]. The family name reflects the fundamental tenet underlying these methods, that is the largest error in ab initio calculations results from basis set truncation. The energy of the chemical system is computed from a series of calculations. The initial calculation starts with geometry optimization and frequency calculation at the HF/6-31G(d′) theory level [6]. The geometry is further optimized at the MP2/6-31G(d′) [7] theory level with single-point energy calculations at QCISD(T)/6-31+(d′) [8], MP4(SDQ)/CBSB4 [9], and MP2/CBSB3. The model also has empirical corrections for spin contamination and a size-consistent high-order correction. An explanation for basis set abbreviation can be found elsewhere [10]. All energies are computed on fully optimized structures of anions, cations, and neutral molecules.

## 3 Results and discussion

First we explored the electronic states of the carbon and fluorine atoms and their difference in energies. Let us first start with the carbon anion. There are five electrons in the outer shell that can be put in one *s* and three *p* orbitals. If all four orbitals are occupied, the carbon anion will be a quartet ($2s^2$, $2p_x^1$, $2p_y^1$, and $2p_1^z$) or if only three are occupied the anion resides in a doublet state ($2s^2$, $2p_x^2$, and $2p_y^1$). The computed total energies and the energy differences for these two states are presented in Table 1. The quartet state is more stable than the doublet, as one would predict from Hund's rule [11], although estimating the energy difference between these two states is not trivial. All traditional ab initio methods predict the energy gap to be too high. The MP2 computed energy is 2.61 eV (Table 1). The complete basis set (CBSQ) method nn computes the energy gap at 1.47 eV, which is identical to the experimental value. There are three possible electronic configurations for neutral carbon with four electrons in the outer shell, all in pairs (singlet), one in a pair (triplet), and all the orbitals occupied with one electron (pentet). Again, considering Hund's rule, the triplet state with a $2s^2$, $2p_x^1$, and $2p_y^1$ occupied orbital should be the most stable, but the question of the energy difference for different electronic configurations arises. As expected, different ab initio methods will offer different energy gaps. The most surprising results stem from the HF ab initio calculations, which suggest that the pentet electron configuration of neutral carbon is slightly more stable than the triplet. The singlet-triplet energy difference is predicted to be too high, while the triplet-pentet electron difference is predicted to be too small. The CBSQ computed values are almost identical to experimental values (Table 2). When neutral carbon is irradiated an electron can be eliminated either from a 2*s* orbital making an quartet, or from the 2*p* orbital making a doublet. It is logical to expect that eliminating an electron from a 2*p* orbital requires less energy; therefore a doublet should be more stable. This was confirmed with our calculations (Table 3). The computed energy difference between these two states was estimated at approximately 5.5 eV. Again the HF, MP2, MP4, and QCISD(T) methods computed an energy difference which is too low while the CBSQ computed energy is almost identical to the estimated values.

**Table 1.** Total energies (a.u.) for the carbon anion in its doublet and quartet state with the energy difference between the two states (eV); $\Delta E_I$ = [(E-doublet)−(E-quartet)] * 27.2116

| Theory | E-doublet | E-quartet | ΔE |
|---|---|---|---|
| HF/6-31G(d′) | −37.557474 | −37.662189 | 2.85 |
| HF/6-31G(d′) (0 K) | −37.557474 | −37.662189 | 2.85 |
| MP2-FC/6-31G(d′) | −37.632996 | −37.729032 | 2.61 |
| QCISD(T)-FC/6-31 + (d′) | −37.734797 | −37.795121 | 1.64 |
| MP4SDQ-FC/CBSB4 | −37.720546 | −37.792054 | 1.95 |
| MP2-FC/CBSB3 | −37.723028 | −37.800413 | 2.11 |
| CBSQ (0 K) | −37.774664 | −37.828855 | 1.47 |
| CBSQ | −37.772304 | −37.826494 | 1.47 |
| Experimental | | | 1.5 |

Let us now evaluate the IP. The older terminology that is well imbedded in the literature is ionization potential although the more appropriate terminology should be ionization energy. Ionization potential is defined as the minimal energy required to remove an electron from a gaseous atom or molecule in its ground state. Furthermore there are two ionization potentials, vertical and adiabatic. The first is based on Koopman's theorem [13] which suggests that the ionization energy is equal to the orbital energy of the ejected electron. The second is the energy difference between chemical systems with and without electrons. Here we are presenting our results for adiabatic ionization potential and EA for the carbon atom. Experimental values [14] for this system are well established and our computed values are compared to them. The IP for carbon computed with ab initio methods is below the experimental values, although the difference is relatively small. As an illustration, the HF/6-31G(d′) computed IP for carbon is 10.73 eV compared to an experimental value of 11.3 eV (Table 4). By increasing the theory level and size of the basis set, the computed value steadily converges to the experimental value with the CBSQ computed value 0.1 eV lower than the experimental value (Table 4). A different picture is obtained in the case of computation of EA for carbon atoms. The HF as well as MP2 methods compute negative carbon EA. One can argue that this is due to inappropriate basis sets that do not have polarization functionals. This is supported by the fact that MP2 ab initio methods with CBSB3 basis sets compute the carbon EA at 1.21 eV; this is close to the experimental value of 1.26 eV for carbon EA (Table 4). Again, an excellent agreement between computed and experimental values is obtained with the CBSQ ab initio method.

**Table 2.** Total energies (a.u.) for neutral carbon in its singlet, triplet, and pentet state with the enegy diference between the three states (eV) $\Delta E_I$ = [(E-singlet)−(E-triplet)] * 27.2116; $\Delta E_{II}$ = [(E-pentet)−(E-triplet)] * 27.2116

| Theory | E-singlet | E-triplet | E-pentet | $\Delta E_I$ | $\Delta E_{II}$ |
|---|---|---|---|---|---|
| HF/6-31G(d′) | −37.588627 | −37.681355 | −37.587664 | 2.52 | 2.55 |
| HF/6-31G(d′) (0 K) | −37.588627 | −37.681355 | −37.587664 | 2.52 | 2.55 |
| MP2-FC/6-31G(d′) | −37.655957 | −37.734578 | −37.607671 | 2.14 | 3.45 |
| QCISD(T)-FC/6-31 + (d′) | −37.701736 | −37.759794 | −37.615558 | 1.58 | 3.92 |
| MP4SDQ-FC/CBSB4 | −37.687736 | −37.756814 | −37.615235 | 1.88 | 3.85 |
| MP2-FC/CBSB3 | −37.685131 | −37.756035 | −37.621836 | 1.93 | 3.65 |
| CBSQ (0 K) | −37.734707 | −37.785153 | −37.629050 | 1.37 | 4.25 |
| CBSQ | −37.732346 | −37.782792 | −37.626689 | 1.37 | 4.25 |
| Experimental | | | | 1.4 | 4.3 |

**Table 3.** Total energies (a.u.) for the carbon cation in its doublet and quartet state with the energy difference between the three states (eV) $\Delta E_I$ = [(E-quartet)−(E-doublet)] * 27.2116

| Theory | E-doublet | E-quartet | ΔE |
|---|---|---|---|
| HF/6-31G(d′) | −37.287110 | −37.152007 | 3.68 |
| HF/6-31G(d′) (0 K) | −37.287110 | −37.152007 | 3.68 |
| MP2-FC/6-31G(d′) | −37.330619 | −37.160360 | 4.63 |
| QCISD(T)-FC/6-31 + (d′) | −37.356940 | −37.163861 | 5.25 |
| MP4SDQ-FC/CBSB4 | −37.352282 | −37.163605 | 5.13 |
| MP2-FC/CBSB3 | −37.342765 | −37.170620 | 4.68 |
| CBSQ (0 K) | −37.373863 | −37.174350 | 5.43 |
| CBSQ | −37.371503 | −37.171990 | 5.43 |
| Experimental | | | 5.50 |

**Table 4.** Ionization potential (IP) and electron affinities (EAs) for carbon; IP = energy difference between the carbon cation in the doublet and carbon in the triplet state; EA = energy difference between carbon in the triplet and carbon anion in the quartet state

| Theory | IP | EA |
|---|---|---|
| HF/6-31G(d′) | 10.73 | −0.52 |
| HF/6-31G(d′) (0 K) | 10.73 | −0.52 |
| MP2-FC/6-31G(d′) | 10.99 | −0.15 |
| QCISD(T)-FC/6-31 + (d′) | 10.96 | 0.96 |
| MP4SDQ-FC/CBSB4 | 11.01 | 0.96 |
| MP2-FC/CBSB3 | 11.25 | 1.21 |
| CBSQ (0 K) | 11.19 | 1.19 |
| CBSQ | 11.19 | 1.19 |
| Experimental | 11.3 | 1.26 |

The fluorine radical (doublet) and fluorine anion (singlet) have only one logical electronic configuration. Any other arrangement would include a higher shell that would be energetically expensive and thus not explored here. On the other hand, a fluorine radical can have two electronic configurations: a singlet $(2s^22p_x^22p_y^2)$ and triplet $(2s^22p_x^22p_y^12p_z^1)$. The ab initio computed total energies for these two fluorine cation states are presented in Table 5. The triplet electronic configuration is more stable with an energy difference of 2.7 eV (Table 5). As expected the HF, MP2, and MP4 methods computed an energy difference that is substantially high. The QCISD(T) method generates an energy that is near the experimental value, though CBSQ produces the best value (Table 5). It was experimentally determined that the IP and EA for the fluorine atom are 17.4 eV [15] and 3.4 eV [15], respectively. As in the case of the carbon atom, the computed fluorine IP with HF, MP2, MP4, and QCISD(T) is lower than the experimental value (Table 6), but with a large basis set such as CBSB3, even MP2 is capable of generating an IP relatively close to the experimental value. This observation is almost identical for the computed fluorine EA. All theory levels except MP2/CBSB3 compute fluorine EAs that are noticeably lower than the experimental value. Again both the fluorine IP and EA are accurately reproduced with the CBSQ ab initio method (Table 6).

**Table 5.** Total energies (a.u.) for the fluorine cation in its singlet and triplet state with the energy difference between the two states (eV); ΔE = [(E-singlet)−(E-triplet)] * 27.2116

| Theory | E-singlet | E-triplet | ΔE |
|---|---|---|---|
| HF/6-31G(d′) | −98.629152 | −98.789240 | 4.36 |
| HF/6-31G(d′) (0 K) | −98.629152 | −98.789240 | 4.36 |
| MP2-FC/6-31G(d′) | −98.750402 | −98.891503 | 3.84 |
| QCISD(T)-FC/6-31+(d′) | −98.803061 | −98.908551 | 2.87 |
| MP4SDQ-FC/CBSB4 | −98.775093 | −98.907370 | 3.60 |
| MP2-FC/CBSB3 | −98.825130 | −98.963945 | 3.78 |
| CBSQ (0 K) | −98.902004 | −99.000266 | 2.67 |
| CBSQ | −98.899643 | −98.997906 | 2.67 |
| Experimental | | | 2.7 |

Let us now explore the energies of various electronically configured CF compounds with only one carbon atom. The first combination involves anion, neutral, or cationic CF compounds. For the CF anion, the carbon has six electrons that can have two electronic configurations, a singlet or triplet. Their computed total energies are presented in Table 7. To the best of our knowledge, the energy difference between these two electron states of the CF anion are not available, therefore, we are offering our best estimation for this molecular system. Because CBSQ has been proven an accurate method for computing the energies for various molecular systems, we believe that 1.07 eV should be highly accurate for the energy difference between singlet and triplet CF anions. Other ab initio methods compute energy differences that have the same pattern that we observed previously in a computational study of various carbon and fluorine electronic configurations. All other ab initio methods compute higher energy differences between singlet and triplet CF anions than the CBSQ estimated energy (Table 7). For a neutral CF molecule there are two possible electron configurations a doublet or quartet. One can assume that the electronic system has a maximal number of unpaired electrons and should be the most stable. However, ab initio calculations

**Table 6.** Total energies (a.u.) for the fluorine anion ($E_A$) in a singlet, fluorine radical ($E_R$) in a doublet state, and fluorine IP EA; IP = energy difference between the fluorine cation in its triplet state and the fluorine radical in its doublet state

| Theory | $E_A$ | $E_R$ | IP | EA |
|---|---|---|---|---|
| HF/6-31G(d′) | −99.350717 | −99.363827 | 15.64 | −0.36 |
| HF/6-31G(d′) (0 K) | −99.350717 | −99.363827 | 15.64 | −0.36 |
| MP2-FC/6-31G(d′) | −99.541442 | −99.507612 | 16.77 | 0.92 |
| QCISD(T)-FC/6-31+(d′) | −99.639920 | −99.530718 | 16.93 | 2.97 |
| MP4SDQ-FC/CBSB4 | −99.637199 | −99.528794 | 16.91 | 2.95 |
| MP2-FC/CBSB3 | −99.724816 | −99.598561 | 17.26 | 3.44 |
| CBSQ (0 K) | −99.766723 | −99.642288 | 17.47 | 3.39 |
| CBSQ | −99.764363 | −99.639927 | 17.47 | 3.39 |
| Experimental | | | 17.4 | 3.4 |

**Table 7.** Total energies (a.u.) for the CF anion in its singlet and triplet states with the energy difference between the two states (eV); ΔE = [(E-singlet)−(E-triplet)] * 27.2116

| Theory | E-singlet | E-triplet | ΔE |
|---|---|---|---|
| HF/6-31G(d′) | −137.050439 | −137.136824 | 2.35 |
| HF/6-31G(d′) (0 K) | −137.048556 | −137.135035 | 2.35 |
| MP2-FC/6-31G(d′) | −137.342685 | −137.409735 | 1.82 |
| QCISD(T)-FC/6-31+(d′) | −137.444886 | −137.488694 | 1.19 |
| MP4SDQ-FC/CBSB4 | −137.432459 | −137.479291 | 1.27 |
| MP2-FC/CBSB3 | −137.532017 | −137.580147 | 1.31 |
| CBSQ (0 K) | −137.611575 | −137.650986 | 1.07 |
| CBSQ | −137.608180 | −137.647577 | 1.07 |

**Table 8.** Total energies (a.u.) for the neutral CF in its doublet and quartet states with the energy difference between the two states (eV); ΔE = [(E-quartet)−(E-doublet)] * 27.2116

| Theory | E-doublet | E-quartet | ΔE |
|---|---|---|---|
| HF/6-31G(d′) | −137.167380 | −137.085748 | 2.22 |
| HF/6-31G(d′) (0 K) | −137.164196 | −137.082663 | 2.22 |
| MP2-FC/6-31G(d′) | −137.442109 | −137.326533 | 3.15 |
| QCISD(T)-FC/6-31+(d′) | −137.479987 | −137.356354 | 3.36 |
| MP4SDQ-FC/CBSB4 | −137.471082 | −137.350009 | 3.30 |
| MP2-FC/CBSB3 | −137.568706 | −137.450009 | 3.23 |
| CBSQ (0 K) | −137.636487 | −137.504915 | 3.58 |
| CBSQ | −137.633171 | −137.501597 | 3.58 |

suggest that the doublet CF radical is more stable than the quartet. The ab initio methods do not agree with the experimental energy difference between these two electronic states (see Table 8). The value we trust is 3.58 eV, as computed by the CBSQ ab initio method. As usual, the most deviance from this value is observed with the HF computational study, while MP2, MP4, and QCISD(T) computed an energy difference that is close to CBSQ values. By elimination of one electron from the neutral CF doublet and quartet, the CF singlet and triplet cation can be obtained. By analogy one can argue that the order of stability should be preserved and the singlet electronic state should be more stable. One can also argue that the energy difference between these two electronic states should be higher than in neutral CF. This was observed just as neutral CF is higher than anionic CF. The latter can be explained by the fact that orbitals for cations are much lower in energy than for anions. Our reasoning is fully supported by ab initio computational studies. All ab initio methods find the singlet CF cation more stable than the triplet CF cation (Table 9). The estimated energy difference is higher than in both the CF anion and radical. The CBSQ energy difference is 4.85 eV (Table 9). Both IPs and EAs for CF neutral molecules are experimentally known [14, 16] and therefore a direct comparison with our computed values was possible. As expected on the basis of our previous computational results, HF and MP2 methods, with a relatively small basis set 6-31G(d′), computed the IP and EA substantially below the experimental value. The EAs are predicted as negative (Table 10). Results closer to experimental values are obtained with the MP2 method when a relatively large basis set (CBSB3) was used. The best agreement between computed and experimental values was again obtained with the CBSQ ab initio method (Table 10).

For $CF_2$ the cation and anion are in a doublet electronic state, while the neutral molecule is a carbene. Carbenes are quite a reactive species that are commonly used in organic synthesis for producing the cyclopropane ring. The stereochemistry of the cyclopropane ring requires the carbene electronic configuration [17]. The computed energy difference for singlet and triplet difluorocarbene is presented in Table 11. According to all ab initio methods singlet carbene is predicted to be more stable. The energy gap between triplet and singlet difluorocarbene varies with theory level. We believe the value of 2.47 eV predicted by the CBSQ ab initio method to be the most accurate. Other ab initio methods compute a lower energy gap with the HF value at only 1.36 eV (Table 11). IP [14] and EA [18] are available for singlet difluorocarbene. As expected, the CBSQ

**Table 9.** Total energies (a.u.) for the CF cation in its singlet and triplet states with the energy difference between the two states (eV); $\Delta E = [(E\text{-triplet})-(E\text{-singlet})]*27.2116$

| Theory | E-singlet | E-triplet | ΔE |
|---|---|---|---|
| HF/6-31G(d′) | −136.843512 | −136.712576 | 3.56 |
| HF/6-31G(d′) (0 K) | −136.839043 | −136.708584 | 3.55 |
| MP2-FC/6-31G(d′) | −137.126766 | −136.959111 | 4.56 |
| QCISD(T)-FC/6-31 + (d′) | −137.155523 | −136.980271 | 4.77 |
| MP4SDQ-FC/CBSB4 | −137.145978 | −136.971611 | 4.74 |
| MP2-FC/CBSB3 | −137.239174 | −137.071414 | 4.57 |
| CBSQ (0 K) | −137.301978 | −137.123751 | 4.85 |
| CBSQ | −137.298672 | −137.120444 | 4.85 |

**Table 10.** IP and EAs for CF; IP = energy difference between the CF cation in its singlet state and CF in the doublet state, EA = energy difference between CF in the doublet and the CF anion in the triplet state

| Theory | IP | EA |
|---|---|---|
| HF/6-31G(d′) | 8.85 | −0.79 |
| HF/6-31G(d′) (0 K) | 8.85 | −0.79 |
| MP2-FC/6-31G(d′) | 8.58 | −0.88 |
| QCISD(T)-FC/6-31 + (d′) | 8.83 | 0.24 |
| MP4SDQ-FC/CBSB4 | 8.85 | 0.22 |
| MP2-FC/CBSB3 | 8.97 | 0.31 |
| CBSQ (0 K) | 9.10 | 0.39 |
| CBSQ | 9.10 | 0.39 |
| Experimental | 9.11 | 0.45 |

**Table 11.** Total energies (a.u.) for the $CF_2$ carbene in its singlet and triplet states with the energy difference between the two states (eV); $\Delta E = [(E\text{-triplet})-(E\text{-singlet})]*27.2116$

| Theory | E-singlet | E-triplet | ΔE |
|---|---|---|---|
| HF/6-31G(d′) | −236.652249 | −236.601924 | 1.37 |
| HF/6-31G(d′) (0 K) | −236.644509 | −236.594458 | 1.36 |
| MP2-FC/6-31G(d′) | −237.143760 | −237.061500 | 2.24 |
| QCISD(T)-FC/6-31 + (d′) | −237.192738 | −237.105890 | 2.36 |
| MP4SDQ-FC/CBSB4 | −237.179169 | −237.094393 | 2.31 |
| MP2-FC/CBSB3 | −237.374107 | −237.289345 | 2.31 |
| CBSQ (0 K) | −237.475757 | −237.385056 | 2.47 |
| CBSQ | −237.471827 | −237.381037 | 2.47 |

**Table 12.** Total energies (a.u.) for the difluoromethylene anion ($E_A$), difluoromethylene cation ($E_C$) both in the doublet state, and difluoromethylene IP and EA; IP = energy difference of the fluorine cation in its triplet state and the fluorine radical in the doublet state

| Theory | $E_A$ | $E_C$ | IP | EA |
|---|---|---|---|---|
| HF/6-31G(d′) | −236.617088 | −236.278889 | 10.16 | −0.96 |
| HF/6-31G(d′) (0 K) | −236.611882 | −236.269670 | 10.20 | −0.89 |
| MP2-FC/6-31G(d′) | −237.101675 | −236.753215 | 10.63 | −1.15 |
| QCISD(T)-FC/6-31 + (d′) | −237.192839 | −236.782527 | 11.16 | 0.00 |
| MP4SDQ-FC/CBSB4 | −237.179092 | −236.768841 | 11.17 | 0.00 |
| MP2-FC/CBSB3 | −237.373635 | −236.965346 | 11.12 | −0.01 |
| CBSQ (0 K) | −237.481607 | −237.054502 | 11.46 | 0.16 |
| CBSQ | −237.477430 | −237.050578 | 11.46 | 0.15 |
| Experimental | | | 11.4 | 0.18 |

**Table 13.** Total energies (a.u.) for the trifluoromethyl $E_A$, the radical ($E_R$), and $E_C$ the radical IP and EA; IP = energy difference between the fluorine cation in its triplet state and the florine radical in its doublet state

| Theory | $E_A$ | $E_R$ | $E_C$ | IP | EA |
|---|---|---|---|---|---|
| HF/6-31G(d′) | −336.108475 | −336.119368 | −335.798133 | 8.74 | −0.30 |
| HF/6-31G(d′) (0 K) | −336.097882 | −336.105825 | −335.782097 | 8.81 | −0.22 |
| MP2-FC/6-31G(d′) | −336.803608 | −336.791894 | −336.485287 | 8.34 | 0.32 |
| QCISD(T)-FC/6-31+(d′) | −336.905335 | −336.846687 | −336.519530 | 8.90 | 1.60 |
| MP4SDQ-FC/CBSB4 | −336.887997 | −336.831170 | −336.502832 | 8.93 | 1.55 |
| MP2-FC/CBSB3 | −337.176567 | −337.121768 | −336.797526 | 8.82 | 1.49 |
| CBSQ (0 K) | −337.316517 | −337.251731 | −336.917423 | 9.09 | 1.76 |
| CBSQ | −337.311918 | −337.247368 | −336.913217 | 9.09 | 1.76 |
| Experimental | | | | ~8.9 | 1.8 |

computed energies are almost identical to the experimental values (Table 12), though other ab initio methods underestimate these two energies. It is obvious that the HF ab initio calculation should be avoided for computing both IPs and EA for fluorinated alkanes.

Finally, let us evaluate IPs and EAs for the trifluoromethyl radical. The logical electronic state for the trifluoromethyl anion is (a singlet), the trifluoromethyl radical (a doublet), and the trifluoromethyl cation (a singlet). Therefore, the energy gaps between various electronic configurations of the same chemical system can not be computed. The IPs and EAs for the $CF_3$ radicals are experimentally estimated [14, 19]. The same pattern observed in other CF compounds is presented here. The CBSQ computed EA is identical to the experimental value while all other ab initio methods produce smaller values. The IP for the $CF_3$ radical was not accurately evaluated and is believed to be 8.9 eV or slightly higher. We have estimated that this value should be 9.09 eV (Table 13). Again all other computational methods predict the $CF_3$ IP to be lower.

In many of our previous studies we have demonstrated that density functional and CBS ab initio methods accurately compute bond dissociation energies for various chemical systems [20], although we have never explored the accuracy of the CBSQ ab initio method in computing the bond dissociation energies for charged molecular systems. Here we present our computational study of fluorinated methyl cations; the values are presented in Table 14. Before we discuss the accuracy of ab initio methods for computation of the bond dissociation energies, it should be pointed out that experimental values have an experimental error of ±0.2 eV at a minimum [21]. The CBSQ computed values for all three CF cations are higher than the experimental values. The difference is around 0.3 eV. Since CBSQ is a highly accurate computational method, we believe that the experimental values for CF cations should be corrected and the C-F bond dissociation energies should be 6.0 eV for $CF_3^+$, 3.0 eV for $CF_2^+$, and 7.8 eV for $CF^+$ (Table 14). The other ab initio values obtained do not predict adjacent energies to what is proposed for C-F bond dissociation energies.

**Table 14.** Bond dissociation energies (eV) for homolytic C-F bond breaking in various fluorinated cations

| Theory | $CF_2^+$ | $CF_2^+$ | $CF^+$ |
|---|---|---|---|
| HF/6-31G(d′) | 4.23 | 1.95 | 5.24 |
| HF/6-31G(d′) (0 K) | 4.04 | 1.82 | 5.12 |
| MP2-FC/6-31G(d′) | 6.11 | 3.23 | 7.85 |
| QCISD(T)-FC/6-31+(d′) | 5.61 | 2.62 | 7.29 |
| MP4SDQ-FC/CBSB4 | 5.58 | 2.56 | 7.21 |
| MP2-FC/CBSB3 | 6.36 | 3.47 | 8.10 |
| CBSQ (0 K) | 6.00 | 3.00 | 7.78 |
| CBSQ | 6.06 | 3.05 | 7.82 |
| Experimental | 5.9 | 2.7 | 7.5 |

## 4 Conclusion

In conclusion, the CBSQ ab initio method is very accurate in the computation of energetic properties of carbon and fluorine molecular systems. The total energies are computed with an estimated energy difference between various electronic states. In some cases there is a lack of experimental data, therefore the obtained values can be used by experimentalist as a reference point. The IPs and EA computed for these systems are identical to the experimental values, confirming that CBSQ is extraordinary reliable for computational energies. The computed C-F bond dissociation energies for $CF_3^+$, $CF_2^+$, and $CF^+$ cations are slightly higher than previously estimated experimentally. Considering the high accuracy of the CBSQ ab initio method it is suggested that the C-F bond dissociation energies for $CF_3^+$, $CF_2^+$, and $CF^+$ are 6.0, 3.0 and 7.8 eV, respectively.

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