



DFT study on the one-electron reduction of CF_3X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) molecules

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ABSTRACT

We present the DFT study on several aspects of the process of one-electron attachment to the CF_3X molecules accompanied by C–X bond dissociation. Three functionals, B3PW91, MPW1PW91 and PBE1PBE, combined with 6-31 + G*, 6-311 + G* and AUG-cc-pVTZ basis sets were used. Dipole moments and adiabatic electron affinities of neutral molecules as well as structural and energetic properties of both forms obtained from the calculations are compared to experimental data. Averaged electron affinity values of 0.45 eV (CF_3Cl), 0.89 eV (CF_3Br) and 1.26 eV (CF_3I) are obtained from the DFT/AUG-cc-pVTZ results. Structural properties of meta-stable anions formed in the gas-phase are found to depend weakly on the X atom, except for the C–X bond lengths, for which we propose d_{CX} values of 2.615 Å for CF_3Cl^- , 2.733 Å for CF_3Br^- and 2.911 Å for CF_3I^- . All harmonic vibrational frequencies are much lower in anions than in molecules. For the radical anions the larger basis sets yield almost identical C–Cl and C–I dissociation energies (~ 0.48 eV with AUG-cc-pVTZ), while C–Br energy is smaller by about 0.03 eV. The smallest basis set suggests similar values but opposite order, i.e. C–Br bond is the strongest, followed by C–Cl and the weakest C–I. The dissociation energies and electron affinities are compared with results obtained with the *Gn* and CBS-QB3 methods. Average energy barriers for the gas-phase reduction process obtained from the intersection of AUG-cc-pVTZ potential energy profiles for the molecules and anions are equal to: 0.34 eV (CF_3Cl), 0.23 eV (CF_3Br) and 0.13 eV (CF_3I).

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1. Introduction

Trifluoromethyl halides, due to their wide-ranging applications in many areas of human life as well as to negative side-effects related to their toxicity and destructive influence on ozone layer, are very important compounds and many scientific works are focused on their various properties and reactions. One of such processes is an electron attachment to the CF_3X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) molecules, which first results in formation of radical anions CF_3X^- , and these dissociate fast to the radical CF_3 and the halide anion X^- . A number of experimental works [1–38] were devoted to explore many aspects of these reactions. Also theoretical techniques were applied to obtain more detailed information about the reactants and the reduction process [34–58]. However, an inspection of the measured and calculated results reveals inconsistency of some estimates and very limited knowledge about others. This especially applies to the radical anions CF_3X^- , which are formed in the reaction course.

In a very few works the energy profiles with respect to the C–X bond length for the CF_3X molecules and anions were studied. In the work of Bertan et al. [45] such theoretical analysis (MP2 method with 4-31G* basis set) was performed for the CF_3Cl system in the

gas-phase and in polar solution. The solvent was modeled as dielectric continuum with dielectric constant $\epsilon = 37$ introduced directly into the quantum calculations. A strong effect of polar solvents was observed mainly on the radical anion profile, which in the gas-phase exhibited very clear energy minimum (about -0.425 eV if the total energy of final products, CF_3 and Cl^- , is taken as a reference level), but in the solution the minimum disappears. In that work the energy barrier for the reduction process in the gas-phase was evaluated as about 0.7 eV.

More extended studies on this subject were undertaken by German and Tikhomirov [51,52], who examined larger number of polyhalogen methanes, among them CF_3Cl and CF_3Br molecules, using the semiempirical PM3 method. In [51] the potential energy surfaces in the gas-phase were presented, while in [52] the continuum approximation was used to take into account the solvation effect. The results obtained with the semiempirical method for the CF_3Cl system differ significantly from finding of Bertan et al. [45]. On the energy profiles presented in [51] for the CF_3Cl^- anion in vacuo and also in [52] for the same anion in the solvent (a mixture of water with acetonitrile characterized with $\epsilon = 52$) one finds two minima, first deeper at $d_{\text{CCl}} = 2.1$ Å, and the second, much weaker, at $d_{\text{CCl}} = 2.8$ Å. According to those semiempirical calculations the first minimum corresponds to the stable anion radical having a structure similar to that in the molecule, while the second minimum results from inversion of the CF_3 part and its weak inter-

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action with the X^- anion. Similar shape of the energy surface in solution was observed for the anion CF_3Br^- . From comparison of these curves with the anion free energy surface in the gas-phase the authors concluded that in the case of perfluoromethyl halides solvation has a rather small effect on the anion profiles, in contrary to the CH_3X molecules also studied in that work.

In a very recent work of Fabrikant and Hotop [39] the R-matrix theory was used to study dissociative attachment of electron to perfluoromethyl halides. The anion potential energy profiles presented there for anions exhibit only one minimum, but details are not discussed.

In this paper the problem of the energy profiles characterizing the process of reduction of CF_3X molecules in the gas-phase is re-examined using selected DFT methods and basis sets. The main goal is to evaluate the energy barriers for these reaction. The most important properties of the CF_3X ($X = Cl, Br, I$) molecules and the corresponding radical anions are also analyzed and compared to experimental and theoretical data available in the literature.

2. Method

In all calculations the C_{3v} geometry was assumed for the molecule and anion, as shown in Fig. 1. The structures were fully optimized by means of bond lengths and angles, respecting the limitations imposed by the C_{3v} symmetry. Three hybrid DFT methods, namely B3PW91 [59,60], MPW1PW91 [60,61] and PBE1PBE [62], were used in combination with three basis sets describing the atoms C, F, Cl, Br: 6-31 + G(d), 6-311 + G(d) and the very large AUG-cc-pVTZ. For the iodide the pseudopotential CEP-4G was used. These methods were selected on the basis of more extended tests performed also with other density functional and basis sets. All calculations were performed using the Gaussian 03 package [63]. The construction of the energy profiles in vacuo included full geometry optimization of the CF_3 part of the system for each CX distance.

Since experimental values available for these systems are often scattered in a relatively wide range, to verify quality of the DFT methods some additional calculations were performed at the G1 [64,65], G2 [66], G3 [67] and CBS-QB3 [68,69] levels available in the Gaussian 03 package. These are the quantum chemistry composite methods which are expected to yield very accurate energies, therefore we used them to calculate bond dissociation energies and electron affinities for the two smaller molecules.

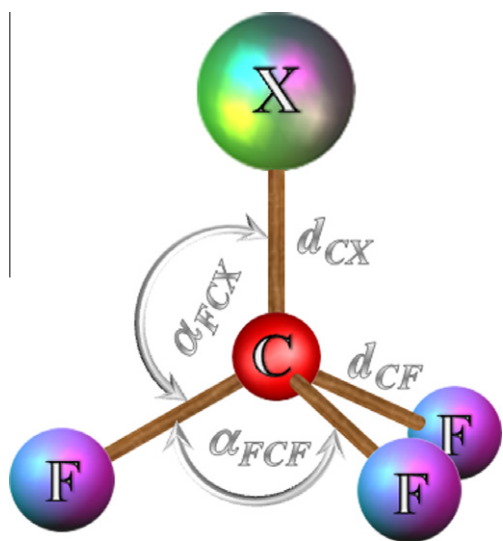


Fig. 1. C_{3v} structure of the CF_3X molecules and anions.

3. Results

3.1. Structural properties of CF_3X molecules and anions

In Table 1 we present the C–X bond lengths obtained from our calculations for the molecules and anions. For comparison, experimental and also theoretical results reported in earlier works are also listed in this table. As can be seen, the reference experimental values for the C–X bond lengths in neutral molecules are scattered in relatively wide intervals, which in fact should be widened by the measurements uncertainty of about 0.02–0.04 Å suggested by the authors. The calculated d_{CX} are more consistent and most of them approach the upper limit set by experimental value. For CF_3Cl and CF_3Br molecules larger basis sets usually predict longer C–X bonds. Exactly opposite trend is observed for CF_3I , which might be an effect of using different basis sets for the iodine atom and the CF_3 part. For this system values obtained with 6-31 + G^* and 6-311 + G^* functions describing CF_3 are too high and only with a very large basis set AUG-cc-pVTZ d_{CI} approach the measured estimates. Some additional tests were performed using for the iodine atom the LANL2DZ pseudopotential, but the results are very similar to those obtained with the CEP-4G description. The average values obtained from all results presented in Table 1 are: 1.759 Å for C–Cl, 1.928 Å for C–Br and 2.164 Å for C–I. The two former numbers are in excellent agreement with experimental values obtained by Typke and Dakkouri [5], Coles and Hughes [1] and Cox et al. [6], while the latter is higher. The averages calculated only from the AUG-cc-pVTZ results are equal to 1.762 Å (CF_3Cl), 1.933 Å (CF_3Br) and 2.149 Å (CF_3I); the latter value is very close to the estimate of 2.1438 Å proposed by Cox et al. [6].

An inspection of all structural parameters of neutral molecules shows that the C–X bond is the most sensitive to the method of calculation, as the differences between the highest and the lowest value obtained for a given molecule reach from 1.1% to 1.5% (calculated with respect to the lowest value). The differences in other parameters, namely the C–F bond lengths and the angles FCF and FCX are much smaller: less than 0.9% for d_{CF} and around 0.1–0.2% for the two angles. Therefore, in Table 2 only the results obtained with one method, namely PBE1PBE/AUG-cc-pVTZ, are shown. According to our calculations, except for the C–X bond length, other structural parameters of CF_3Br and CF_3I molecules are almost identical and the differences are less than 0.2%.

The agreement between the DFT and experimental results for the neutral molecules is promising with respect to evaluation of similar properties of the corresponding radical anions. Their existence in the gas-phase was observed in a number of measurements [17,31–33,35,38], nevertheless their structural properties could not be measured and the only source of information on this subject are theoretical works. In the past most often the calculations were performed for the smallest CF_3Cl system and only two groups performed comparative studies for all three molecules. The results obtained in the present work at the DFT level differ significantly from the values obtained by Roszak et al. [41,42] in their MP2 calculations. It can be seen in Table 1 that all methods tested in the present work predict the C–X bonds in radical anions to be longer than most earlier calculations. Only for the CF_3Cl^- anion two larger estimates were reported, one obtained by Roszak et al. [42] with the B3LYP density functional, which is relatively close to our results, and the highest one found by Bertran et al. [45] at the MP2 level with a rather small basis set 4-31G. Again we calculated average values of d_{CX} from the AUG-cc-pVTZ results and these are: 2.615 Å for CF_3Cl^- , 2.733 Å for CF_3Br^- and 2.911 Å for CF_3I^- . In general the structural parameters obtained for the anions are more sensitive to the methods used than for the molecules, the differences between the highest and lowest values ranging from 1.1% to 1.2% for d_{CF} , and from 0.45% to 0.65% for the two angles.

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