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# Structure and stability of the $CF_3^{2+}$ dication

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## Abstract

The structure of the $CF_3^{2+}$ dication was studied by means of different ab initio methods. The previously reported $D_{3h}$ structure was found to be a minimum only at the Hartree–Fock level, while it corresponds to a higher order saddle point on correlated potential energy surfaces. The calculated adiabatic ionization energy for $CF_3^{2+}$ leading to a $C_{2v}$ symmetric dication of 26.80 eV is in very good agreement with the experimental value of 26.30 ± 0.4 eV. (Int J Mass Spectrom 185/186/187 (1999) 701–706) © 1999 Elsevier Science B.V.

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## 1. Introduction

Long-lived molecular dications have attracted considerable attention from both experimentalists [1,2] and theoreticians [3,4] during the past two decades. These dications sometimes exhibit unusual structures and reactivities and not only in this context they represent a challenging topic in gas phase ion chemistry. The $CF_n^+$ and $CF_n^{2+}$ series of cations and dications [5] are of particular interest, e.g. because of their importance in plasma etching processes [6,7]. Furthermore, it is believed that $CF_n^{X+}$ ions play a key role in the depletion of ozone in the outer atmosphere [8].

Recently we have shown that discrepancies in the thermochemical data for the $CF_2^{2+}$ dication can be solved by highly accurate quantum chemical calculations [9]. Such discrepancies do seemingly not appear for the energetics of the $CF_3^{2+}$ dication. The first measurements of appearance energies (AE) of $CF_3^{2+}$ led to 42.7 ± 0.3 eV [10]. This value was slightly refined by more recent measurements which resulted in an AE ($CF_3^{2+}$) of 41.8 ± 0.3 eV [11]. Beynon and co-workers [12] determined the ionization energy (IE) of $CF_3^{2+}$ as 26.3 ± 0.4 eV by a direct $Q_{\min}$ measurement using the charge stripping technique. Later, the reactivity of $CF_n^{2+}$ dications was studied by Leone and co-workers [13–15] in collision experiments with a series of collision gases. These reactions led for the $CF_3^{2+}$ ion only to dissociative charge transfers and contrary to the $CF_2^{2+}$ ion, no ionization energy of the singly charged cation could be derived. Nothing is known about the structure of the $CF_3^{2+}$ ion from spectroscopic measurements. However, interesting

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Dedicated to Professor Mike Bowers on the occasion of his 60th birthday.

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features are expected because of its complicated electronic structure.

The probably most recent ab initio and density functional theory (DFT) calculations on $CF_3^{2+}$ were carried out by de la Vega and San Fabian at rather modest levels of theory, i.e. the uncorrelated Hartree–Fock (HF)/6-31G* [16] level and with electron correlation partially included through second order Møller-Plesset perturbation theory (MP2/6-31G*) [17]. In both cases the $CF_3^{2+}$ dication was reported to be a highly symmetric, planar molecule possessing $D_{3h}$ point group symmetry. This is in strong disagreement with our recent findings, where higher level ab initio calculations point to a $C_{2v}$ distorted structure of this species [9]. This discrepancy motivated us, besides the chemical interest intrinsic to this system, to consider a closer examination of the problem.

A full configuration interaction (CI) treatment is obviously invariant to the choice of the molecular orbital basis. However, practical calculations are limited to a truncated CI or similar approaches and consequently the results are heavily dependent on the reference orbital set used. In addition, for open shell systems, symmetry broken (SB) Hartree–Fock solutions (i.e. solutions where the wave function has a lower symmetry than the underlying molecular skeleton) may artificially stabilize distorted molecular frames even at correlated levels of calculation. It refers to the fact, that the exact wave function is symmetry adapted (SA), while for approximate variational wave functions the symmetry adaptation represents a further constrain which may lead only to a higher energy [18]. The advantages and disadvantages of the use of SA and SB wave functions have been intensively discussed in the literature, e.g. in a excellent review by Paldus and Cizek [19] and, very recently, by Ayala and Schlegel [20].

On the other hand, the existence of symmetry distorted molecular frames of polyatomic molecules described by Jahn-Teller and pseudo-Jahn-Teller effects is well documented and understood [21]. Because of its electronic structure (see below) the $CF_3^{2+}$ dication is a suitable candidate for such an investigation. It was already noted by de la Vega [16] that the use of a SB wave function leads to lower HF energies and stretches the CF bonds in the $D_{3h}$ symmetrical $CF_3^{2+}$. The discrepancy between the reported $D_{3h}$ structure of the $CF_3^{2+}$ dication and our own findings which point to a $C_{2v}$ distorted skeleton [9] could be a reflection of the symmetry broken HF reference in the correlated calculation. Recently we have been able to show that the single-reference based coupled cluster ansatz with single and double excitations and a perturbative estimate of the triple excitations (CCSD(T)) [22] is suitable to eliminate almost completely the effect of symmetry breaking in $HOOH^+$ [23]. Nevertheless, it is not a priori clear if the $C_{2v}$ structure is not intrinsic to the system and if phenomena like pseudo Jahn-Teller effects (i.e. coupling between the ground and excited states) are possibly active. In this communication we report a theoretical investigation of the $CF_3^{2+}$ dication with particular emphasis on distortions to lower point group symmetries.

## 2. Computational details

The calculations were performed with the GAUSSIAN'94 [24] and MOLPRO96 [25] program packages as installed on IBM, HP and CRAY computers. Dunning's correlation consistent triple-zeta basis set (cc-pVTZ) with two sets of *d*- and one set of *f*-type polarization function as implemented in the GAUSSIAN'94 and MOLPRO96 programs was used for these purposes [26]. It is well established that a basis set of at least this size are required for a quantitatively reasonable description of structures and energies in correlated ab initio calculations [27].

In anticipation of the possible occurrence of symmetry breaking we used two entirely different approaches i.e. the CCSD(T) method and the popular (unrestricted) B3LYP [28] parametrized hybrid density functional method [29], which involves a semi-empirical combination of the "*exact*" and gradient-corrected Becke exchange [30] together with Lee-Yang-Parr correlation [31] functionals. This approach, includes, albeit in an only approximate manner, exchange and correlation effects. Even in very pathological cases, where other single reference based methods fail, these two approaches were found rather insensitive to symmetry breaking [20,23,32].

For the CCSD(T) calculations the unrestricted Hartree-Fock (UHF) based strategy as implemented in GAUSSIAN94 as well as the MOLPRO96 R-CCSD(T) code [33] employing restricted open-shell Hartree–Fock (ROHF) reference orbitals were used. All but the 1s electrons of the carbon and fluorine atoms were correlated in the CCSD(T) calculations. The geometry was fully optimized at these levels, using numerical first and second derivatives of the energy. The harmonic frequencies were calculated with the UCCSD(T) code of the GAUSSIAN94 program using an analogues procedure based on numerical differentiation.

For the HF and B3LYP methods the geometry was optimized and the harmonic frequencies calculated using analytical first and second derivatives of the corresponding energies. From previous studies we expect reasonable B3LYP geometries [34–36] and the comparison of the two different approaches in calculating the harmonic frequencies should lead to further insight. All calculations were performed exploiting the highest possible abelian symmetry point group, i.e. $C_{2v}$ even though the full point groups, including $C_{3v}$ and $D_{3h}$, were used as symmetry restrictions in the structure determinations, were indicated. Symmetry adapted and symmetry broken wave functions were used as initial guesses in order to account for the effect of electronic symmetry breaking.

## 3. Results and discussion

The Jahn-Teller effect in $CF_4^+$ and the stability towards the dissociation in $CF_3^+$ and F is widely studied theoretically [16,17,37] and experimentally [38–41]. The threefold degenerate ground state ($^2T_1$) of $CF_4^+$ is above (0.65 eV) the dissociation limit of $CF_3^+ + F$ [41]. de la Vega and San Fabian [17] investigated this process at the correlated (MP2) ab initio level in the context of the Jahn-Teller distortion. In this study, the authors reported only the $D_{3h}$ symmetrical structures of $CF_3^+$ ($^1A_1'$ state) and $CF_3^{2+}$ ($^2A_2'$ state). Since this state of the dication is not spatially degenerate, no (first order) Jahn-Teller effect is expected. The ionization process induced large changes in the C–F bond length. At the MP2/6-31G* level of theory $r_{CF} = 1.246$ Å in $CF_3^+$ which increases to 1.270 Å in $CF_3^{2+}$ [17]. Further, the UHF/6-31G** computed geometries of the $CF_3^{2+}$ dication were largely dependent on the wave function used. The calculation using symmetry adapted orbitals resulted in $r_{CF}$ of 1.219 Å, while use of the SB reference led to $r_{CF}$ of 1.244 Å. The UHF energy gap between the SA and SB structures was found to be 46.3 m Hartree or 29 kcal mol$^{-1}$ accompanied by a somewhat larger spin contamination ($\langle S^2 \rangle = 0.783$) for the SA case. Further, calculation employing the SB wave function leads to an unphysical and huge dipole moment (2.183 D) indicating a charge localization within the $D_{3h}$ symmetry of the molecular frame. Of course, the SA calculation results in a vanishing dipole moment.

The geometry-optimized structures resulting from our calculations are summarized in Table 1. Using the cc-pVTZ basis set we nicely reproduce the SCF symmetry-breaking behavior reported earlier [17]. For the $D_{3h}$ structure ($^2A_2'$ state) the bond length are 1.210 Å (SA) and 1.246 Å (SB) with an energy gap of 45.1 m Hartree. However, the problem seemingly disappears at the correlated levels. No differences could be found at the B3LYP level for the SA and SB solutions, akin to the results described in [20]. Both calculations gave $r_{CF} = 1.246$ Å and identical total energies. The $\langle S^2 \rangle$ expectation value of 0.755 indicate that spin contamination is almost negligible. The B3LYP optimized structure is virtually identical with the result of the CCSD(T) calculation ($r_{CF} = 1.248$ Å). No differences were found between the results of the UCCSD(T) calculation performed based on SA and/or SB SCF solutions ($\langle S^2 \rangle = 0.789$ and $\langle S^2 \rangle = 0.752$, respectively) using the GAUSSIAN program and the corresponding RCCSD(T) SA calculation using the MOLPRO package. Regarding the use of UHF or ROHF single determinant wave functions for the post-SCF calculations one may find contradicting opinions in the literature [22,42]. It is often stated, that the UHF spin orbitals are superior to the ROHF MO's. On the other hand, examples might be pre-

Table 1
Equilibrium geometries (Å and degrees), computed total energies [$E_h$] and expectation values of the $S^2$ operator for $CF_3^+$ and $CF_3^{2+}$ evaluated at the UHF, RHF, B3LYP, RCCSD(T), and U-CCSD(T) levels with the cc-pVTZ basis set

| Method | | | $E_{tot}$ | $\langle S^2 \rangle$ | $r_{CF}$ | $r_{CF*}$ | $\omega$ |
|---|---|---|---|---|---|---|---|
| $CF_3^+$ ($^1A_1'$) | RB3LYP | $D_{3h}$ (SA) | −337.363 771 | ··· | 1.236 | ··· | 120.0 |
| | RCCSD(T) | $D_{3h}$ (SA) | −336.850 232 | ··· | 1.233 | ··· | 120.0 |
| $CF_3^{2+}$ ($^2A_2'$) | UHF | $D_{3h}$ (SA) | −334.972 416 | 0.785 | 1.210 | ··· | 120.0 |
| | UHF | $D_{3h}$ (SB) | −335.017 540 | 0.753 | 1.246 | ··· | 120.0 |
| | UB3LYP | $D_{3h}$ (SA/SB) | −336.442 114 | 0.755 | 1.246 | ··· | 120.0 |
| | RCCSD(T) | $D_{3h}$ (SA) | −335.911 298 | ··· | 1.248 | ··· | 120.0 |
| | UCCSD(T) | $D_{3h}$ (SA/SB) | −335.911 882 | 0.789 | 1.248 | ··· | 120.0 |
| $CF_3^{2+}$ ($^2B_2$) | RHF | $C_{2v}$ (SA) | −335.067 454 | ··· | 1.158 | 1.514 | 110.1 |
| | UHF | $C_{2v}$ (SA) | −335.072 924 | 0.757 | 1.158 | 1.516 | 109.4 |
| | UB3LYP | $C_{2v}$ (SA) | −336.447 184 | 0.753 | 1.186 | 1.564 | 109.9 |
| | RCCSD(T) | $C_{2v}$ (SA) | −335.933 308 | ··· | 1.186 | 1.552 | 109.9 |
| | UCCSD(T) | $C_{2v}$ (SA) | −335.933 842 | 0.759 | 1.186 | 1.552 | 109.9 |

sented in which the UHF reference fails to describe the shape of the surface of the equilibrium region as soon as the spin contamination becomes severe. However, this is not the case in the present calculations and all three CC calculations lead basically to the same results.

If the $D_{3h}$ symmetry restriction is removed in the geometry optimization a $C_{2v}$ symmetric minimum in a $^2B_2$ state (antisymmetric with respect to the mirror plane $\sigma'$ perpendicular to the planar molecule) is smoothly reached. This structure is characterized by two short ($r_{CF}$ = 1.186 Å) and one long ($r_{CF}$ = 1.564 Å) CF bonds at the DFT level. The structures obtained from the CCSD(T) methods are very similar and actually yield identical results whether the restricted Hartree-Fock (RHF) or a UHF determinant is used as the reference: $r_{CF}$ = 1.186 Å and $r_{CF}$ = 1.552 Å. As expected, the uncorrelated UHF and ROHF calculations lead to qualitatively similar pictures, only the bond distances are in general somewhat shorter (see Table 1). Most importantly, the $C_{2v}$ structure is in all cases more stable than the corresponding $D_{3h}$ one. This stabilization is rather huge at the UHF level, amounting to 63.1 and 34.7 kcal/mol with the symmetry adapted and symmetry broken wave functions, respectively. In distinct contrast, the B3LYP density functional favors the less symmetric species by merely 3.2 kcal/mol. At our most reliable levels of theory, i.e. RCCSD(T) and UCCSD(T) the $C_{2v}$ system is predicted to be more stable than the $D_{3h}$ alternative by 13.8 kcal/mol, pointing to deficiencies not only of the HF but also of the B3LYP methods.

The $^1A_1'$ ground state of the $CF_3^+$ is characterized in the HF picture by the closed shell wave function . . . $(e')^4$ $(e'')^4$ $(a_2')^2$. However, the energetical spacing between these five frontier orbitals is very small. Following Koopmans' theorem, the ionization requiring the least amount of energy should proceed (at least in principle) from the highest occupied MO, which is of $a_2'$ symmetry and hence should lead to a $^2A_2'$ ground state of $CF_3^{2+}$. Indeed, this state is lower than a $^2E''$ state at the $D_{3h}$ geometry. The $C_{2v}$ ground state of the dication is of $^2B_2$ symmetry and correlates with the $^2A_2'$ state in $D_{3h}$ [43]. Thus, the reduction of the symmetry of the $CF_3^{2+}$ dication is not the consequence of a (first-order) Jahn-Teller distortion.

The UHF/SCF, B3LYP and UCCSD(T) harmonic vibrational frequencies for the $D_{3h}$ and $C_{2v}$ symmetric structures of doubly positively charged $CF_3$ are listed in Table 2. In general, there is good agreement between the B3LYP and UCCSD(T) results, whereas the UHF data show deviations which are in particular significant for the degenerate $e'$ vibrations. In addition, the UHF method characterizes the $D_{3h}$ species as a minimum with only real frequencies, in contrast to the two other techniques, which predict the $D_{3h}$ structure to be a higher order saddle point having two degenerate ($e'$) imaginary frequencies. The $e'$ frequencies seem to be most problematic also for the B3LYP and UCCSD(T) levels of theory, note the

Table 2
Harmonic frequencies [cm$^{-1}$] at the corresponding equilibrium geometries for $CF_3^{2+}$ evaluated at the UHF, B3LYP, and UCCSD(T) levels with the cc-pVTZ basis set

| | $D_{3h}$ $CF_3^{2+}$ ($^2A_2'$) | | | $C_{2v}$ $CF_3^{2+}$ ($^2B_2'$) | | |
|---|---|---|---|---|---|---|
| Mode[a] | UHF (SA) | UB3LYP (SA) | UCCSD(T) (SA) | UHF (SA) | UB3LYP (SA) | UCCSD(T) (SA) |
| $v_1$ ($e'/b_2$) | 554.7 | $i426.3$ | $i1279.7$ | 428.6 | 321.4 | 355.9 |
| $v_2$ ($e'/a_1$) | 554.7 | $i426.3$ | $i1279.7$ | 533.1 | 371.3 | 455.1 |
| $v_3$ ($a_2''/a_1$) | 762.4 | 690.7 | 686.5 | 711.6 | 605.5 | 656.9 |
| $v_4$ ($e'/b_1$) | 2227.5 | 757.6 | 591.0 | 744.5 | 653.4 | 669.5 |
| $v_5$ ($e'/a_1$) | 2227.5 | 757.6 | 591.0 | 1406.5 | 1260.0 | 1285.5 |
| $v_6$ ($a_1'/b_2$) | 1127.1 | 989.2 | 978.2 | 2167.8 | 1951.4 | 1995.2 |

[a] Numbers in parenthesis give the irreducible representations of the corresponding vibrational modes.

huge difference between the magnitude of the imaginary frequency of 426 cm$^{-1}$ at B3LYP and 1279 cm$^{-1}$ at the UCCSD(T) level of calculation. If instead of B3LYP the "pure" BLYP functional is employed, an even lower imaginary frequency of 351 cm$^{-1}$ is predicted. Possible reasons for this discrepancy could be problems in the purely numerical differentiation of the UCCSD(T) energies or factors inherent to the chosen methods.

For the current situation with a symmetrical $D_{3h}$ structure as a second order saddle point surrounded by three degenerate $C_{2v}$ minima, one should expect a regular first order saddle point which connects the minima without having to pass the central $D_{3h}$ structure. If we assume in the $C_{2v}$ structure a charge distribution in which the two positive charges are mostly localized at the two fluorines having the short bond to the central carbon, this transition structure corresponds to the migration of these charges through an allyl type saddle point. Indeed, such a transition structure was found at both correlated methods and is characterized by two long (1.290 Å at B3LYP and 1.295 Å at UCCSD(T)) and one short (1.187 Å at B3LYP and 1.183 Å at UCCSD(T)) C–F bond. Again, the B3LYP calculated imaginary harmonic frequency is smaller ($i43.3$ cm$^{-1}$, $b_2$) than the value resulting from the CCSD(T) calculation ($i558.8$ cm$^{-1}$). The barrier calculated at UCCSD(T) for the degenerate interconversion is 8.6 kcal mol$^{-1}$ with respect to the $C_{2v}$ minima and thus should be high enough to allow a spectroscopic characterization of the $C_{2v}$ states.

Finally a further, important argument in favor of a $C_{2v}$ rather than a $D_{3h}$ molecular skeleton of the $CF_3^{2+}$ dication is the excellent agreement between the calculated and experimental ionization energy. At CCSD(T), we compute an adiabatic ionization energy of $CF_3^+$ of 26.80 eV compared to the experimental value of 26.30 ± 0.4 eV [12]. On the other hand, the calculated ionization energy for the $D_{3h}$ structure amounts to 27.40 eV, about 1 eV off the experimentally deduced result.

## 4. Summary

Quantum chemical calculations employing the conventional wave function based CCSD(T) approach and the B3LYP density functional establish a $C_{2v}$ symmetric equilibrium geometry rather than the hitherto predicted $D_{3h}$ structure for the electronic ground state of the $CF_3^{2+}$ dication. The latter isomer is characterized by a pair of degenerate imaginary frequencies and represents a second order saddle point. A regular transition state connecting the three identical $C_{2v}$ minima was located some 9 kcal mol$^{-1}$ above the minimum structure. While calculations for the highly symmetric $D_{3h}$ species are plagued by severe symmetry breaking problems at the uncorrelated Hartree–Fock level, no unphysical wave functions of lower symmetry than the molecular skeleton were obtained from the more sophisticated theoretical treatments.

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