F_4^+: A Stable Three-Electron Bonded Complex and a Challenge for Standard ab Initio Computational Methods

Philippe C. Hiberty* and Nathalie Berthe-Gaujac

Contribution from The Laboratoire de Chimie Théorique,† Université de Paris-Sud,
91405 Orsay Cedex, France

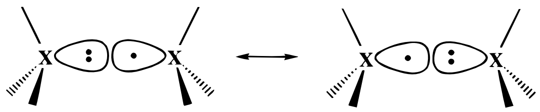
Received: December 9, 1997; In Final Form: February 13, 1998

Qualitative considerations based on a simple molecular-orbital model point to the prediction that the radical cation complex F_4^+ should be stable, with a significant bonding energy, relative to dissociation to the F_2 and F_2^+ fragments. A rectangular minimum is indeed characterized at the ab initio MP2 level, as well as a linear conformer displaying nearly free rotation about the central F−F bond. The Møller−Plesset results are, however, shown to be inconsistent and very poorly converged as the order of perturbation is increased, and to be subject to very strong spin contamination with additional problems of local symmetry breaking in the linear conformer. Higher level calculations of the quadratic configuration interaction or coupled-cluster type, with inclusion of single and double excitations and perturbative treatment of triples (QCISD(T) and CCSD(T)), are performed in their spin-unrestricted and spin-restricted forms. All high-level calculations yield optimized geometries and bonding energies which are consistent with each other and point to the firm conclusion that the F_4^+ complex should be stable either in a rectangular or in a linear conformation, with dissociation energies of the order of 13−16 kcal/mol.

Introduction

A growing interest has been noted for a decade in the nature and stability of three-electron (3-e) bonds that consist of two bonding σ electrons and one antibonding σ^* electron. Among the various species that owe their stabilities to such bonds, the radical cation dimers of the type $A{\therefore}A^+$ form an important subclass, with bonding energies often ranging from 20 to 50 kcal/mol.[1,2] Particularly well known are the noble gas dimer cations, which all are experimentally observed, and some disulfur or diphosphorus radical cations of the types $R_2S{\therefore}SR_2^+$ and $R_3P{\therefore}PR_3^+$.[3,4] However, the ab initio computational studies of Clark[1] and Radom[2] have shown that all compounds of the $H_nX{\therefore}XH_n^+$ type (X = N, O, F, P, S, Cl; n = 1 to 3), which are isoelectronic to the noble gas dimer cations, are bound relative to the separate XH_n and XH_n^+ dissociation products.

What characterizes all these species is the presence of at least one lone pair on the X atom of H_nX that corresponds to an orbital which is doubly occupied in H_nX and singly occupied in H_nX^+. For three-electron bonding to occur, these two orbitals must point toward each other, so that they may overlap efficiently and exchange one electron as in the two-structure resonating scheme below.



1 **2**

In valence bond terms, the 3-e bond owes its stability to the resonance energy resulting from the mixing of **1** and **2** in the ground state of $H_nX{\therefore}XH_n^+$. Because resonance is favored when both resonance structures have equal weights, homodimeric radical cations are more commonly observed than heterodimeric ones,[1,5] although many examples of the latter have also been characterized,[5] not to mention neutral radical-molecule adducts.

Larger symmetrical 3-e bonded complexes, such as $(N_2O)_2^+$, $(CO_2)_2^+$, $(SO_2)_2^+$ and $(COS)_2^+$,[6] $(C_2H_4S)_2^+$,[7] and N_4^+,[8] have also been found to be stable, all of them bearing lone pairs. By contrast, it is rather surprising that the simple F_4^+ complex has, to our knowledge, never been characterized, either experimentally or theoretically, while simple qualitative considerations immediately predict this species to be stable relative to dissociation to F_2 and F_2^+ (vide infra). On the theoretical side, one possible reason for the lack of reported data might well originate from the great difficulties and misleading predictions encountered with this system at the most commonly used standard levels of the theory, as will be shown below. In this context, the aim of the present paper is first to get some qualitative understanding of the possible interactions between F_2 and its radical cation, then to investigate the possibility of a stable three-electron bonded F_4^+ complex by means of ab initio calculations at an appropriate level of theory.

Why Should F_4^+ Be Stable at All? A Qualitative Analysis

The qualitative aspects of three-electron bonding are best understood in the framework of extended Hückel theory, with overlap integrals included, even though qualitative valence bond theory leads to exactly equivalent formulas.[2,9] In the simple cases of noble gas dimer cations $A{\therefore}A^+$ or species of the type $H_nX{\therefore}XH_n^+$, the overall ion−molecule interaction can be reduced to the interaction of two fragment orbitals that are nonbonding and quasi-atomic in nature, leading to one bonding and one antibonding combination as in Figure 1. In the extended Hückel framework, the net energetic stabilization thereby achieved, $D_e(A_2^+)$, is given by eq 1:

---

† Associated with the CNRS, URA 506.

S1089-5639(98)00466-6 CCC: $15.00

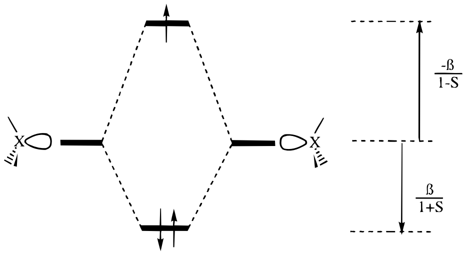


Figure 1. Qualitative molecular-orbital interaction diagram for the $H_nX\therefore XH_n^+$ case. The indicated energy gaps are the stabilization/destabilization of the bonding and antibonding MOs, relative to the nonbonding level.

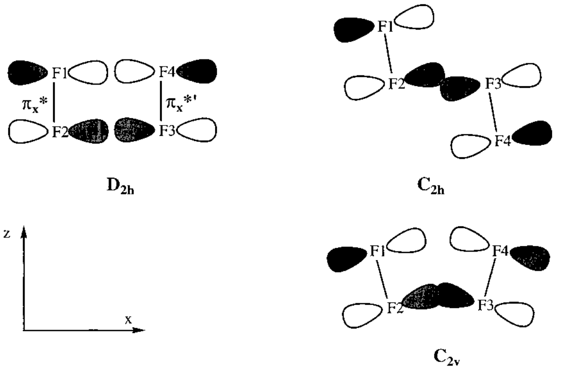


Figure 2. Interacting π^* fragment molecular orbitals in the D_{2h}, C_{2h}, and C_{2v} planar approaches of the F_2 and F_2^+ fragments.

$$D_e(A_2^+) = 2\beta/(1 + S) - \beta/(1 - S) \approx \beta(1 - 3S) \qquad (1)$$

where β is the usual reduced resonance integral, S is the overlap between the interacting orbitals of each center, and the denominator $(1 - S^2)$ has been dropped for simplicity. Equation 1 shows that the interaction is always stabilizing provided the interatomic distance is sufficiently large. By assuming β to be proportional to the overlap integral S, one can show by differentiation[2] that the three-electron bonding energy reaches its maximum for an optimal S value of 1/6, a value typical of rather long interfragment separation.

The case of F_4^+ is a little more complex, in that more than one pair of fragment orbitals are expected to interact as the two fragments approach each other. Indeed, in this case the highest occupied orbitals of the F_2 and F_2^+ fragments are not simple atomic orbitals but delocalized MOs, more specifically antibonding π orbitals, i.e., π_x^* and $\pi_x^{*\prime}$. Considering a planar approach as in Figure 2, so as to maximize the three-electron interaction between π_x^* and $\pi_x^{*\prime}$, it is apparent that another pair of fragment orbitals, namely the π_x and π_x' in-plane bonding π orbitals of F_2 and F_2^+, overlap as well, and that their four-electron repulsion must be taken into account. Neglecting the interactions between the remaining fragment MOs,[10] the net MO interacting diagram appears as in Figure 3, where the same β has been taken for each pair of interaction orbitals since they are both composed of atomic orbitals of the same nature. Still using the rules of qualitative theory, the net energetic balance of the overall interaction is the sum of a three-electron attractive term, $\beta(1 - 3S)$, and a four-electron repulsive term, $-4\beta S$, leading to eq 2 which shows that the interaction *is necessarily stabilizing* at some distance, provided the overlap is smaller than a critical value of 1/7.

$$D_e(F_4^+) \approx \beta(1 - 7S) \qquad (2)$$

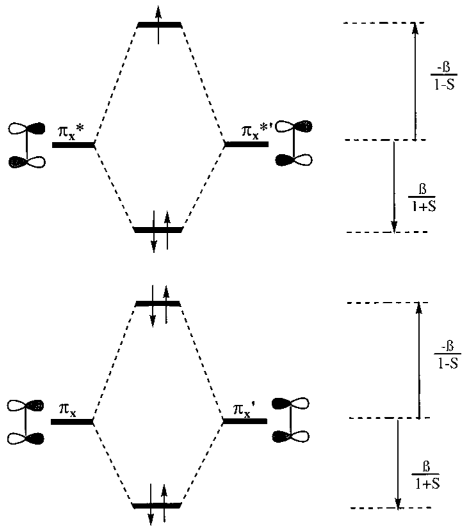


Figure 3. Qualitative molecular-orbital interaction diagram for the F_4^+ case.

For more quantitative predictions, some useful comparisons can be made between eq 1, which applies to the $HF\therefore FH^+$ system, and eq 2, which applies to F_4^+. First, the optimal S value for maximizing the bonding energy in eq 2 appears by differentiation to be only 1/14, therefore smaller than in eq 1, showing that the F−F optimal distance should be longer in F_4^+ than it is in $HF\therefore FH^+$. Pursuing the same type of qualitative reasoning even allows us to compare the bonding energies of both systems, by replacing S in eqs 1 and 2 by the respective optimal S values of 1/6 and 1/14:

$$\beta = kS \qquad (3a)$$

$$D_e(HFFH^+) \approx kS(1 - 3S);\ S = 1/6 \qquad (3b)$$

$$D_e(F_4^+) \approx kS(1 - 7S);\ S = 1/14 \qquad (3c)$$

$$D_e(F_4^+)/D_e(HFFH^+) \approx 6/14 \qquad (3d)$$

Thus, knowing the bonding energy of ca. 45 kcal/mol and the F−F optimal bond length of 1.80 Å[1,2] for $HF\therefore FH^+$, the above qualitative considerations predict the F_4^+ system to be stable relative to dissociation to F_2 and F_2^+ by a significant quantity, of the order of ca. 19 kcal/mol (eq 3d), and with an F−F interfragment bond length somewhat longer than 1.80 Å. Last, one may try to predict the most probable geometries for the stable three-electron bonded conformers, by choosing the conformations that maximize the overlap between the π^* fragment MOs.[11] According to this criterion, a rectangular D_{2h} conformation and a Z-shaped C_{2h} one can be a priori considered, the latter presumably displaying very facile rotation around the F−F interfragment bond (Figure 2). Rotating the dihedral angle of the C_{2h} conformer by 180° would lead to a third planar conformation, of C_{2v} type; however, this latter conformer is expected to collapse with a very small barrier, if any at all, to the D_{2h} conformer, since this motion would further optimize the interaction between the π^* fragment MOs as is apparent in Figure 2.

Theoretical Methods

Some Theoretical Difficulties To Be Anticipated. The dissociation products, F_2 and F_2^+, are known as two fairly hard molecules for which good values of the dissociation energy and bond length can be obtained. In 6-31G(d) basis set, the bond length for F_2^+ varies by 0.18 Å according to whether it is optimized at the spin-unrestricted Hartree−Fock (UHF) or second-order Møller−Plesset (UMP2) level, the experimental value lying halfway between.[12] The inaccuracy remains at higher orders, even in larger basis sets, due to a rapid deterioration of the convergence in the Møller−Plesset series as R increases, with large oscillations developing in the series.[12] In addition, this cation radical is subject to a severe symmetry-breaking effect, by which the lowest Hartree−Fock solution is of lower symmetry than the nuclear framework and tends to localize the odd electron on one of the two fluorine atoms. As a consequence, it has been found that the bond lengths calculated at the UMP4 level differ by over 0.1 Å according to the symmetry of the UHF reference function.[13] The problem is easily solved in highly symmetrical conformations such as the isolated F_2^+ radical or the D_{2h} conformation of F_4^+, by enforcing the symmetry of the wave function. On the other hand, in low symmetry conformations, some subtle form of excessive localization of the odd electron may persist, this time with no simple remedy. Suppose that the two fragments approach each other in a geometry of low symmetry, e.g., C_{2h}. Each fragment displays a local quasi-symmetry, slightly perturbed by the presence of the other fragment. Therefore, even though the four atoms are not equivalent, there should remain a good deal of odd-electron delocalization in each fragment. However, as the UHF method tends to ignore the stabilizing effect of electron delocalization in F_2^+, it is likely that the odd electron will be found too much localized at this level, even if not formally in conflict with the symmetry of the supersystem. Thus, one can expect the UMP2 and UMP4 results to be worse for the C_{2h} than for the D_{2h} conformations of F_4^+, resulting in an imbalanced surface.

Additional problems that can be expected on the F_4^+ potential surface are the spin contamination in the F_2^+ entity[12] and the charge-transfer nature of the $F_2-F_2^+$ interaction, a phenomenon that requires further dynamical electron correlation[14] relative to the separate entities F_2 and F_2^+. It follows that F_4^+ meets all conditions to be a particularly challenging test case for which the commonly used MP series has all chances to be in serious error. Thus, it is clear that higher levels of theory, like quadratic configuration interaction (QCI) or coupled cluster (CC) theory, will be required to investigate the potential surface of F_4^+ and to make firm predictions about the stability of this complex relative to separate F_2 and F_2^+. It will also be useful to use both spin-unrestricted and spin-restricted forms of the theory, to estimate the consequences of spin contamination.

Technical Details. As the preceding analysis shows that a careful treatment of electron correlation is crucial for a balanced description of the F_4^+ potential surface, we have chosen to privilege this aspect of the level of theory over considerations of basis set quality. Therefore, all calculations have been performed in the standard 6-31G(d) basis set of double-ζ + polarization quality, whose rather modest size is certainly insufficent for high accuracy but should not lead to qualitative errors. The Møller−Plesset perturbation theory has been used in its spin-unrestricted form, at the second and fourth order (UMP2 and UMP4), and, after annihilation of the spin contamination by projection (PMP2 and PMP4), all geometries being optimized at the UMP2 level. The quadratic configuration interaction theory[15] has also been used in its spin-unrestricted form, with inclusion of all single and double excitations and perturbative treatment of triple excitations (UQCISD(T)).[15] Finally, our highest level uses the coupled cluster theory,[16−19] in both its spin-unrestricted (UCC) and spin-restricted (RCC) forms.[17]

TABLE 1: Optimized Geometries for the F_4^+ Complex and Dissociation Products, at Various Levels of Theory

conformation	$\langle S^2\rangle^a$	F1−F2	F2−F3	∠F1−F2−F3	Φ^b
		F_2			
UMP2	0.0	1.421			
UQCISD(T)	0.0	1.443			
UCCSD(T)	0.0	1.444			
RCCSD(T)	0.0	1.444			
experiment[c]		1.412			
		F_2^+			
UMP2	0.7646	1.411			
UQCISD(T)	0.7643	1.351			
UCCSD(T)	0.7642	1.350			
RCCSD(T)	0.75	1.352			
experiment[d]		1.305			
		F_4^+ (D_{2h})			
UMP2	0.7646	1.429	2.218	90.0	0.0
UQCISD(T)	0.7645	1.399	2.208	90.0	0.0
UCCSD(T)	0.7645	1.397	2.207	90.0	0.0
RCCSD(T)	0.75	1.398	2.209	90.0	0.0
		F_4^+ (C_{2h})			
UMP2	0.8115	1.434	1.978	101.3	180.0
UQCISD(T)	0.8441	1.406	1.986	106.6	180.0
UCCSD(T)	0.8341	1.412	1.990	106.6	180.0
RCCSD(T)	0.75	1.409	2.021	106.9	180.0
		F_4^+ (C_{2v})			
UMP2	0.8092	1.426	2.011	101.6	0.0

[a] Expectation value of $\langle S^2\rangle$ for the UHF wave function. [b] Dihedral angle F1−F2−F3−F4. [c] From ref 21. [d] From ref 22.

The geometries have been optimized by using a gradient technique. The linear conformations have been optimized assuming planarity in a first step, to avoid difficulties in the optimization process due to the presumably very facile rotation around the F−F interfragment bond (vide supra). Then, a potential surface scan along this latter mode has been performed at the MP2 level to verify that the rotation is quasi-free. Accordingly, the geometry optimizations at higher levels of theory have been performed with a constraint of planarity. All calculations have been carried out using the Gaussian 92[20] system of programs.

Results of Møller−Plesset Calculations

Dissociation Products. The optimized bond lengths of F_2 and F_2^+ are displayed in Table 1, as calculated at various levels of theory. All results on F_2^+ refer to calculations with enforced symmetry, to get rid of the symmetry-breaking artifact.

It is seen that the UMP2 level of theory performs differently for F_2 and F_2^+. While the optimized bond length of the former is fortuitously very close to experiment, that of the second is too long by 0.106 Å, so that both bond lengths come out very similar, at variance with experiment. The spin contamination in F_2^+ is significant, with an expectation value of 0.765 for the spin-squared operator ($\langle S^2\rangle$) to be compared with the value of 0.75 required for a pure doublet.

***D_{2h}* Conformation.** The geometry of the F_4^+ complex is shown in Table 1, as calculated at various computational levels, in D_{2h} and C_{2h} conformations. At the UMP2 level, the geometry displays some intrafragment bond lengths (F1−F2 and F3−F4) in the expected range, i.e., close to the UMP2-optimized bond lengths of the F_2 and F_2^+ separate fragments, and an interfragment F2−F3 distance of 2.218 Å, significantly larger than 1.80 Å (the F−F distance in $HF\therefore FH^+$), in accord with the qualitative predictions.

The spin contamination is important but not overwhelming, of the same order of magnitude as in F_2^+. Accordingly, the

TABLE 2: Absolute Energies, in Hartrees, for the Various Conformations of the F_4^+ Complex and the Dissociation Products[a]

method	F_4^+ (D_{2h})	F_4^+ (C_{2h})	F_4^+ (C_{2v})	F_2	F_2^+
UMP2	−397.566 971 (25.8)	−397.510 766 (−9.5)	−397.513 567 (−7.7)	−199.034 891	−198.490 938
UMP4	−397.577 283 (18.4)	−397.553 109 (3.2)	−397.555 328 (4.6)	−199.051 156	−198.496 867
PMP2	−397.570 264 (25.6)	−397.519 098 (−6.4)	−397.521 742 (−4.8)	−199.034 891	−198.494 549
PMP4	−397.578 423 (18.5)	−397.558 557 (6.0)	−397.560 600 (7.3)	−199.051 156	−198.497 848
UQCISD(T)	−397.569 385 (16.1)	−397.565 328 (13.5)		−199.051 502	−198.492 260
UCCSD	−397.539 862 (13.0)	−397.537 733 (11.6)		−199.041 492	−198.477 713
UCCSD(T)	−397.568 611 (16.1)	−397.563 869 (13.1)		−199.051 405	−198.491 612
RCCSD	−397.537 412 (12.8)	−397.536110 (12.0)		−199.041492	−198.475491
RCCSD(T)	−397.566 912 (16.1)	−397.563 304 (13.9)		−199.051 405	−198.489 821

[a] The dissociation energies relative to F_2 and F_2^+ are indicated in parentheses, in kcal/mol.

annihilation of unwanted spin states by projection, at the PMP levels, has little consequences on the dissociation energies.

At both the MP2 and MP4 levels, the F_4^+ system appears to be quite stable in its D_{2h} conformation, by 18−25 kcal/mol relative to dissociation (Table 2); however, the large difference of ca. 7 kcal/mol between the second- and fourth-order results indicates that the MP series is far from being converged, and casts some serious doubts on the validity of the calculations.

Linear Conformations. The planar-constrained Z-shaped complex displays a C_{2h} geometry with nearly the same intrafragment bond length as the D_{2h} conformer, but a shorter interfragment distance, 1.978 Å. While this might lead one to expect a larger bonding energy, the C_{2h} conformer is on the contrary higher in energy than the separate F_2 and F_2^+ fragments, by 9.5 kcal/mol. The C_{2h} minimum is therefore some 35 kcal/mol higher in energy than the D_{2h} one at the MP2 level, a rather surprising feature which can receive no apparent qualitative explanation in terms of orbital interactions and can, therefore, be taken as the first warning that the MP calculations are not valid. A second warning comes from the very important spin contamination, as indicated by the spin-squared expectation value of 0.812.

Relaxing the constraint of planarity leads to a nearly free rotation about the central F−F bond, from 180° to 0°, ending at a minimum of C_{2v} symmetry (Figure 2), lying only 1.8 kcal/mol below the C_{2h} conformer and displaying rather similar geometrical features. However, as mentioned above, the C_{2v} conformer can be expected either to be unstable or to collapse with a very small barrier to the D_{2h} minimum, and indeed higher levels of the theory confirm this prediction (vide infra). Therefore, the rest of the discussion for linear conformations focuses on the C_{2h} conformation.

The convergence in the MP series appears as even worse than in the D_{2h} conformation, with a difference of about 13 kcal/mol between the UMP2 and UMP4 dissociation energies. The annihilation of unwanted spin states further increases the bonding energies at both the MP2 and MP4 levels, ending in a PMP4 positive bonding energy of 6.0 kcal/mol (Table 2).

The dissociation energy curve has been explored at the MP2 level, by optimizing the geometries of various Z-shaped planar conformers, at the UMP2 level, for various fixed F2−F3 interfragment distances. The resulting UMP2 and PMP2 reaction profiles, shown in Figure 4, display an energy rise followed by a rather unrealistic energy collapse, leading to energies *lower* than those of the separate fragments while the three-electron bond is practically broken, as a population analysis of the wave functions would show (all the charge is located on a single fragment for F2−F3 distances larger than 2.7 Å). Thus, the Møller−Plesset calculations appear as particularly unadapted to the F_4^+ potential surface, in many aspects. To summarize: (i) the MP series is not converged; (ii) the treatment of different regions (C_{2h} vs D_{2h}) of the potential surface is apparently not balanced, the C_{2h} conformations being disfavored, probably due to artifacts of local symmetry-breaking type leading to excessive localization of the odd electron; (iii) the spin contamination is large and symmetry-dependent; (iv) the shape of the potential surface is at variance with qualitative expectations. For all these reasons, it is clear that higher levels of theory are necessary to draw firm conclusions on the stability of the F_4^+ complex.

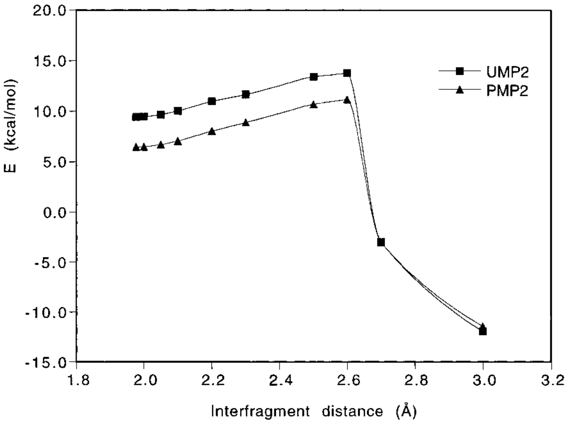


Figure 4. Energy profiles for the dissociation of the Z-shaped F_4^+ complex to F_2 and F_2^+, as calculated at the UMP2 and PMP2 levels. Energies in kcal/mol, relative to the separate fragments.

Quadratic CI and Coupled Cluster Calculations

Quadratic CI and coupled cluster methods are two increasingly popular techniques for the treatment of electron correlation effects, the former being a cost-effective approximation of the second. Both methods are typically carried out including all single and double excitations (QCISD and CCSD) and involve some additional terms that are equivalent to including the higher excitations needed for size consistency. Even better accuracy is obtained by including the triple excitations, which may be treated in a perturbative way, leading to the QCISD(T) and CCSD(T) methods. Both these techniques are generally recognized to be the most accurate, yet computationally tractable, schemes, the latter being perhaps more accurate and more widely applicable than the former.[23] Interestingly for the problem in hand, the coupled cluster method has been shown to recover well from symmetry-breaking artifacts, and to provide results for the F_2^+ radical cation that are not too dependent on the symmetry of the orbitals.[24]

Let us first consider the spin-unrestricted quadratic CI results, UQCISD(T). The optimized bond lengths of F_2 and F_2^+ (Table 1) are now well differenciated at this level, in agreement with experiment, with values of 1.443 and 1.351 Å, respectively. They are somewhat too long relative to the experimental values of 1.412 and 1.305 Å; however, this is due to the rather modest size of the basis set rather than to a deficiency of the computational method. Indeed, our F_2 bond length is close to the full CI estimation in a similar basis set,[25] and some UQCISD(T) calculations of F_2^+ in a larger basis set of 5s4p2d type yield a bond length of 1.330 Å and an excellent vibrational frequency.[12] As for the F_4^+ complex, both its D_{2h} and C_{2h} conformations display interfragment bond lengths that are quite logically intermediate between the bond lengths of F_2 and F_2^+. The other optimized geometrical parameters are in agreement with the UMP2-optimized values. The C_{2v} conformation is found to collapse without barrier to the D_{2h} minimum, in agreement with qualitative expectations. Therefore, all high-level calculations will be limited in the following to the D_{2h} and C_{2h} conformations, the latter being considered as representative of all linear complexes.

In sharp contrast with the Møller−Plesset level, the UQCISD(T) level yields dissociation energies (Table 2) that are close to each other for the D_{2h} and C_{2h} conformations, in accord with physical intuition since the nature of three-electron bonding is the same in both cases. The value of 16.1 kcal/mol for the D_{2h} conformation may a priori be taken with confidence, as the spin contamination remains acceptable, with an expectation value $\langle S^2 \rangle$ of 0.765 for the spin-squared operator. On the other hand, the spin contamination for the C_{2h} conformer clearly passes the acceptable limits, with a $\langle S^2 \rangle$ value of 0.844. Thus, the dissociation energy of 13.5 kcal/mol, for F_4^+ in its C_{2h} conformation, must be taken with some reservation.

For the coupled cluster calculations, the geometries have been optimized at the CCSD(T) level that includes triple excitations,[18,19] and some single point calculations at the lower CCSD level have been further performed to check the stability of the relative energies against varying the theoretical level.

As can be seen from Table 1, the geometry optimizations performed at the spin-unrestricted UCCSD(T) level confirm the geometric parameters arising from the UQCISD(T) level, for the dissociation products F_2 and F_2^+ as well as the D_{2h} and C_{2h} conformations of the F_4^+ complex. As regards the dissociation energies (Table 2), that of the D_{2h} conformation is almost unchanged relative to the UQCISD(T) level, while that of the C_{2h} conformation slightly diminishes, from 13.5 to 13.1 kcal/mol. Now the spin contamination remains important for the C_{2h} conformation whose $\langle S^2 \rangle$ expectation value remains as high as 0.834, hardly smaller than the UQCISD(T) value. Clearly, neither the geometric parameters nor the dissociation energy of the C_{2h} conformation of F_4^+ can be considered as definitive, so long as spin-unrestricted forms of the theory are used.

To definitely get rid of the spin contamination problem, the CCSD(T) calculations were repeated in a spin-restricted scheme, referred to as RCCSD(T). The results of the geometry optimizations, displayed in Table 1, show that no significant differences are found between the spin-restricted and spin-unrestricted calculations, for the molecules displaying moderate spin contamination at the UCCSD(T) level, like F_2^+ and F_4^+ in its D_{2h} conformation. The C_{2h} conformation, on the other hand, is found to display a slightly larger interfragment bond length at the RCCSD(T) level than at UCCSD(T). The same remarks hold for the dissociation energies, which are exactly the same at both levels for the D_{2h} conformation but differ for the C_{2h} conformation. Yet in this latter case, the difference between spin-restricted and spin-unrestricted results is rather small, despite the very large spin contamination found at the UCCSD(T) level.

The CCSD values for the dissociation energies are rather different from CCSD(T), confirming the well-established fact that the effect of triple excitations is crucial for achieving good accuracy. However, the differences are not so large as to cast doubts on the validity of the CCSD(T) results. Finally, an estimate of the basis set superposition error (BSSE) was made by performing a counterpoise calculation on the D_{2h} structure at the restricted open-shell Hartree−Fock level,[26] according to the method of Boys and Bernardi.[27] The BSSE error was found to be very small, 1.1 kcal/mol, relative to the above-reported bonding energies.

Discussion and Conclusion

The fluorine-containing compounds are known to necessitate quite large basis sets, in addition to an appropriate treatment of electron correlation, for an accurate calculation of geometric parameters and bonding energies. However, while an improper treatment of electron correlation sometimes leads to qualitatively erroneous results, to our knowledge the use of the 6-31G(d) basis set for molecules made of atoms of the first line of the periodic table only results in bond lengths being too large and bonding energies being too small, but does not affect the qualitative shapes of the potential surfaces. Thus, the quantitative values for the geometrical parameters and bonding energies arising from the best computational levels used in this study might certainly be quantitatively refined by using some series of basis sets of increasing qualities; however, the qualitative conclusions should remain unchanged.

The D_{2h} conformation of the F_4^+ complex is the one that causes lesser problems. The spin contamination remains within acceptable limits and the symmetry-breaking artifact is easily avoided owing to the high symmetry of the molecule. Our highest computational levels, UQCISD(T), UCCSD(T), and RCCSD(T), provide geometrical parameters in good agreement with each other, and the bonding energies converge to a value of ca. 16 kcal/mol which can be taken with confidence, if not for the basis set deficiencies.

The C_{2h} conformation is a priori more difficult to deal with, because of a predictable artifact leading to excessive localization of the odd electron within the fragments. The spin contamination is very large at the unrestricted levels; however, the results of the three above high computational levels are surprisingly close to each other, yielding a bonding energy of ca. 13−14 kcal/mol. The rotational barrier around the interfragment F−F bond appears to be nearly free, so that the specific optimal rotational angle has not been searched at these levels.

As anticipated from a preliminary survey of the theoretical difficulties likely to be encountered, the commonly used Møller−Plesset theory appears to fail dramatically for the F_4^+ potential surface. At second order, the D_{2h} conformation is found to be too stable relative to the dissociation products, while the C_{2h} conformation is on the contrary too high in energy. In both cases, the MP4 relative energies are very different from MP2 ones, and the effects of spin projection are exceedingly large in the C_{2h} case. All in all, the Møller−Plesset error appears to be even worse in the C_{2h} than in the D_{2h} conformation.

The present work is, of course, not claimed to report an exhaustive study of the F_4^+ potential surface. It, however, points to the firm conclusion that the F_4^+ complex is stable relative to dissociation to F_2 and F_2^+, and is linked by interactions of three-electron type in the conformations that can be logically expected from a qualitative analysis. Remarkably, the qualitative model provides an order of magnitude for the bonding energy, 19 kcal/mol, which turns out to be in good agreement with the ab initio calculated values of 13−16 kcal/mol. It is hoped that the present study will stimulate further research to achieve experimental observation of the F_4^+ complex.

References and Notes

(1) Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672 and references therein.

(2) Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1988**, *110*, 4931.

(3) (a) Janssen, R. A. J.; Aagaard, O. M.; van der Woerd, M. J.; Buck, H. M. *Chem. Phys. Lett.* **1990**, *171*, 127. (b) Aagaard, O. M.; de Waal, B. F. M.; Cabbolet, M. J. T. F.; Janssen, R. A. J. *J. Phys. Chem.* **1992**, *96*, 614.

(4) For leading references, see: (a) Asmus, K.-D. In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; Chatgilialoglu, C., Amus K.-D., Eds.; Plenum Press: New York and London, 1990; p 155. (b) Gilbert B. C. In ref 4a, p 135. (c) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436 and references therein.

(5) An account of the literature on homodimeric and heterodimeric radical ions and neutral radicals can be found in: (a) refs 1 and 2. (b) Hiberty, P. C.; Humbel, S.; Danovich, D.; Shaik, S. *J. Am. Chem. Soc.* **1995**, *117*, 9003. (c) Abu-Raqabah, A.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3293.

(6) (a) McKee, M. L. *Chem. Phys. Lett.* **1990**, *165*, 265. (b) McKee, M. L. *J. Phys. Chem.* **1990**, *94*, 8553. (c) McKee, M. L. *Chem. Phys. Lett.* **1991**, *179*, 559.

(7) Qin, X.-Z.; Meng Q.-C.; Williams, F. *J. Am. Chem. Soc.* **1987**, *109*, 6778.

(8) Sohlberg, K. *J. Mol. Struct. (THEOCHEM)* **1995**, *339*, 195.

(9) Shaik, S.; Hiberty, P. C. *Adv. Quantum Chem.* **1995**, *26*, 99.

(10) At an F2−F3 distance of 2 Å, the overlap between two 2s AOs or between two parallel 2p AOs, respectively, located on the F2 and F3 atoms, is about four times smaller than the overlap between two 2p AOs that point toward each other.

(11) The three-electron bond is favored when the optimal overlap S between the π^* fragment orbitals is attained at the largest possible interfragment distance, so as to minimize the repulsive interactions between the other fragment orbitals. This implies choosing conformations that maximize the $\pi_x^*-\pi_x^{*\prime}$ overlap.

(12) Tozer, D. J.; Handy, N. C.; Amos, R. D.; Pople, J. A.; Nobes, R. H.; Xie, Y.; Schaefer, H. F. *Mol. Phys.* **1993**, *79*, 777.

(13) Murphy, R.; Schaefer, H. F.; Nobes, R. H.; Radom, L.; Pitzer, R. S. *Int. Rev. Phys. Chem.* **1986**, *5*, 229.

(14) Hiberty, P. C.; Humbel, S.; Archirel, P. *J. Phys. Chem.* **1994**, *98*, 11697.

(15) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

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

(17) For a comparison between UCCSD and RCCSD results in open-shell systems, see: Stanton, J. F. *J. Chem. Phys.* **1994**, *101*, 5371.

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

(19) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513.

(20) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision C3*, Gaussian, Inc.: Pittsburgh, PA, 1992.

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

(22) Tuckett, R. P.; Dale, A. R.; Jaffrey, D. M.; Jarrett, P. S.; Kelly, T. *Mol. Phys.* **1983**, *49*, 475.

(23) Raghavachari, K.; Anderson, J. B. *J. Phys. Chem.* **1996**, *100*, 12960.

(24) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *95*, 6652.

(25) Laidig, W. D.; Saxe, P.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 887.

(26) Davidson, E. R. *Chem. Phys. Lett.* **1973**, *21*, 565.

(27) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.