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Electronic structures and geometries of the XF_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{At}$) fluorides

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The potential energy surfaces of the group 17 XF_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{At}$) fluorides have been investigated for the first time with multiconfigurational wave function theory approaches. In agreement with experiment, bent T-shaped C_{2v} structures are computed for ClF_3 , BrF_3 and IF_3 , while we predict that an average D_{3h} structure would be experimentally observed for AtF_3 . Electron correlation and scalar relativistic effects strongly reduce the energy difference between the D_{3h} geometry and the C_{2v} one, along the XF_3 series, and in the $\text{X} = \text{At}$ case, spin-orbit coupling also slightly reduces this energy difference. AtF_3 is a borderline system where the D_{3h} structure becomes a minimum, *i.e.* the *pseudo* Jahn-Teller effect is inhibited since electron correlation and scalar-relativistic effects create small energy barriers leading to the global C_{2v} minima, although both types of effects interfere.

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I. INTRODUCTION

During the past decades, several computational works concerning the geometries of group 17 element XF_3 fluorides (where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{At}$, or even element 117), were reported.¹⁻⁹ These systems are not only of fundamental interest since they can be the subject of industrial applications. ClF_3 is a strong oxidizer, used as a fluorinating agent, and involved nowadays in the synthesis of uranium hexafluoride. BrF_3 is only used as a fluorinating agent in organic synthesis, while no application involving IF_3 is yet known. Several attempts to synthesize astatine fluorides turned out to be unsuccessful.¹⁰ The determination of the geometries of these known and hypothetical XF_3 systems is a task of fundamental interest in theoretical chemistry. The valence shell electron pair repulsion model^{11,12} supports bent T-shaped C_{2v} geometries (see Figure 1). Experimentally, such geometries were evidenced for ClF_3 ^{13,14} and BrF_3 ¹⁵ in the gas phase, and also in the condensed state of IF_3 .¹⁶ Regarding the $(117)\text{F}_3$ system, a planar D_{3h} structure is predicted from computations,^{4,5,9} while AtF_3 is a borderline system where the T-shaped C_{2v} and the D_{3h} structures are almost isoenergetic.^{2,4,5,9} For the XF_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) systems, such a D_{3h} structure is unstable due to the *pseudo* Jahn-Teller effect (PJTE).¹⁷ The detailed description of the PJTE in these cases was first given by Schwerdtfeger.² In the AtF_3 case, the D_{3h} situation corresponds to a local minimum,^{5,9} meaning that the PJTE is in this case inhibited by other electronic factors.

FIG. 1. Ball and stick representations of T-shaped C_{2v} (left) and planar D_{3h} (right) XF_3 geometries. [Color code: maroon ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{At}$), light blue (F)].

From a quantum mechanical perspective, non-relativistic (NR), scalar-relativistic (SR) and spin-orbit coupling (SOC) calculations have been performed^{1,2,4,5,9} in order to determine critical points on the ground state potential energy surfaces (PESs) of these XF_3 systems, as well as for determining energy differences between them, especially the one between the D_{3h} and the T-shaped C_{2v} structures, $\Delta E^{D_{3h}-C_{2v}}$. However, for some systems, important

critical points of the PES are still not reported or discussed. Regarding most of the transition states (TSs), their nature (*i.e.* their connectivities with minima of the PESs) was generally not rigorously established. The most emblematic case is the AtF₃ system where important aspects are still a matter of debate in the literature. For instance, very recently Yang and Wang⁹ stated that the T-shaped C_{2v} structure is the only candidate to be observed through experiments. But one may think at first glance that their reasoning is a bit odd. Strong issues are related to the existence of the D_{3h} structure as a true minimum, *e.g.* about the effects that inhibit the PJTE in this case. Different factors such as electron correlation, SR effects and SOC are able to significantly affect $\Delta E^{D_{3h}-C_{2v}}$. It is well known that numerous properties of At species are highly sensitive to SOC.¹⁸⁻²³ Thus, the most recent investigations^{5,9} had focused on the relationship between SOC and the PJTE at the D_{3h} structure. However, no definite statement has yet been made.⁹ Indeed, one needs to consider the different factors not solely at the D_{3h} structure, but also how they affect the PES in its close vicinity in order to reach a relevant conclusion. Furthermore, all previous theoretical studies made use of single-determinantal methods while the reliability of such approaches has not been verified in difficult cases like AtF₃.

In this article, we aim at resolving the above-mentioned points through multiconfigurational wave function theory (WFT) calculations, via a contracted spin-orbit configuration interaction approach, and additional spin-orbit density functional theory (SO-DFT) calculations. Note that the two-step spin-orbit WFT approach have been already validated in iodine and astatine containing systems.^{24,25} Since this work also deals with the ClF₃ and BrF₃ systems, we will start by validating the choice of the exchange-correlation functionals used to explore the PESs of interest. The obtained geometries of the critical points will be used for subsequent multiconfigurational WFT calculations, aiming at studying the dependence of the results on the degrees of freedom associated to this methodology. Finally, based on multiconfigurational calculations, we will discuss the role of electron correlation, scalar relativistic effects, and SOC along the XF₃ series in order to clarify and complement the conclusions of previous investigations^{4,5,9} on the respective role of these effects on the PESs of the studied systems.

II. METHODOLOGY

A. DFT calculations

The critical points of the PESs corresponding to the ground state of the XF_3 ($\text{X} = \text{Cl-At}$) systems were optimized using NR-DFT ($\text{X} = \text{Cl}$), SR-DFT and SO-DFT ($\text{X} = \text{Br-At}$) approaches. NR- and SR-DFT calculations have been performed using the GAUSSIAN09 program package,²⁶ while all the SO-DFT ones were carried out with the NWChem program package.²⁷ Vibrational harmonic frequencies have been determined to establish the nature of the different critical points. Afterwards, the connectivities between TSs and minima were established through the computation of intrinsic reaction coordinate (IRC) paths at NR or SR levels.

The M06-2X²⁸ and PBE0^{29,30} hybrid exchange-correlation functionals were considered, since these two functionals showed good performance on the XF_3 ($\text{X} = \text{I-117}$) fluorides.⁹ In order to further discuss the role of the fraction of “exact” exchange on the performance of DFT functionals on these systems, this fraction has been also varied in a hybrid PBE functional, PBEh(x), where x denotes the percentage of exact exchange.

In the SR-DFT and SO-DFT calculations, energy-consistent small-core ECP n MDF pseudopotentials^{31,32} were used to mimic the effects of the $n = 60$ core electrons of At, $n = 28$ core electrons of I, and $n = 10$ core electrons of Br. Note that in the SO-DFT calculations, the pseudopotentials account for both scalar relativistic effects and SOC. For describing the explicitly treated electrons (25 in the neutral atoms), the aug-cc-pVTZ-PP-2c basis sets³³ were used for the At and I atoms, while the aug-cc-pVTZ-PP one³¹ was used for Br. All-electron aug-cc-pVTZ basis sets^{34,35} were used for the Cl and F atoms.

B. WFT calculations

All the WFT calculations were performed with the ORCA program package.³⁶ Regarding the ClF_3 and BrF_3 systems, reference values for $\Delta E^{D_{3h}-C_{2v}}$ were obtained with the CCSD(T) method by means of geometry optimizations. For ClF_3 , the relativistic effects were neglected and TZVP basis sets were used.³⁷ For BrF_3 , scalar relativistic effects were taken into account via the use of the Douglas-Kroll-Hess Hamiltonian³⁸⁻⁴⁰ and accordingly, the segmented all-electron relativistically contracted SARC-TZVP-DKH basis set were used.⁴¹

Two-step WFT calculations were then performed. In the first step, a set of spin-orbit free (SOF) states is computed at a multiconfigurational level, here using the state-averaged complete active space self-consistent field (SA-CASSCF) approach.^{42,43} The calculations were performed on the previously optimized (SO-)DFT structures. In the second step, the spin components of the SOF states are used to build a state-interaction matrix, consisting of correlated energies on the diagonal, and off-diagonal SOC matrix elements computed within a mean-field approximation.^{44,45} An important degree of freedom concerns the method used to compute the correlated energies, which can be SA-CASSCF or the n -electron valence state second-order perturbation theory (NEVPT2) method.⁴⁶ The latter accounts for more dynamic correlation and usually does not suffer from the occurrence of intruder states. The SARC-TZVP-DKH basis sets^{41,47} were used for all atoms in these calculations, and scalar relativistic effects were accounted for via the Douglas-Kroll-Hess Hamiltonian.^{38–40}

Regarding the CASSCF calculations, two active spaces have been considered: (i) a minimal one (in view of SOC calculations) comprising only 2 electrons and the np orbitals of the central atom, leading to CASSCF(2/3) calculations, and (ii) a larger one comprising 20 electrons and the np and $2p$ orbitals of the central and F atoms, leading to CASSCF(20/12) calculations. In the SA-CASSCF(2/3) calculations, two state-averaging schemes have been considered: the full one consisting of the $M_{S_{\max}}$ components of the 6 singlet (S) and 3 triplet (T) spin states (6S3T), and a subset of it, containing the ground SOF state plus all the essentially singly-excited states, *i.e.* 3S and 2T states (3S2T). For the SA-CASSCF(20/12) calculations, only one averaging scheme has been considered, namely 21S20T. Note that this averaging-scheme fulfills the following conditions for all the studied XF_3 systems, (i) it does not artificially break the symmetry in the D_{3h} structures, (ii) it includes all the essentially singly excited states, and (iii) the enlargement of the state-averaging space and of the corresponding state-interaction space hardly affect the computed SOC ground state energy stabilizations.

Furthermore, specific Hartree-Fock (HF) and NEVPT2 calculations were performed at NR and SR levels in order to highlight the role of scalar relativistic effects, electron correlation and SOC on the stability of some structures. These calculations made use of fully uncontracted SARC-TZVP-DKH basis sets in order to avoid any bias introduced by the contraction scheme.

III. RESULTS AND DISCUSSION

A. DFT study

We start our analysis by looking at the performance of the M06-2X and PBE0 functionals in determining the geometries of the D_{3h} and T-shaped C_{2v} structures, as well as the energy difference between them ($\Delta E^{D_{3h}-C_{2v}}$). With both functionals, the T-shaped C_{2v} structures are minima of the PESs for all the studied XF_3 systems. The D_{3h} structure is a second-order saddle point in the $X = \text{Cl-I}$ cases, with one doubly-degenerate e' imaginary frequency. In contrast, the D_{3h} structure is found to be a (weak) local minimum in the AtF_3 case. These results are compared to experimental data, when available, as well as to (SO-)CCSD(T) reference calculations (see Table I). Since the CCSD(T) equilibrium geometries are in very good agreement with the experimental ones for the ClF_3 and BrF_3 T-shaped C_{2v} structures, both sets of results can be alternatively used to assess the quality of the (SO-)DFT results. Table I reveals that both the PBE0 and M06-2X functionals lead to geometries in very good agreement with the (SO-)CCSD(T) ones, and when available, with the experimental data. For instance, the obtained deviation with the PBE0 functional regarding the equilibrium bond lengths with respect to the (SO-)CCSD(T) ones is less than 2% for each studied system. However, important discrepancies with the CCSD(T) results appear in some cases for $\Delta E^{D_{3h}-C_{2v}}$. While (SO-)PBE0 gives reasonable energy differences compared to (SO-)CCSD(T) for the whole XF_3 series, the (SO-)M06-2X results deviate more and more from $X = \text{At}$ to $X = \text{Cl}$. For ClF_3 , the $\Delta E^{D_{3h}-C_{2v}}$ value computed with the M06-2X functional is too large by $\sim 30 \text{ kJ mol}^{-1}$ with respect to the CCSD(T) value. One can conclude that the PBE0 functional is overall more adequate than the M06-2X one for studying PESs in the XF_3 ($X = \text{Cl-At}$) series.

In order to highlight the role of the fraction x of exact exchange in hybrid functionals, we monitored the r_e bond length (D_{3h} case) and $\Delta E^{D_{3h}-C_{2v}}$ while varying x in PBEh(x) functional, from 20 to 100 % (see Figure 2). Using B3LYP as the reference functional, Yang and Wang⁹ had performed a similar study but restricted to the case of AtF_3 . We find similar trends in the whole XF_3 series, *i.e.* both r_e and $\Delta E^{D_{3h}-C_{2v}}$ diminish with the fraction of exact exchange. When comparing to the (SO-)CCSD(T) results, we find, for instance in the case of AtF_3 , a different optimal fraction, $\sim 35 \%$ for r_e and $\sim 40 \%$ for $\Delta E^{D_{3h}-C_{2v}}$, with

TABLE I. Geometrical parameters of the D_{3h} and T-shaped C_{2v} structures computed at various levels of theory, and associated energy differences.

System	Method	D_{3h}	T-shaped C_{2v}			$\Delta E^{D_{3h}-C_{2v}}$ (kJ mol ⁻¹)
		$r_e(\text{\AA})$	$r_{eq}(\text{\AA})$	$r_{ax}(\text{\AA})$	$\alpha(^{\circ})$	
ClF ₃	NR-M06-2X	1.713	1.592	1.696	86.6	128.4
	NR-PBE0	1.728	1.603	1.706	87.4	91.5
	SR-CCSD(T)	1.738	1.605	1.703	87.1	96.7
	Expt. ¹³	-	1.598	1.698	87.5	-
BrF ₃	SO-M06-2X	1.815	1.715	1.802	85.4	93.2
	SO-PBE0	1.825	1.725	1.812	86.4	60.2
	SR-CCSD(T)	1.828	1.725	1.811	86.0	70.7
	Expt. ¹⁵	-	1.721	1.810	86.2	-
IF ₃	SO-M06-2X	1.956	1.866	1.940	83.0	79.2
	SO-PBE0	1.965	1.878	1.950	83.8	55.0
	SO-CCSD(T) ⁹	1.941	1.853	1.926	83.3	67.8
AtF ₃	SO-M06-2X	2.059	1.993	2.059	89.1	10.3
	SO-PBE0	2.068	2.012	2.068	91.0	2.4
	SO-CCSD(T) ⁹	2.046	1.987	2.046	89.1	7.7

respect to the ~ 55 % obtained in Ref. 9. This discrepancy is due to the use of another reference functional. Therefore, the good performance of hybrid functionals for computing geometries and energy differences in the XF₃ series is not only related to the fraction of exact exchange since different functionals with very different fractions of exact exchange can lead to a similar accuracy. From Figure 2, one would conclude that the recommended fractions of exact exchange would range from 20–30 % (ClF₃ case) to 35–45 % (IF₃ case) for PBEh(x). Overall, one could recommend to use the PBEh(35) functional. However, not much improvement would be reached compared to the standard PBE0 functional ($x=25$), which has therefore been used in the rest of this work.

We now question the nature of the Y-shaped C_{2v} TSs on the PESs of the XF₃ systems, that were previously reported by Yang and Wang.⁹ Table II displays the computed geometrical parameters using both functionals, as well as the energy difference of these Y-shaped TSs

FIG. 2. Evolution of the energy differences between the C_{2v} and D_{3h} structures ($\Delta E^{D_{3h}-C_{2v}}$) and of the D_{3h} bond lengths (r_e) as a function of the fraction of exact exchange (x) introduced in the PBEh(x) functional.

with respect to the T-shaped C_{2v} global minima. The comparison with the D_{3h} structure shows for the ClF₃, BrF₃ and IF₃ cases that the r_{ax} bond lengths are smaller than r_e , the r_{eq} bond lengths are larger than r_e and the α bond angles are larger than 120° . Such Y-shaped TSs are expected to be involved in the pseudo-rotations between two equivalent T-shaped C_{2v} global minima, as suggested in the ClF₃¹ and IF₃⁹ cases. We confirm this hypothesis through IRC calculations as displayed in Figure 3. Note that going from the D_{3h} to the T-shaped C_{2v} structure via a Y-shaped C_{2v} TS does not involve a drastic change in the electronic configuration.

Regarding the AtF₃ system, a Y-shaped C_{2v} TS also exists but its structure exhibits an α bond angle smaller than 120° , an r_{ax} bond length larger than r_e , and an r_{eq} bond length

FIG. 3. Energies along the IRC paths starting from Y-shaped C_{2v} TSs, computed at NR- or SR-PBE0 levels (the T-shaped C_{2v} energies are chosen as the zeroes of energy).

TABLE II. Geometrical parameters of the Y-shaped C_{2v} TSs computed at various levels of theory, and associated energy differences $\Delta E^{\text{TS}-C_{2v}}$.

System	Method	$r_{\text{eq}}(\text{\AA})$	$r_{\text{ax}}(\text{\AA})$	$\alpha(^{\circ})$	$\Delta E^{\text{TS}-C_{2v}} (\text{kJ mol}^{-1})$
ClF ₃	NR-M06-2X	1.770	1.676	130.9	121.5
	NR-PBE0	1.762	1.703	128.7	89.3
BrF ₃	SO-M06-2X	1.848	1.793	128.7	90.8
	SO-PBE0	1.843	1.814	125.6	59.9
IF ₃	SO-M06-2X	1.981	1.940	127.8	77.9
	SO-PBE0	1.978	1.958	124.4	54.9
	SO-CCSD(T) ⁹	1.960	1.930	126.4	67.3
AtF ₃	SO-M06-2X	2.053	2.060	117.8	11.1
	SO-PBE0	2.047	2.075	108.7	3.1
	SO-CCSD(T) ⁹	2.039	2.049	116.0	7.8

smaller than r_e . Furthermore, this TS is (slightly) higher in energy than the D_{3h} structure, in contrast to what is observed for ClF₃, BrF₃ and IF₃. Hence, this TS exhibits a different nature and it was suggested to connect T-shaped C_{2v} and D_{3h} minima by Yang and Wang.⁹ Note that differences appear between the results presented in Table II and the energy profiles displayed in Figure 3 since SOC is neglected in these IRC calculations. In the AtF₃ system,

FIG. 4. C_s TS structure of AtF_3 with displacement vectors traced for the imaginary frequency (left) and energy along the IRC path starting from the C_s TS and computed at SR-PBE0 level (right). The energy of the T-shaped C_{2v} minimum is chosen as the zero of energy.

SOC notably stabilizes the Y-shaped C_{2v} and the D_{3h} structures compared to the T-shaped one.

In the literature, the potential existence of TSs connecting T-shaped C_{2v} minima in AtF_3 was not considered. At SR levels, we have identified a C_s TS with an out-of-plane distorted geometry (see Figure 4). This C_s TS actually connects two T-shaped C_{2v} minima, as shown by the IRC profile (see Figure 4). SOC significantly stabilizes the TS and modifies its geometrical parameters close to a C_{3v} structure at the SO-M06-2X level, and leads to the practical impossibility of converging on a C_s structure at the SO-PBE0 level. The optimized SR-DFT and SO-DFT geometrical parameters of the C_s TS are compiled in Table III.

In close connection with the C_s TS structure, a second-order saddle point belonging to the C_{3v} symmetry point group was evidenced. The doubly-degenerate imaginary frequencies are $57i$ and $67i \text{ cm}^{-1}$ at the SO-M06-2X and SO-PBE0 levels, respectively. Note that in the limit of a doubly-degenerate zero-frequency normal mode, this C_{3v} structure would correspond to a “monkey”^{48,49} saddle point associated with the trifurcation toward the three possible C_s TS structures. Such situation was for instance suggested in (tetracoordinated) AX_4 systems,⁵⁰ even if the existence of “monkey” saddle points can be seriously questioned since

it would violate some rules.^{51,52} The fact that we failed to optimize the C_s TS structure at the SO-PBE0 level could be related to the near degeneracy with the C_{3v} structure. The near degeneracy between the C_s and C_{3v} geometries is also an indication for the existence of an effective “monkey” C_{3v} saddle point in AtF_3 , even if no definitive conclusion can actually be given on this point.

TABLE III. AtF_3 geometrical parameters of the C_s TS computed at SO-DFT and SR-DFT (in parenthesis) levels of theory, corresponding imaginary harmonic frequency, and associated energy difference $\Delta E^{\text{TS}-C_{2v}}$.

Method	$r_{\text{in}}(\text{\AA})$	$r_{\text{out}}(\text{\AA})$	$\nu_1(\text{cm}^{-1})$	$\Delta E^{\text{TS}-C_{2v}} (\text{kJ mol}^{-1})$
SO-M06-2X	2.061 (1.957)	2.062 (2.063)	106i (314i)	156.4 (256.0)
SO-PBE0	(1.969)	(2.078)	(308i)	(242.8)

Schematic representations of the connectivity maps for the ground state PESs of the studied XF_3 systems are shown in Figure 5. For $\text{X} = \text{Cl-I}$, the D_{3h} structure is a second-order saddle point and three equivalent T-shaped C_{2v} global minima are connected via Y-shaped C_{2v} TSs. For AtF_3 , the D_{3h} structure is a “weak” local minimum, while three equivalent T-shaped C_{2v} structures correspond to global minima of the PES. Between the D_{3h} and each T-shaped C_{2v} structure, there is a very small energy barrier associated to a Y-shaped C_{2v} TS. At SR levels, each pair of T-shaped C_{2v} minima are connected via a C_s TS leading to a large energy barrier. When SOC is included in M06-2X calculations, the C_s structure is brought very close in terms of geometry and energy to a more symmetric C_{3v} one. Note that dissociation energies corresponding to the formation of either $\text{XF} + \text{F}_2$ or $\text{XF}_2 + \text{F}$ are reported in Table SI.⁵³ All the critical points reported in Figure 5 are found lower in energy than the lowest dissociation limit for each XF_3 system.

Finally, we find that the inclusion of entropic and thermal contributions significantly reduces the difference in stability between the D_{3h} and C_{2v} minima. At $T = 298 \text{ K}$ and $P = 1 \text{ atm}$, the difference in free energy is 3.6 and 0.3 kJ mol^{-1} at the SO-M06-2X and SO-PBE0 levels, respectively. Given the accuracy of the used approaches, it becomes impossible to conclude on the nature of the AtF_3 most stable structure (C_{2v} or D_{3h}). However, since the free energy difference between these structures and the associated energy barriers are so small, it would be impossible to experimentally distinguish between these two

structures, and therefore, an average D_{3h} geometry would be seen in the experiments, if they were possible.

FIG. 5. Schemes of the connectivity maps between the important critical points of the PESs of the XF_3 systems, $\text{X} = \text{Cl-I}$ (left), $\text{X} = \text{At}$ (right). [Color code: blue is used for minima, green for TSs and red for second-order saddle points.]

B. WFT study

The dependence of the results with respect to computational degrees of freedom was first assessed by means of single-point calculations on previously obtained DFT geometries. Since in two-step WFT calculations the SOC is introduced *a posteriori*, it is straightforward to distinguish SOF and SOC contributions to $\Delta E^{D_{3h}-C_{2v}}$. In Tables SII–SIV and IV, SOC stabilizations of the T-shaped C_{2v} and the D_{3h} structures, namely $E_{\text{SOC}}^{C_{2v}}$ and $E_{\text{SOC}}^{D_{3h}}$ are reported. It is therefore possible to quantify SOC effects ($\Delta E_{\text{SOC}}^{D_{3h}-C_{2v}}$) on $\Delta E^{D_{3h}-C_{2v}}$.

Tables SII and SIII collect energy parameters computed at the NEVPT2(2/3) and NEVPT2(2/3)+SOC levels of theory, with 6S3T and 3S2T averaging schemes. As expected, both schemes lead to quite similar results. At these levels, $\Delta E^{D_{3h}-C_{2v}}$ is rather constant in the series from $\text{X} = \text{Cl}$ to $\text{X} = \text{I}$, while it is much smaller in the AtF_3 case. According to the reference CCSD(T) results, a significant decrease of $\Delta E^{D_{3h}-C_{2v}}$ is expected from ClF_3 to BrF_3 , which is not reproduced at the considered NEVPT2(2/3) levels. This fact is probably due to the size of the active space, which may not be large enough to well describe covalency

in the states of interest. As expected, the absolute values of $E_{\text{SOC}}^{C_{2v}}$ and $E_{\text{SOC}}^{D_{3h}}$ increase with the atomic number. The SOC stabilization of C_{2v} and D_{3h} structures being practically equivalent from $X = \text{Cl-I}$, no significant SOC contribution to $\Delta E^{D_{3h}-C_{2v}}$ is observed in Tables SII and SIII. The AtF_3 case is more ambiguous since $\Delta E_{\text{SOC}}^{D_{3h}-C_{2v}}$ is of the same order of magnitude as the NEVPT2(2/3) $\Delta E^{D_{3h}-C_{2v}}$, leading to an almost vanishing $\Delta E^{D_{3h}-C_{2v}}$ value at the NEVPT2(2/3)+SOC level. It is thus clear that increasing the active space is actually needed for determining which of the C_{2v} and the D_{3h} structures is lower in energy at the NEVPT2+SOC level of theory.

SA-CASSCF(20/12) and NEVPT2(20/12) results obtained with active spaces which also include the $2p$ orbitals (and electrons) of fluorine atoms are presented in Tables SIV and IV. The comparison between the two sets of data highlights the importance of the electron correlation that was not treated within the active space. While this correlation enlarges $\Delta E^{D_{3h}-C_{2v}}$ in the ClF_3 and BrF_3 cases, it markedly diminishes it in the IF_3 and AtF_3 cases. At the SA-CASSCF(20/12)+SOC level, the expected trend regarding $\Delta E^{D_{3h}-C_{2v}}$ values within the series is not reproduced, while it appears correct at the NEVPT2(20/12)+SOC level, with values in good agreement with the (SO-)CCSD(T) ones. The SOC contribution to the energy lowering of the C_{2v} and D_{3h} structures is negligible for ClF_3 and BrF_3 , is moderate for IF_3 ($\sim 5 \text{ kJ mol}^{-1}$), and appears quite important for AtF_3 ($\sim 60 \text{ kJ mol}^{-1}$). As previously noted, SOC does not contribute much to $\Delta E^{D_{3h}-C_{2v}}$, since this coupling stabilizes in a very similar way the C_{2v} and D_{3h} minima. However, the $\Delta E_{\text{SOC}}^{D_{3h}-C_{2v}}$ value in the AtF_3 case, which is about -0.7 kJ mol^{-1} , appears somewhat small compared to previous DFT calculations: the energy difference between the D_{3h} and T-shaped C_{2v} minima is reduced by 8.8(11.6) kJ mol^{-1} when comparing SO-PBE0(SO-M06-2X) results. This issue is most probably related to the neglect of the geometry relaxation when computing the NEVPT2(20/12) and NEVPT2(20/12)+SOC energies (SO-PBE0 geometries are used).

It is worth noting for the whole series that in the SA-CASSCF(20/12) ground-state wave functions, the weights of the HF configurations are always larger than 80%. Due to the use of state-averaged orbitals, the SOF wave functions may look more multiconfigurational than what they should actually be. This means that these ground SOF states are essentially single-configurational in all the series. In addition, regarding the SOC wave functions, they are dominated by the ground-SOF-singlet spin component. In the AtF_3 case, where SOC effects are the largest ones, the $|M_S| = 1$ components of the first two excited SOF triplet

states correspond to 16% of the ground SOC wave function for the D_{3h} minimum, while the ground-SOF-singlet spin component weights 83%. We definitively conclude that the ground SOC wave functions are essentially single-configurational in this series, which justifies the use of single-determinantal or single-reference approaches such as the SO-DFT and SO-CCSD(T) ones.

TABLE IV. Contributions (in kJ mol^{-1}) to $\Delta E^{D_{3h}-C_{2v}}$ computed at the NEVPT2 and NEVPT2+SOC levels using SA-CASSCF(20/12) references and 21S20T state-averaging and state-interaction spaces. The reference (SO-)CCSD(T) $\Delta E^{D_{3h}-C_{2v}}$ values are also recalled for convenience.

System	NEVPT2	NEVPT2+SOC				(SO-)CCSD(T)
	$\Delta E^{D_{3h}-C_{2v}}$	$E_{\text{SOC}}^{D_{3h}}$	$E_{\text{SOC}}^{C_{2v}}$	$\Delta E_{\text{SOC}}^{D_{3h}-C_{2v}}$	$\Delta E^{D_{3h}-C_{2v}}$	$\Delta E^{D_{3h}-C_{2v}}$
ClF_3	88.6	-0.1	-0.1	-0.0	88.6	96.7
BrF_3	72.0	-1.2	-1.0	-0.2	71.8	70.7
IF_3	66.2	-6.1	-5.4	-0.7	65.5	67.8 ⁹
AtF_3	7.4	-58.8	-58.1	-0.7	6.7	7.7 ⁹

FIG. 6. Scheme representing the two different pathways used to define the contributions of scalar relativistic effects (SRE) and electron correlation (EC) on $\Delta E^{D_{3h}-C_{2v}}$.

In order to shed light on important factors affecting the $D_{3h} - C_{2v}$ energy difference within

the series, namely scalar relativistic effects (SRE) and electron correlation (EC), NR-HF, SR-HF, NR-NEVPT2(20/12) and SR-NEVPT2(20/12) calculations have been performed with uncontracted SARC-TZVP-DKH basis sets (see Table V). It allows us to define SRE and EC contributions to the SR $\Delta E^{D_{3h}-C_{2v}}$ values through two paths: (i) Path₁ in which SRE are first introduced at the non-correlated HF level, prior to introducing EC at the SR level, and (ii) Path₂ in which EC is introduced in the absence of SRE and SRE are later introduced at the NEVPT2 correlated level (see Figure 6). If SRE and EC were additive, both paths would yield the same SRE and EC contributions to $\Delta E^{D_{3h}-C_{2v}}$. One concludes that it is not the case by looking at the data reported in Table V, *i.e.* SRE and EC interfere. In the X = Cl-I cases, $\Delta E^{D_{3h}-C_{2v}}$ is more affected by EC than by SRE. In contrast, an opposite behavior is observed in the AtF₃ case, which furthermore displays a particularly large interference between SRE and EC: the sum of SRE(HF) and EC(NR) contributions is about ~ 20 kJ mol⁻¹ over the sum of the EC(SR) and SRE(NEVPT2) contributions. Note that although the NR-HF $\Delta E^{D_{3h}-C_{2v}}$ values are too large compared to the SR-NEVPT2 ones, they already exhibit a correct trend within the series. Indeed, the simultaneous treatment of both SRE and EC affects in a similar way the $\Delta E^{D_{3h}-C_{2v}}$ values (with respect to the NR-HF ones), with only a small noticeable difference for the ClF₃ case (SRE and EC decrease more $\Delta E^{D_{3h}-C_{2v}}$ than in the other cases).

TABLE V. Contributions (in kJ mol⁻¹) of scalar relativistic effects (SRE) and electron correlation (EC) to $\Delta E^{D_{3h}-C_{2v}}$ according to the two pathways represented in Figure 6.

	NR-HF	Path ₁		Path ₂		SR-NEVPT2	
XF ₃	$\Delta E^{D_{3h}-C_{2v}}$	SRE(HF)	EC(SR)	EC(NR)	SRE(NEVPT2)	SRE + EC	$\Delta E^{D_{3h}-C_{2v}}$
ClF ₃	185.8	-4.1	-92.6	-93.6	-3.1	-96.7	89.1
BrF ₃	149.7	-14.7	-63.1	-65.9	-11.9	-77.8	71.9
IF ₃	142.5	-29.4	-46.3	-51.1	-24.5	-75.7	66.8
AtF ₃	80.5	-52.3	-22.1	-31.5	-42.9	-74.4	6.1

In order to assess the existence of the low TS connecting D_{3h} and C_{2v} minima in the AtF₃ system, one has to go beyond single-point calculations. We have considered scans of the ground state PES between the D_{3h} and C_{2v} structures *via* NEVPT2(20/12) and NEVPT2(20/12)+SOC calculations. Three variables naturally arise, namely α , r_{ax} and r_{eq}

FIG. 7. Representation of the NEVPT2(20/12) (left) and NEVPT2(20/12)+SOC (right) ground state PESs of AtF₃. The energy scale is expressed in kJ mol⁻¹ and the T-shaped C_{2v} energies are chosen as the zeroes of energy.

which were all varied in contrast to previous studies.^{2,5,9} In order to approximately determine the minimum energy path, a non-uniform grid has been defined by interpolations between the D_{3h} and C_{2v} structures. In Figure 7, contour plots of the resulting surfaces are represented. Note that for each r_{eq} value corresponds a different r_{ax} value. The approximate structures of the D_{3h} and C_{2v} minima at NEVPT2+SOC level do not differ much from the ones optimized at the SO-PBE0 level. As can also be seen, the Y-shaped C_{2v} TS is evidenced between the D_{3h} and C_{2v} minima at both NEVPT2 and NEVPT2+SOC levels. Its approximate structure complies with the previous findings: α smaller than 120°, r_{ax} larger than r_e and r_{eq} smaller than r_e (not explicitly shown on Figure 7). Notable SOC effects on the PES are evidenced by the comparison of the NEVPT2 and NEVPT2+SOC scans displayed in Figure 7. It is clear that the energy difference between the D_{3h} and C_{2v} minima, and to a lesser extend, the one between the Y-shaped C_{2v} TS and the C_{2v} minimum are decreased, *i.e.* the PES is “flattened” by SOC. This does agree with the reference SO-CCSD(T) calculations, where SOC reduces about 8 kJ mol⁻¹ the energy difference between the D_{3h} and C_{2v} minima.⁹

Finally, we have analyzed the factors affecting the energy difference between the Y-shaped C_{2v} TS and the D_{3h} minimum by means of single-point calculations, performed on the SO-PBE0 geometries. The results gathered in Table VI show that SRE and EC are the main contributions and are both responsible for the existence of the Y-shaped TS. Indeed, SRE and

EC tend to enlarge the energy difference, resulting in a C_{2v} TS lying at higher energy than the D_{3h} minimum. As for the $\Delta E^{D_{3h}-C_{2v}}$ energy difference, some interference appear between SRE and EC which actually lead to a smaller energy difference than if the effects were additive. SOC does not seem to affect much the energy difference, an energy increase of only 0.3 kJ mol⁻¹ is calculated. The latter prediction is quite consistent with previous DFT results: the comparison of SR-PBE0 (SR-M06-2X) and SO-PBE0 (SO-M06-2X) results, points out that SOC increases the energy difference between the Y-shaped C_{2v} TS and the D_{3h} minimum by 0.6 (0.1) kJ mol⁻¹. It is worth noting that previous SO-CCSD(T) calculations led to a small decrease of about 1 kJ mol⁻¹.⁹ Thus, it comes out that spin-dependent relativistic effects are definitely small and somewhat bland on the relative energy of the Y-shaped C_{2v} TS with respect to the one of the D_{3h} minimum.

TABLE VI. Energy difference (in kJ mol⁻¹) between the Y-shaped TS and the D_{3h} minimum of AtF₃ ($\Delta E^{TS-D_{3h}}$) computed at different levels of theory (SO-PBE0 geometries are considered).

XF ₃	NR-HF	SR-HF	NR-NEVPT2	SR-NEVPT2	SR-NEVPT2+SOC
AtF ₃	-12.0	-2.5	-6.2	1.8	2.2

IV. CONCLUSION

In this work, the topological properties of the PESs and the molecular geometries of the XF₃ (X = Cl–At) fluorides have been studied with DFT and WFT based methods. From a methodological point of view, several conclusions arise. First, the PBE0 functional appears better suited to describe the whole series than the M06-2X one. Regarding the multiconfigurational WFT calculations, the ground spin-orbit-free states are found to be essentially closed-shell and single-configurational, especially in the X = Br–At cases. While spin-orbit coupling introduces some open-shell character to the AtF₃ wave function, the latter remains dominated by the ground spin-orbit-free spin-singlet HF configuration. It is an indisputable support for all the previous studies on these systems that made use of single-determinantal or single-reference methods.^{1,2,4,5,9} Furthermore, we have demonstrated the suitability of the two-step spin-orbit configuration interaction calculations, where spin-orbit coupling is introduced *a posteriori* as a perturbation of spin-orbit-free effects, for investigating

the XF_3 PESs, although such an approach is sometimes said to be problematic for systems containing heavy p -elements as At.⁵⁴

With respect to the PES explorations, new critical points have been evidenced and notably in the AtF_3 system, three equivalent C_s TSs connecting the C_{2v} minima between them. In the $\text{X} = \text{Cl-I}$ cases, Y-shaped TSs connect two equivalent T-shaped C_{2v} minima, while in the AtF_3 system, each Y-shaped TS connects a T-shaped C_{2v} minima and the D_{3h} minimum. The calculated energy difference between the C_{2v} and D_{3h} minima is very small, and considering the thermal and entropic contributions, no definitive conclusion can actually be given on the nature of the AtF_3 most stable structure. However, we firmly consider that the D_{3h} minimum would be the average structure seen from experiment, if they were possible, since the Y-shaped TSs results in trifling energy barriers between the three equivalent T-shaped C_{2v} minima.

Based on WFT calculations, we found in all the studied systems that scalar relativistic effects and electron correlation strongly reduce the energy differences between the T-shaped C_{2v} and the D_{3h} structures by more than a factor of two. While in the $\text{X} = \text{Cl-I}$ cases, electron correlation plays a more important role, scalar relativistic effects are the main contributors to the energy differences of interest in the AtF_3 system. As expected in the $\text{X} = \text{Cl-I}$ cases, no significant spin-orbit coupling effects were found, and the latter led to a weak reduction of the energy difference when $\text{X} = \text{At}$. Furthermore, both scalar relativistic effects and electron correlation inhibits the *pseudo* Jahn-Teller effect in the AtF_3 system by creating an energy barrier between the emerging D_{3h} minimum and the C_{2v} minima, although both effects interfere. In agreement with DFT calculations, the spin-orbit coupling effects are found negligible regarding this point.

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