Effective Monkey Saddle Points and Berry and Lever Mechanisms in the Topomerization of SF_4 and Related Tetracoordinated AX_4 Species

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The topomerization mechanisms of the SF_4 and SCl_2F_2 sulfuranes, as well as their higher (SeF_4, TeF_4) and isoelectronic analogues PF_4^-, AsF_4^-, SbF_4^-, $SbCl_4^-$, ClF_4^+, BrF_4^+, $BrCl_2F_2^+$, and IF_4^+), have been computed at B3LYP/6-31+G* and at B3LYP/6-311+G*. All species have trigonal bipyramidal (TBP) C_{2v} ground states. In such four-coordinated molecules, Berry rotation exchanges both axial with two equatorial ligands simultaneously while the alternative "lever" mechanism exchanges only one axial ligand with one equatorial ligand. While the barrier for the lever exchange in SF_4 (18.8 kcal mol^{-1}) is much higher than that for the Berry process (8.1 kcal mol^{-1}), both mechanisms are needed for complete ligand exchange. The $F_{ax}F_{ax}$ and $F_{eq}F_{eq}$ isomers of SF_2Cl_2 have nearly the same energy and readily interconvert by BPR with a barrier of 7.6 kcal mol^{-1}. The enantiomerization of the $F_{ax}F_{eq}$ chiral isomer can occur by either the Berry process (transition state barrier 8.3 kcal mol^{-1}) or the "lever" mechanism via either of two C_s transition states, based on the TBP geometry: $Cl_{ax} \leftrightarrow Cl_{eq}$ or $F_{ax} \leftrightarrow F_{eq}$ exchanges with barriers of 6.3 and 15.7 kcal mol^{-1}, respectively. Full scrambling of all ligand sites is possible only by inclusion of the lever mechanism. Planar, "tetrahedral", and triplet forms are much higher in energy. The TBP C_{3v} structures of AX_4 either have two imaginary frequencies (NIMAG = 2) for the X = F, Cl species or are minima (NIMAG = 0) for the X = Br, I compounds. These "effective monkey saddle points" have degenerate modes with two small frequencies, imaginary or real. Although a strictly defined "monkey saddle" (with degenerate frequencies exactly zero) is not allowed, the flat C_{3v} symmetry region serves as a "transition state" for trifurcation of the pathways. The BPR mechanism also is preferred over the alternative lever process in the topomerization of the selenurane SeF_4 (barriers 5.9 vs 12.1 kcal mol^{-1}), the tellurane TeF_4 (2.1 vs 6.4), and the interhalogen cations ClF_4^+ (2.5 vs 14.8), BrF_4^+ (4.7 vs 11.3), $BrF_2Cl_2^+$ (14.6 vs 17.4), and IF_4^+ (1.4 vs 6.0), as well as for the series PF_4^- (7.0 vs 9.0), AsF_4^- (9.3 vs 17.2), and SbF_4^- (3.8 vs 5.3 kcal mol^{-1}), all computed at B3LYP/6-311+G* with the inclusion of quasirelativistic pseudopotentials for Te, I, and Sb. The heavier halogens increasingly favor the lever process, where the barrier (2.6 kcal mol^{-1}) pertaining to the effective monkey saddle point (C_{3v} minimum for $SbCl_4^-$) is less than that for the Berry process (8.2 kcal mol^{-1}).

1. Introduction

First reported in 1911, SF_4,[1] the prototypical sulfurane, has a C_{2v} structure. This can be based on a trigonal bipyramid (TBP) with one equatorial site vacant.[2,3] An alternative C_{3v} form, with a missing axial site, also can be based on TBP but is expected to be higher in energy. This would comply with the VSEPR model,[4] which favors structures with equatorial lone pairs in which the bond−lone pair repulsion is minimized.[4]

Indeed, the low-temperature NMR of SF_4 shows two fluorine signals of equal area.[5−14] Like other sulfuranes, SF_4 is a nonrigid molecule which undergoes rapid exchange of ligand positions as revealed by its dynamic NMR spectra at higher temperatures.[5] Muetterties and Phillips showed in 1957[6] that the 30 MHz ^{19}F NMR spectrum of SF_4 coalesces at −47 °C into a single broad resonance which gradually sharpens to a narrow singlet at higher temperatures.[6] However, accurate measurements of the topomerization barrier were complicated for many years from difficulties due to impurities[6a,7] and to the intervention of bimolecular

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reactions,[6a,8] and by conflicts in the interpretation of data. Consequently, experimentally determined activation energies for the intramolecular rearrangement[15−19] of SF_4 range from 4[6,8] (for intermolecular exchange) to 16 kcal mol^{-1} [9] as deduced from the calculation of the NMR relaxation times from the signal coalescence temperatures at different temperatures. A barrier of 10 kcal mol^{-1} was obtained from IR studies in 1971 by a fitting of the potential function for the vibrational mode pertaining to the angle distortion between equatorial fluorines.[10] More recent measurements at different gas pressures gave values in a much narrower range, from 11.7[14] to 13.7[20] kcal mol^{-1}; 11.2 kcal mol^{-1} [14] was deduced in the liquid phase.

These values are consistent with computed barrier heights for the BPR process in SF_4, 10.6 kcal mol^{-1} at HF/6-31G$^{(*)}$ [19a] (the 6-31G* basis set was used for S), 10.3 kcal mol^{-1} at MP2/DZP, and 9.0 kcal mol^{-1} with an LSDA functional.[19b] Density functional calculations consistently give values that are 2−4 kcal mol^{-1} lower than the MP2/DZP results.[21]

Klemperer[13] provided conclusive evidence in 1975 that "Berry pseudorotation" (BPR)[16−18] was the mechanism by which the fluorines in SF_4 are interchanged. This mechanism, first proposed for ligand exchange in PF_5 in 1959[16a] (eventually also verified by Klemperer et al. in 1975),[13] results for such pentacoordinated systems in a total scrambling by a 5-fold repetition of the BPR topomerization step.[22]

"Turnstile rotation" (TR) was proposed by Ugi and Ramirez as an alternative to BPR in five-coordinated systems.[22b,c] The turnstile process involves an internal rotation of a ligand pair relative to the other three ligands in mutually opposite directions[22,23] and, like BPR, results in a simultaneous exchange of both axial with two equatorial ligands in pentacoordinated compounds.[22]

In tetracoordinated compounds like SF_4 with an additional lone pair at the central atom, a single BPR or TR step either would result in a TBP minimum structure with three equatorial ligands and a vacant axial position or does not result in total scrambling of the ligand positions, since only a simultaneous pairwise exchange of both axial ligands with the equatorial ligands is involved.[15,22] To achieve a full ligand scrambling in such SF_4-like systems without involving minima with vacant apical sites, Musher[24] and Minyaev and Minkin[25,26] independently considered several mechanistic alternatives, involving only single axial−equatorial exchange of ligands, in 1975.

The best alternative, termed the "lever" mechanism,[25−28] was computed for SF_4 by Minkin and Minyaev at extended Hückel and CNDO/2 levels in 1975[25] (we located the transition state at B3LYP/6-311+G* in 1994).[28] This mechanism resembles in outcome two consecutive "turnstile" steps. However, in contrast to the TR, only three ligands rotate with respect to the remaining ligand and the central atom. As this mechanism involves a single axial−equatorial exchange of ligands, it would allow a total scrambling of all ligand positions.

Indeed, low-energy mechanisms for the enantiomerization of SABCD and SA_2BC chiral halosulfuranes, like **a**,[29] **b**,[30] and **c**[31] in Scheme 1, appear to be absent, since such optically active sulfuranes[29−34] could be resolved.[30] The ^{19}F NMR data for **a** in solution is consistent with the presence of two nonequivalent sulfur-bound fluorines, because two signals are given by the two CF_3 groups.[29] A single Berry rotation step was considered for the $F_{ax} \leftrightarrow F_{eq}$ exchange of the two fluorines,[29] but racemization of **a** was not observed.

Solutions of the similar compound, (*S*)-chlorosulfurane **b**,[30] racemize only slowly on standing at room temperature (the lower limit of the barrier of uncatalyzed racemization is 25 kcal mol^{-1}).[30] Martin and Balthazor anticipated the possibility of a five-step enantiomerization of **b** on the basis of the Berry process.[30] If the Berry process would afford racemization of **b**, why it does it not for **a**?

Similarly, in spirobicyclic sulfuranes like **d**[35] and **e**,[36] with identical axial and equatorial ligands, rapid interconversion of enantiomeric forms was observed (racemization barrier: 7.5 kcal mol^{-1} at −100 °C).[35,36] While **d** displays four ^{19}F NMR peaks below −100 °C, only two F peaks appear above −100 °C.[35] But even at 200 °C no further coalescence to a single signal was observed, ruling out facile single axial−equatorial exchange of ligands.[35] Spirobicyclic **e** also enantiomerizes rapidly with an experimental barrier of 9 kcal mol^{-1}.[36] However, isomerization of **f**,[37] with an endo ethyl substituent, to the diastereomer with an exo ethyl substituent proceeds with a much higher barrier of 30 kcal mol^{-1} at 84 °C! Why?

We decided that the problem of sulfurane racemization would be adressed best by studying a simple model for a chiral sulfurane computationally. Hence, we considered the (unknown) mixed sulfur halide SF_2Cl_2 in the present work.

The potential energy surface of the isoelectronic and isostructural ClF_4^+ was examined recently at SCF/DZP and at MP2/DZP.[27] While the reported MP2 data was suspect (e.g., with a D_{4h} global minimum and a C_{3v} minimum, 79.6 kcal mol^{-1} above

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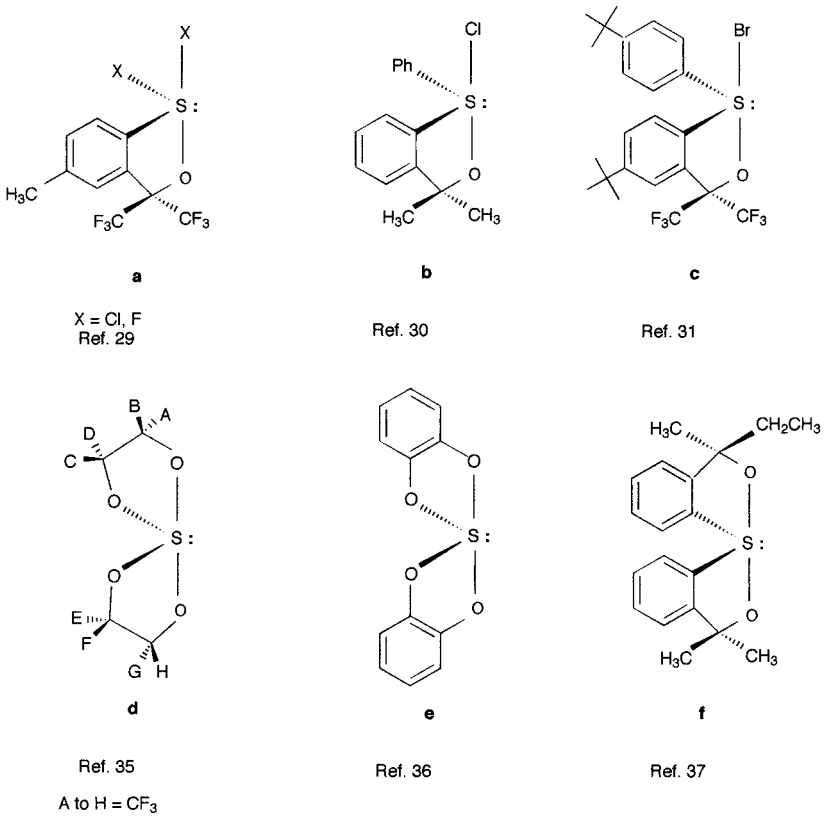
Scheme 1



the C_{2v} minimum), the reported activation barrier for the BPR process in ClF_4^+ is 6.7 kcal mol^{-1}, and 39.5 kcal mol^{-1} for the lever mechanism (with a C_s transition state based on the TBP geometry) at SCF/DZP and with sequential axial−equatorial exchange of fluorine atoms. In C_{3v}, a second-order saddle point was found on a flat hilltop, only 0.6 kcal mol^{-1} (at the SCF/DZP level) higher in energy than the lever TS.[27] Gradient lines, corresponding to the imaginary frequencies of that C_{3v} stationary point, were supposed to connect to three permutational isomers of the C_s TS's and the C_{2v} minima.

As pseudorotation also has been observed in arsenanes,[38,39] selenuranes,[40] and PF_4^- (the computed barrier at MP2/DZP, 10.2, agrees with the 10.3 kcal mol^{-1} observed experimentally),[21] we extended our investigation to known members of the isoelectronic series: SF_4, SeF_4,[41,42] TeF_4,[43] ClF_4^+,[44,45] BrF_4^+,[45] IF_4^+,[45] PF_4^-,[21] AsF_4^-,[46] and SbF_4^-.[47] For comparison, we have also studied the related $BrF_2Cl_2^+$ system and the $SbCl_4^-$ anion, to seek possible trends in the topomerization barriers for related systems.

Questions we answer in the present work are: Why do some optically active sulfuranes isomerize rapidly while others do not? We invoke the lever mechanism for explanation. Which of the two mechanisms, Berry and lever, governs the topomerizations in SF_4-like systems? While the Berry process always is lower in energy, the combination of both mechanisms is necessary to achieve complete ligand exchange.

Table 1. Total Energies (hartree) and Zero Point (ZPE) and ZPE-Corrected Relative Energies (kcal mol^{-1}) of SF_4 Species at the (U)B3LYP/6-31+G* and CCSD(T)/6-31G* Levels[a]

structure[b]	NIMAG	sym	E_{tot}	E_{rel}	ZPE
1	(0)	C_{2v}	−797.49964	0.0	6.8
			−795.99458[c]		
2	(1)	C_{4v}	−797.48647	8.1	6.8
			−795.98009[c]		
3	(1)	C_s	−797.46978	18.8	5.9
4	(2)	D_{4h}	−797.39907	62.7	4.7
5[d]	(0)	D_{4h}	−797.41289	53.5	5.8
6	(2)	C_{3v}	−797.46913	19.2	5.7
7	(2)	C_{3v}	−797.42591	46.3	4.8
8	(3)	T_d	−797.41082	55.7	3.5

[a] The number of imaginary frequencies (NIMAG) is given in parentheses. [b] See Figure 1 (for species **1**−**4** and **6**−**8**). [c] At the CCSD(T)/6-31G* level. [d] Triplet, run at UB3LYP/6-31+G*.

2. Computational Methods

The GAUSSIAN-94 program[48] was employed for geometry optimizations at B3LYP/6-31+G* (for all stationary points in the SF_4 and SCl_2F_2 systems, Tables 1 and 2) and at the B3LYP/6-311+G** DFT

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Table 2. Total Energies at B3LYP/6-31+G* (hartree) and Zero Point (ZPE) and ZPE-Corrected Relative Energies (kcal mol^{-1}) (in Square Brackets) of SCl_2F_2 Species[a]

structure[b]	NIMAG	sym		E_{tot}	ZPE
9	(0)	C_{2v}	F_{ax}	−1518.19543 [0.0]	4.9
10	(0)	C_{2v}	Cl_{ax}	−1518.19296 [2.2]	5.1
11	(0)	C_1		−1518.19179 [2.4]	5.0
12	(1)	C_s	F_{ax}	−1518.18047 [8.7]	4.4
13	(1)	C_s	Cl_{ax}	−1518.16550 [18.1]	4.1
14	(1)	C_s		−1518.17851 [10.7]	5.0
15	(1)	C_{2v}		−1518.09312 [63.8]	4.5
16	(1)	C_{2v}		−1518.18075 [9.2]	4.9
17	(1)	C_1	Cl_{ax}	−1518.16562 [17.8]	4.0
18	(2)	C_{2v}		−1518.11114 [52.2]	4.2
19	(2)	D_{2h}		−1518.12240 [44.4]	3.5
20	(3)	C_s		−1518.14769 [28.0]	2.9

[a] The number of imaginary frequencies (NIMAG) is given in parentheses. [b] See Figure 6.

Table 3. Relative Energies for the Lever and BPR Mechanisms in Interhalogen Cations ClF_4^+, BrF_4^+, and $BrF_2Cl_2^+$, Computed at B3LYP/6-31+G*, Including ZPE Corrections at the Same Level[a]

system	species	NIMAG	sym	E_{rel}
ClF_4^+	**21**	0	C_{2v}	0.0
	22 lever	1	C_s	14.8
	23 BPR	1	C_{4v}	2.5
	24	2	C_{3v}	2.5
	25	2	D_{4h}	50.5
	26	3	D_{2d}	45.2
BrF_4^+	**27**	0	C_{2v}	0.0
	28 lever	1	C_s	11.3
	29 BPR	1	C_{4v}	4.7
	30	2	D_{4h}	76.3
$BrF_2Cl_2^+$	**31**	0	C_{2v}	0.0
	32	0	C_1	11.3
	33 lever	1	C_s	17.4
	34 lever	1	C_1	20.5
	35 BPR	1	C_s	14.6
	36	2	D_{2h}	36.0

[a] The number of imaginary frequencies (NIMAG) and point group symmetries are given.

level (for the C_{2v}, C_s, C_{4v} and C_{3v} stationary points of SF_4, Table 1, of ClF_4^+, Table 3, and of PF_4^-, Table 5). CCSD(T)[49] single-point computations are reported on the B3LYP/6-31+G* geometries of SF_4 (Table 1). Hay and Wadt[50] pseudopotentials (which include a relativistically fitted effective core potential (RECP) for the core and inner valence electrons), in combination with the 6-311+G* basis set, have been applied for the valence shells of Se, Te, As, Sb, and I and all electrons on F (Table 5). The reliability of combining B3LYP with the RECP + DZVP basis was checked for $TeCl_4$ in 1998 and has been found satisfactory, although not as good as the combination of other methods and basis sets.[51] To assess the validity of the "mixed" basis

Table 4. Comparison of Transition States for the Lever and BPR Mechanisms in the Tetrafluorophosphate Anion PF_4^-, Computed at B3LYP/6-31+G* and B3LYP/6-311+G* Including ZPE Corrections of the Relative Energies at the Same Level[a]

species	NIMAG	sym		E_{rel}	E_{exp}
37	0	C_{2v}		0.0	
	0		−741.05718[b]	0.0	
38 lever	1	C_s		16.1	
	1		−741.03119[b]	16.3	
39 BPR	1	C_{4v}		9.3	10.3[c]
	1		−741.04118[b]	10.0	
40	2	C_{3v}		17.2	
	2		−741.02959[b]	17.3	
41	2	D_{4h}		54.5	
42	3	D_{2d}		50.2	

[a] The number of imaginary frequencies (NIMAG) and point group symmetries are given. [b] B3LYP/6-311+G* level. [c] Reference 42.

Table 5. Comparison of Relative Energies at B3LYP/6-311+G* (kcal mol^{-1}) (without ZPE Corrections) of C_{2v} Minima, C_{4v} (Berry) and C_s (Lever) Transition States, and C_{3v} "Effective Monkey Saddle Points" on the Potential Energy Surfaces of Isoelectronic Tetracoordinated Species with a Central Atom from Group 15, 16, or 17[a]

	E_{rel}			
system	C_{2v}	C_{4v}	C_{3v}	C_s
PF_4^-	0.0(0)	9.3(1)	17.2(2)	16.1(1)
AsF_4^-	0.0(0)	7.0(1)	9.0(2)	9.0(1)
SbF_4^- [b]	0.0(0)	3.8(1)	5.3(0)	5.3(1)
$SbCl_4^-$ [c]	0.0(0)	8.2(1)	2.6(2)	2.6(1)[d]
SF_4	0.0(0)	8.2(1)	19.1(2)	18.7(1)
SeF_4	0.0(0)	5.9(1)	12.1(2)	12.0(1)
TeF_4 [b]	0.0(0)	2.1(1)	6.4(2)	6.5(1)
ClF_4^+	0.0(0)	2.4(1)	15.6(2)	15.6(1)[e]
BrF_4^+	0.0(0)	4.8(1)		12.0(1)
IF_4^+ [b]	0.0(0)	0.0(1)[f]	6.0(0)	6.5(1)
IF_4^+ [c]	0.0(0)	1.4(1)		8.8(1)

[a] The number of imaginary frequencies (determining the nature of the stationary points) is given in parentheses. [b] LANL2DZ basis set on the heavy element, 6-31+G* basis set on F. [c] Quasirelativistic ECP on all atoms, see ref 52. [d] ΔE to the C_{3v} form 3×10^{-3} kcal mol^{-1}. [e] The difference in energy (ΔE) to the C_{3v} form is less than 0.04 kcal mol^{-1}. [f] ΔE to the C_{2v} form is less than 0.01 kcal mol^{-1}.

set, we carried out additional computations on IF_4^+ and $SbCl_4^-$ by use of a large-core quasirelativistic pseudopotential (fitted to atomic properties, rather than relativistic all-electron Dirac−Fock calculations)[52] on all atoms in combination with DZP valence shell basis sets.[53] Analytical second derivative calculations,[54] performed with GAUSSIAN 94 (G94) using standard basis sets and with GAUSSIAN 98[55] for the computations with pseudopotentials, established the nature of all stationary points at the respective level. The corresponding zero point energies (ZPE) were used to correct the relative energies of the SF_4 and SCl_2F_2 species. Intrinsic reaction coordinate (IRC)[56] calculations have been carried out with G94 (bond angle data of intermediate structures along the IRC path are given in Table A in the Supporting Information).

3. Results and Discussion

Sulfuranes. SF_4. The computed bond angles of the C_{2v} isomer of SF_4, **1** (Figure 1), are in close agreement with the electron diffraction[57] and microwave data (SF_{ax} 1.646 Å, SF_{eq} 1.545 Å, $\angle F_{eq}SF_{eq}$=101.6°, $\angle F_{ax}SF_{ax}$=173.1° [58]). The computed bond

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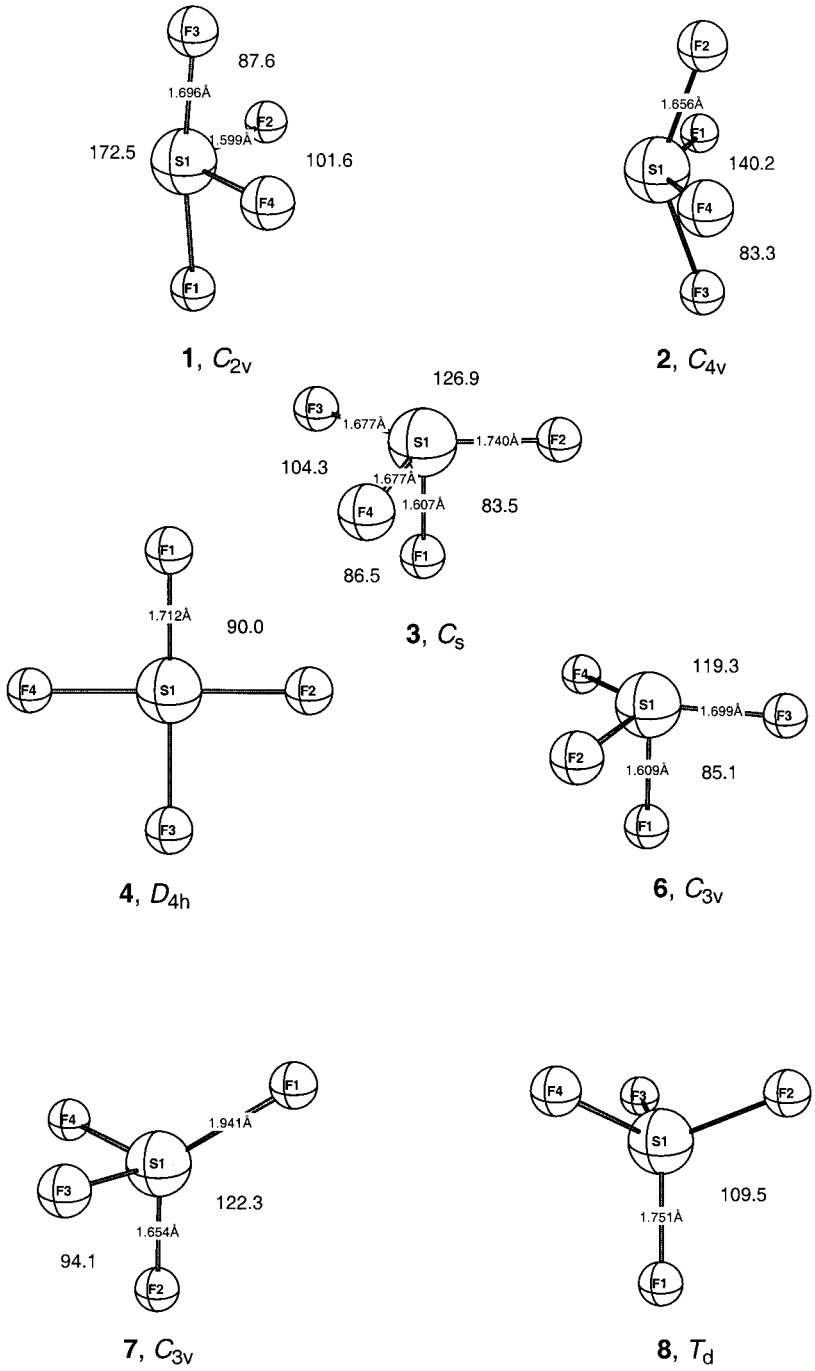

Figure 1. B3LYP/6-31+G* optimized structures of seven stationary points on the SF_4 PES.

lengths are somewhat longer (about 4%), than the experimental distances.

The barrier to Berry pseudorotation (also see eq **3**, Figure 3) is 8.1 kcal mol^{-1}, which confirms the CCSD(T)/6-31G*//B3LYP/6-31+G* result, 7.9 kcal mol^{-1}, via the C_{4v} transition state **2** (Table 1). An alternative transition state **3**, with C_s symmetry, has a 18.8 kcal mol^{-1} relative energy with respect to **2** (Table 1).

In contrast to earlier RHF calculations on SF_4,[19] the planar D_{4h} form **4** (Figure 1) has two imaginary frequencies (Table 1). The RHF solution for **4** is triplet unstable (see, e.g., ref 59), and the D_{4h} triplet $^3A_{2u}$ state, **5**, at UB3LYP/6-31+G* is a minimum, 9.2 kcal mol^{-1} lower in energy than the $^1A_{1g}$ singlet **4**. However, the geometry and energy of C_{3v} **6** (NIMAG = 2) is very close to that of **3** (Table 1). Density functional theory computations gave the $^3A_1$ C_{4v} structure at E_{rel} = 63.1 kcal

(55) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

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(58) Kimura, K.; Bauer, S. H. *J. Chem. Phys.* **1963**, *39*, 3172.

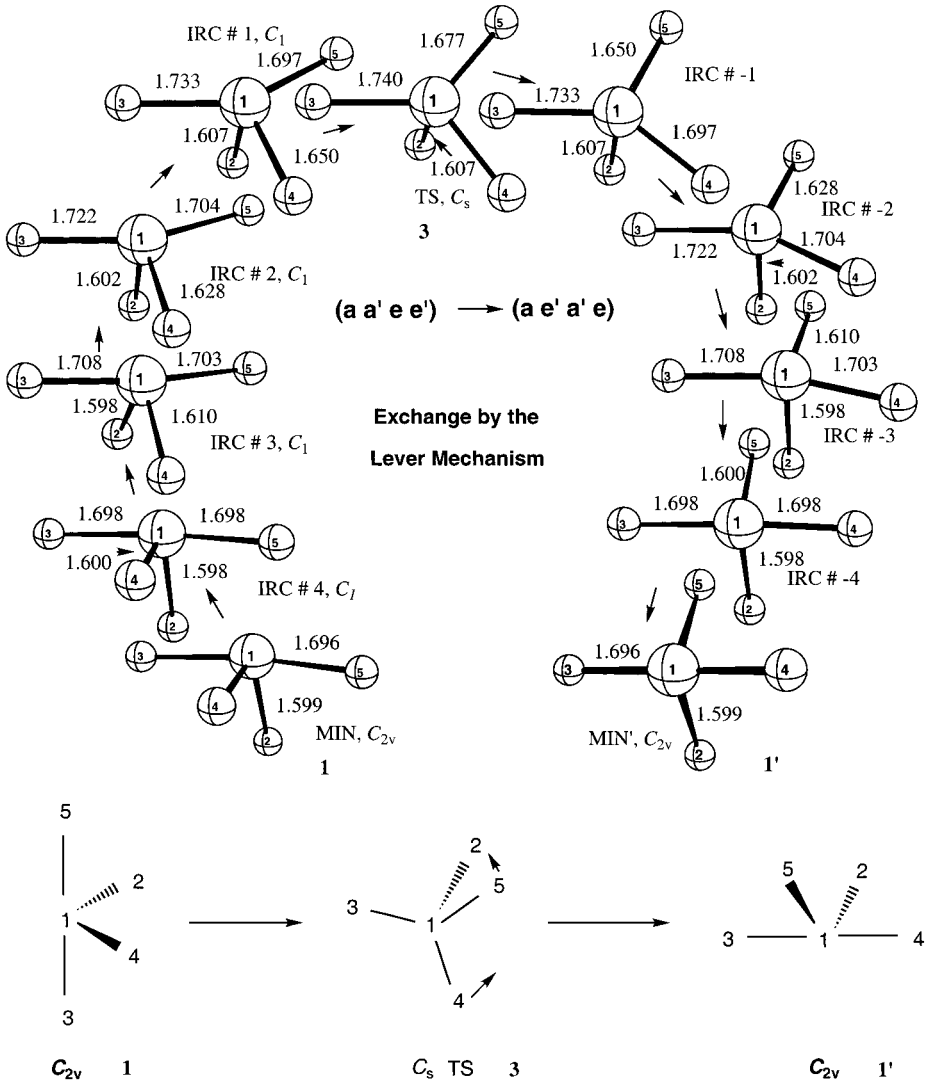

Figure 2. Illustration of the ligand permutation in SF_4 by the lever mechanism, as obtained from the IRC path. Several intermediate structures are shown together with their point group symmetries.

mol^{-1} with respect to **1**.[19b] Other stationary points on the singlet potential surface have more than one imaginary frequency and are all less stable than **3** (Table 1).[60] The geometry of the C_{3v} form, **7**, is close to tetrahedral (with one S−F bond extended), but T_d **8** is a third-order saddle point. Both **7** and **8** are lower in energy than **4** (Table 1).

Other stationary points reported earlier for the SF_4 and ClF_4^+ potential energy surfaces include the D_{4h} form for SF_4 and the D_{4h} and T_d forms for ClF_4^+, which were found to be much higher in energy (SF_4 D_{4h}, relative energy 108.8 kcal mol^{-1} and NIMAG = 1 at HF/6-31G;[61] ClF_4^+ D_{4h}, NIMAG = 1, 59.5, T_d, NIMAG = 3, 138.0 kcal mol^{-1},[27] both at the SCF/DZP level). Inversion in SF_4[19a,25,26,61] and ClF_4^+,[27] involving the (high-energy) D_{4h} structure, has been discussed.

Figure 2 shows some of the structures along the TS **3** IRC path. A wagging motion of the F4−S1−F5 moiety with respect to the F3−S1−F2 reference frame occurs, resulting in the shift of F5 from an axial into an equatorial position (as the F3−S1−F5 angle decreases). The F3−S1−F2 angle remains virtually unchanged. The same motion brings the originally equatorial ligand F4 into an axial position, increasing the F3−S1−F4 angle. All other bond angles and bond lengths adjust to these changes. Note that the originally equatorial ligand F2 temporarily becomes apical in the transition state before it returns to an equatorial position, but one which is spatially inverted with respect to the initial position.

Figure 3 gives a schematic overview over the ligand permutational isomerism in penta- and tetracoordinated TBP or ψ-TBP compounds. The TR process, like BPR, results in a simultaneous exchange of two equatorial ligands with two axial ligands. The outcome of BPR and TR are different in asymmetrically substituted phosphoranes or related five-coordinated compounds, but simultaneous exchange of two axial−equatorial ligand pairs occurs in both mechanisms.[22] In such pentacoordinated TBP molecules with five different ligands, an inversion of configuration is possible by a unique sequence of five BPR steps (with five different fixed points).[22] Similar to BPR, TR results in five-step enantiomerization.[22]

The initially equatorial vacant sites in a tetracoordinated TBP species always are the "fixed points" for Berry rotation, because structures with axial vacant sites are expected to be less stable.[30,34] The fact that this does not result in complete

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(60) That C_{3v}, D_{2d}, and T_d symmetry structures are much higher in energy than the C_{4v} form also has been found for SH_4.[3,15]
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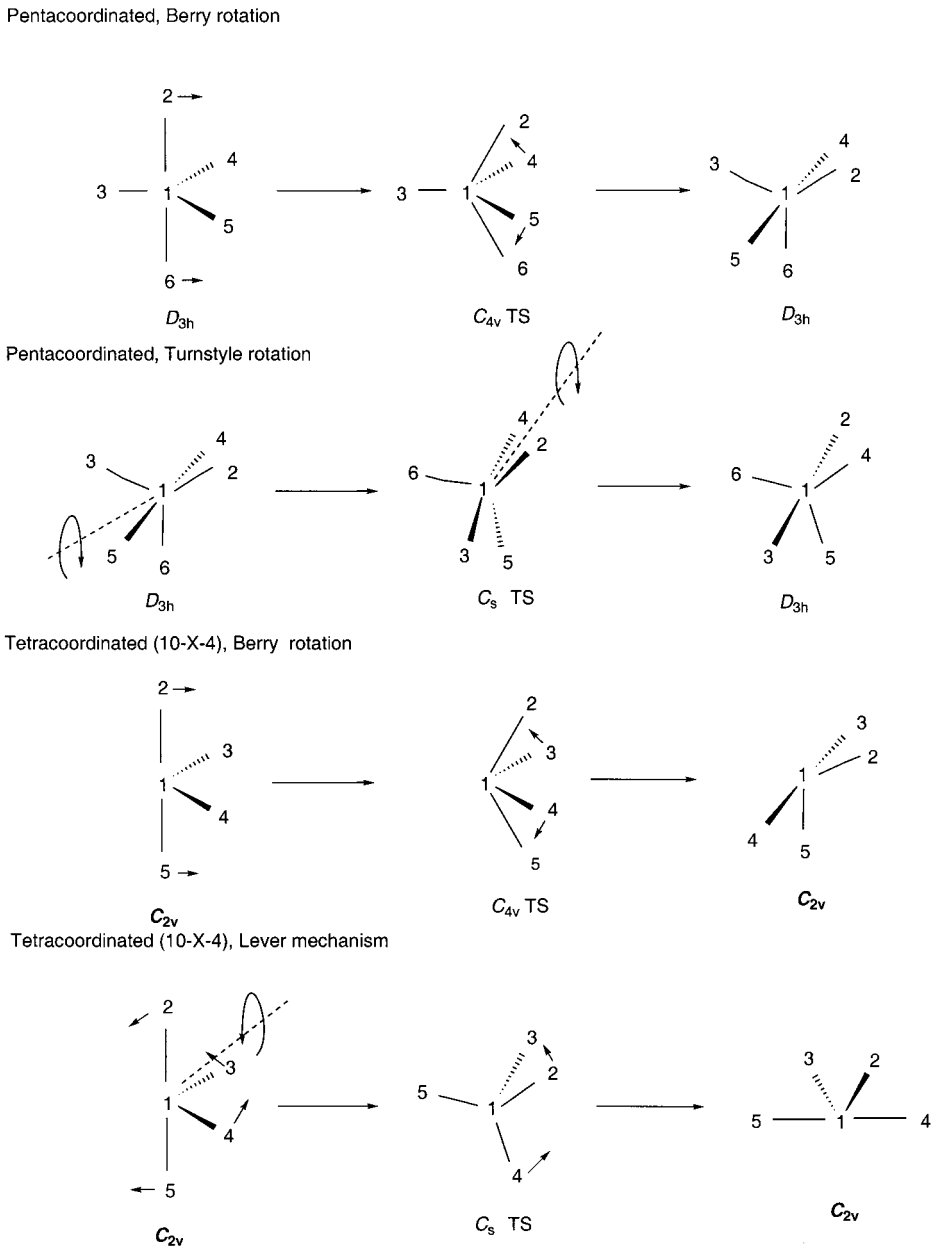

Figure 3. Schematic overview of BPR and lever processes in AX_4 compounds, as well as the BPR and TR processes in AX_5 molecules. BPR and TR in AX_5 molecules both result in double axial−equatorial exchange.

scrambling explains the lack of signal coalescence to a single F peak in the NMR spectrum of compound **d** (Scheme 1) and the absence of rapid racemization of compounds **a** and **b**.[29,30,34]

The "lever" process (Figure 3), unlike the TR in pentacoordinated molecules, involves only a single exchange of one axial with one equatorial ligand, accompanied by an additional exchange of the resulting two equatorial positions. The lever process may bear some resemblance to the turnstyle rotation, because the topomerization might be described as a rotation of the ligand triple 2−3−4 (Figure 3, below) around a ψ-axis through the central atom, exchanging $2_{ax} \leftrightarrow 2_{eq}$, $4_{eq} \leftrightarrow 4_{ax}$ and $3_{eq} \leftrightarrow 3'_{eq}$, while keeping the 1−5 axis in a fixed frame. However, the actual IRC path (Figure 2) reveals that the lever mechanism is not similar to the turnstyle rotation in pentacoordinated systems.

Ugi et al.[22] called such a hypothetical single-exchange process in pentacoordinated systems "M3" (named after Muetterties, who first conceived such a possibility[62]). In five-coordinated species, M3 is tantamount to a sequence of two consecutive TR steps, abbreviated as $(TR)^2$. However, M3 was ruled out by the Whitesides−Mitchell experiment, which precluded single axial−equatorial exchanges for five-coordinated phosphoranes.[22a,63] Indeed, two consecutive TR rotations (with the vacant site as part of a ligand "pair", rotating with regard to the rest of the molecule) would achieve the same ligand permutation as the lever mechanism in a single step. As a consequence, the lever mechanism in four-coordinated molecules involves only two possible reaction paths for every BPR process (with either one of the equatorial ligands becoming apical in the transition state); in contrast there are four equivalent TR processes in five-coordinated molecules.[22]

The IRC (minimum energy) path for the lever process (Figure 4, Table A in the Supporting Information) is symmetric around the transition structure. E.g., angle F3−S1−F5 ($F3_{ax}$, $F5_{ax} \leftrightarrow$

(62) (a) Muetterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 1636. (b) Also see a group theoretical treatment of this problem: Nourse, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 2063.

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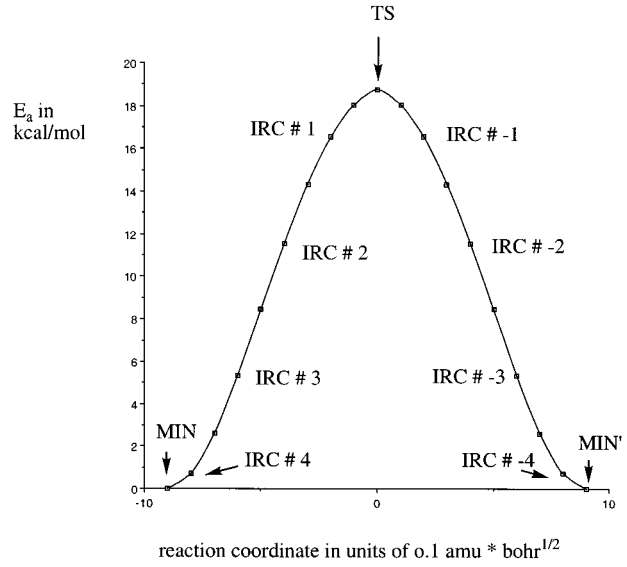

Figure 4. IRC path energy profile, symmetric around the transition state (vertical axis, energy of activation in kcal/mol; horizontal axis, reaction coordinate in 0.1 $m_p^{1/2}a_0$).

$F3_{eq}$, $F5_{ax}$) exchanges its role with F3−S1−F4 ($F3_{ax}$, $F4_{eq}$ ↔ $F3_{ax}$, $F4_{ax}$), and F2−S1−F4 exchanges its role with F2−S1−F5, both with one equatorial fluorine ($F2_{eq}$) and one axial fluorine ($F4_{ax}$, $F5_{ax}$).

Even an arbitrary sequence of the lever process does not lead to inversion of an AX_4 structure, as illustrated in Figure 5: an arbitrary sequence of three lever steps only generates the identity operation on the reactant structure. Intuitively, a sequence of single axial−equatorial exchanges acting first on one and then on the other axial ligand is anticipated to give the enantiomer of a chiral SABCD or SA_2BC SF_4-like sulfurane or a related system. But as Figure 5 shows, any sequence of lever steps only leads back to the initial configuration, rather than to the enantiomer. To achieve not only full ligand scrambling but also inversion, a combination of one BPR with two lever steps is required. The two other possible combinations Berry−lever−lever and lever−Berry−lever lead to identical results.

SCl_2F_2. To elucidate the enantiomerization mechanisms in chiral sulfuranes, we have chosen a simple model, SCl_2F_2 (although experimentally unknown), for a PES search. Figure 6 shows 12 stationary points on the B3LYP/6-31+G* potential surface (see Table 2 for energies).

The $F_{ax}F_{ax}$ C_{2v} minimum **9** (Figure 6) is the most stable, in accord with the higher apicophilicity of fluorine with respect to chlorine.[34] But despite the apicophilicity rule, the energies of $F_{eq}F_{eq}$ **10** and the enantiomeric pair $F_{ax}F_{eq}$ **11** (2.2 and 2.4 kcal mol^{-1} relative to **9**) are nearly the same.

Because of the inherently lower symmetry of SCl_2F_2 (than SF_4), there are in principle four different transition states for the lever process and two Berry rotation transition states (Figure 6). Two C_s TS's, **12** (with apical F, for Cl_{ax} ↔ Cl_{eq} exchange) and **13** (with apical Cl, for F_{ax} ↔ F_{eq} exchange) (Figure 6), are involved in the enantiomerization of **11** (verified by IRC calculations) by the lever process with 6.3 and 15.7 kcal mol^{-1} barriers, respectively. The alternative interconversion of **11** and its enantiomer **11′** (with exchanges F_{ax} ↔ F_{eq} and Cl_{ax} ↔ Cl_{eq} occurring at the same time) by the BPR proceeds via the nonplanar C_s TS **14** with a barrier of 8.3 kcal mol^{-1}, close to that for the favored lever process. While direct inversion of **11** might proceed via planar C_{2v} **15**, this is 61.4 kcal mol^{-1} higher in energy than **11** (Figure 6).

Achiral **9** and **10** are interconverted by the BPR process (by simultaneous F_{ax} ↔ F_{eq} and Cl_{ax} ↔ Cl_{eq} exchange), proceeding via a C_{2v} transition state **16** with E_{rel} = 9.2 kcal mol^{-1} with respect to **9**. Only the lever mechanism interconverts the chiral $F_{ax}F_{eq}$ and the achiral $F_{ax}F_{ax}$ isomers via the C_1 TS **17** (with apical chlorine and Cl_{eq} ↔ F_{ax} exchange) with a 17.8 kcal mol^{-1} barrier with respect to **9**. An IRC calculation established the **9** ↔ **17** ↔ **11** pathway and ruled out the alternative **10** ↔ **17** ↔ **11** process.

We have been unable to locate the other conceivable C_1 transition structure for the Cl_{ax} ↔ F_{eq} exchange and with apical F. On the basis of comparisons with the energies of C_s species **12** (F apical) and **13** (Cl apical, Table 2), this hypothetical C_1 TS should be lower in energy than **17**. The IRC calculations also confirmed that all three TBP C_s TS's **12**, **13**, and **17** correspond to the same type of lever permutation process, exemplified by TS **3** for SF_4.

There are two planar C_{2v} forms: **18** has two imaginary frequencies (Table 2) and is 11.6 kcal mol^{-1} lower in energy than **15**. Species **19**, a planar conformation with D_{2h} symmetry (Figure 6), is even lower in energy and also has two imaginary

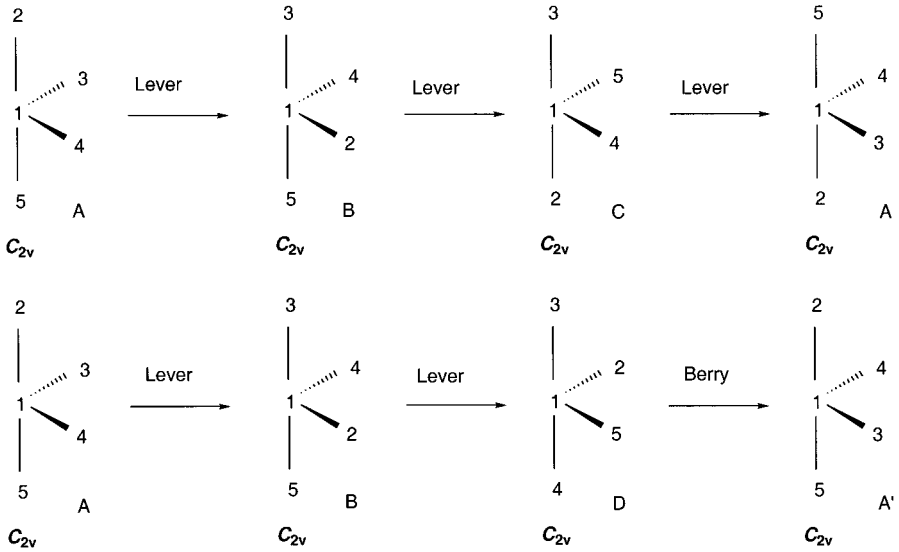

Figure 5. Three consecutive lever steps give the identity operation. Only a combination of one Berry with two lever steps permits enantiomerization of a chiral AX_4 TBP system.

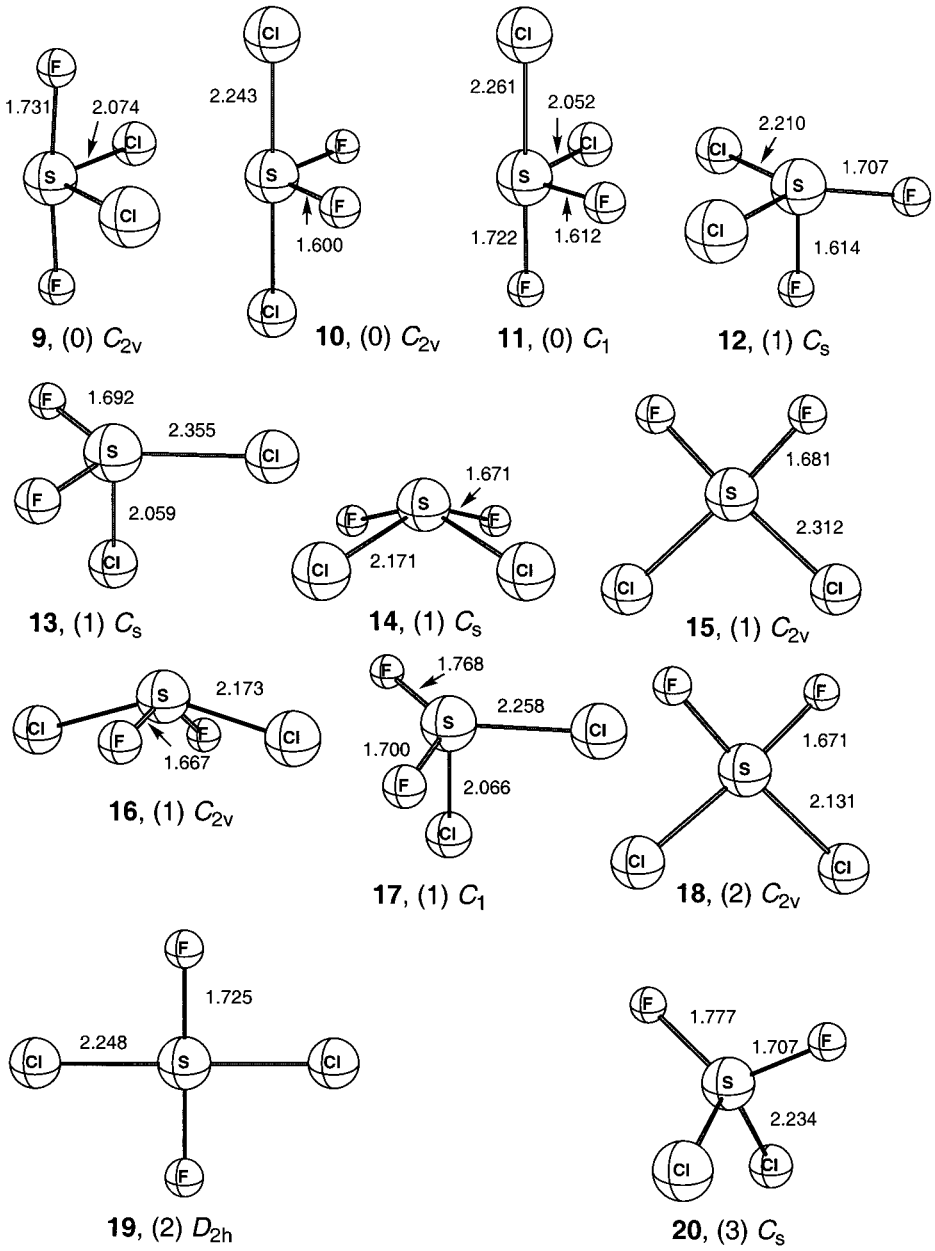

Figure 6. B3LYP/6-31+G* optimized structures of 12 stationary points on the SCl_2F_2 PES.

frequencies (Table 2). The nonplanar C_s form **20** (which resembles the T_d conformation **8** of SF_4) has three imaginary modes but is only 28.0 kcal mol^{-1} less stable than **9**! Figure **7** displays all the reaction network possibilities corresponding to the transition structures we have located for topomerization in SCl_2F_2 schematically. Enantiomerization **11** ↔ **11′** might occur in four different ways, among which, however, only the single Berry and one of the lever processes are competitive. In contrast to SF_4, the barriers for Berry and for both lever mechanisms are low. Hence, SCl_2F_2 should racemize rapidly. This contrasts with the findings[29,30] for dichloro-substituted **a** and **b** (Scheme 1), which are optically stable. This is only understandable if the replacement of the two fluorines in SCl_2F_2 by more electropositive ligands to give SCl_2RR' results in a larger increase in the barrier of the lever process than in that for the Berry process.

The much higher activation barriers for the lever mechanism in sulfuranes than those for the Berry rotation (as in SF_4) explain the resistance of the known optically active sulfuranes, like **a** and **b**, to racemize, and of **f** to isomerize (Scheme 1).

Interhalogens. The C_{2v} global minimum of ClF_4^+, **21** (Figure 8), first mentioned in 1968 on the basis of indirect evidence[64a] and NMR spectroscopically characterized in 1973,[64,65b] is isoelectronic and isostructural with SF_4.[64,65] We have found a TS **22** with C_s symmetry, with a geometry similar to the C_s TS in SF_4 and with a relative energy to the global minimum of 14.8 kcal mol^{-1}. An IRC calculation, starting from **22**, established the "lever mechanism" as being the process involved. However, the C_{4v} TS for Berry rotation, **23**, is much lower in energy (2.5 kcal mol^{-1}, Table **3**). The C_{3v} NIMAG = 2 species **24** is almost isoenergetic with the C_s TS ($\Delta E = 0.04$ kcal mol^{-1}!). The D_{4h} species **25** has two imaginary frequencies. One imaginary mode

(64) (a) Roberto, F. Q: Mamantov, G. *Inorg. Chim. Acta* **1968**, *2*, 317. (b) Christe, K. O.; Pilipovich, D. *Inorg. Chem.* **1969**, *8*, 391 (c) Shamir, J. *Struct. Bonding* **1979**, *37*, 141.

(65) (a) Christe, K. O.; Hon, J. F.; Pilipovich, D. *Inorg. Chem.* **1973**, *12*, 84. (b) Christe, K. O.; Sawodny, W. *Inorg. Chem.* **1973**, 12, 2879. (c) Christe, K. O.; Sawodny, W. 6th International Symposium on Fluorine Chemistry, Durham, England, July 1971. (d) Stein, L. In *Halogen chemistry* Gutmann, V., Ed.; Academic Press: London, 1967; Vol. 1, pp 133−224.

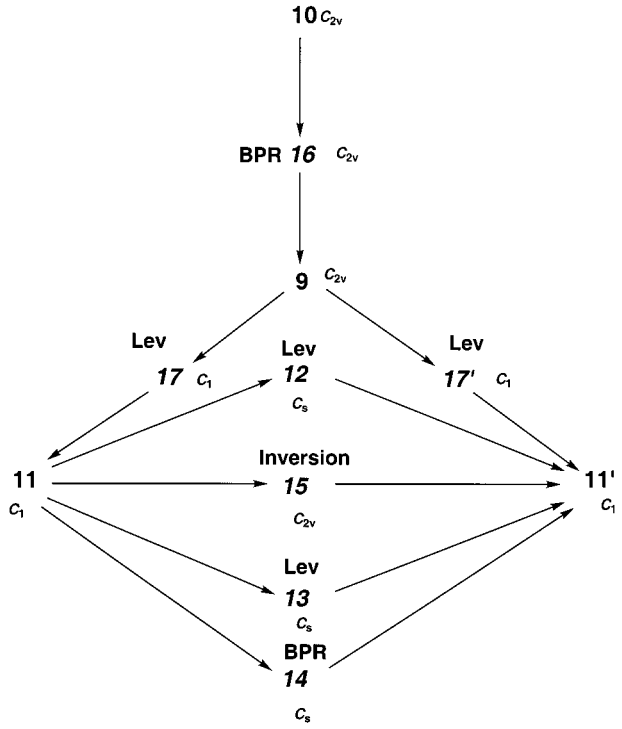

Figure 7. Schematic representation of the reaction path network in the SCl_2F_2 system.

(-992.5 cm^{-1}) connects two enantiomeric (inverted) BPR TS's (Figure 9). The other (-90.9 cm^{-1}) leads to a D_{2d} structure **26** (Figure 8), 7.4 kcal mol^{-1} lower in energy than **25**.[66]

The results for BrF_4^+,[65] first mentioned speculatively in 1967[65d] and tentatively characterized in 1971,[65c] are similar to those for ClF_4^+ (Figure 8 and Table 3) and include a C_{2v} minimum **27**, a C_s "lever" TS **28**, a BPR C_{4v} TS **29**, and a D_{4h} second-order saddle point **30**. The barriers are 11.3 kcal mol^{-1} for the lever process and 4.7 kcal mol^{-1} for the Berry rotation, while the D_{4h} form relative energy is quite high, 76.3 kcal mol^{-1}.

In contrast to the SCl_2F_2 system, no bound $BrF_2Cl_2^+$ stationary points (Table 3) with two anti or two apical chlorine atoms could be located; this drastically reduces the number of species (and possible topomerization routes). There are only three minima, C_{2v} **31** ($F_{ax}F_{ax}$) and a C_1 enantiomeric pair **32** ($F_{ax}F_{eq}$). Two lever mechanism transition states exist, one C_s form **33** for $F_{ax} \leftrightarrow F_{eq}$ exchange (for the **32** $\leftrightarrow$ **32′** enantiomerization) and one C_1 transition state **34** for the **31** $\leftrightarrow$ **32** interconversion ($F_{ax} \leftrightarrow Cl_{eq}$ exchange). With the heavier halogen ligands, the preference of the Berry over the lever mechanism diminishes; the Berry rotation TS (for enantiomerization of **32** by simultaneous $F_{ax} \leftrightarrow F_{eq}$ and $Cl_{ax} \leftrightarrow Cl_{eq}$ exchange) is found to be only 2.8 kcal mol^{-1} lower in energy than the lever TS **33** (Table 3). Remarkably, the relative energy of the planar D_{4h} form **36** with NIMAG = 2 is only 36.0 kcal mol^{-1} with respect to **31**.

PF_4^-. The tetrafluorophosphate anion, prepared by the reaction of $[N(CH_3)_4]^+F^-$ and PF_3 in excess PF_3 as the solvent, also was studied computationally by the same authors.[21] The potential energy surface of PF_4^- (Table 4, Figure 9) is similar to that of the isoelectronic SF_4 (Figure 1, Table 1) and ClF_4^+ and BrF_4^+ (Figure 8, Table 3). The global minimum is again a C_{2v} structure (**37**, Figure 10). The difference in the activation barriers for the lever process in PF_4^- (C_s TS **38**, 16.1 kcal mol^{-1}) and the Berry process (C_{4v} TS **39**, 9.3 kcal mol^{-1}) is much smaller, if compared to the situation in SF_4 and in the AF_4^+ interhalogen cation examples (Tables 1, 3, and 4). Species **40** is a TBP C_{3v} form with two imaginary frequencies, only 1.1 kcal mol^{-1} higher in energy than TS **38**, while D_{4h} **41** is much higher in energy (Table 4) and also has two imaginary frequencies. But instead of the D_{2d} form **26** in ClF_4^+, there is a T_d form **42**, similar to that in SF_4 and lower in energy than **41**.

Christe et al.[21] found a barrier to the BPR process in PF_4^- of 10.2 kcal mol^{-1} at the MP2/DZP level, somewhat higher than our value and in better agreement with experiment (10.3 kcal mol^{-1} [42]).

Trends in Lever and Berry Activation Barriers. In order to reveal possible trends in the activation energies for the alternative lever and Berry processes, we have compared the relative energies of the C_{2v}, C_{4v} (Berry TS), C_{3v}, and C_s (lever TS) stationary points for the series PF_4^-, AsF_4^-, SbF_4^-, $SbCl_4^-$, SF_4, SeF_4, TeF_4, ClF_4^+, BrF_4^+, IF_4^+ (Table 5 and Figure 11). The activation barriers for both Berry and lever mechanisms decrease down the group, with the exception of the interhalogens. Going from the left to the right in the periodic table, the preference of the Berry mechanism increases.

Increasing the number of chlorine ligands disfavors the Berry process (Tables 2, 3 and 5), depending on the central atom. While in $BrF_2Cl_2^+$, the Berry mechanism is still preferred, the barriers for the lever and the Berry process become nearly equal for SCl_2F_2, whereas for $SbCl_4^-$ the lever mechanism is favored.

While the energy difference between the C_s lever TS's and the C_{3v} structures also diminishes with the heavier elements (Table 5), the nature of the C_{3v} form changes from a second-order saddle point for the lighter elements to a minimum for the heaviest systems. In IF_4^+, the energies of the C_{2v} (minimum) and C_{4v} (transition state) become virtually identical. However, at a different level of theory[52,53] we have found IF_4^+ in C_{4v} to be 1.4 kcal mol^{-1} higher in energy than in C_{2v} (Table 5).

Effective Monkey Saddle Points in AX_4 Species. Gradient lines connect the C_{3v} structures with three lever (C_s) transition states (which are either second-order saddle points, Figure 12, or minima, Figure 13), reached by only small distortions (like the letter Y) of the equatorial bonds. This situation has been described earlier for ClF_4^+ [27] and for ClF_3.[67] According to our computations (Table 5), the energy difference between the C_s and the C_{3v} structures becomes as small as 0.04 kcal mol^{-1}, even without ZPE correction (IF_4^+, where the C_{3v} minimum lies in a deeper trough, is an exception). An idealization of the PES around the central C_{3v} form is illustrated in Figure 14, showing three valleys that meet on a hilltop. This is called a "monkey saddle".[68] A monkey saddle point with three valleys is characterized by the absence of any negative curvature and a doubly degenerate zero eigenvalue of the Hessian (i.e., a degenerate zero frequency).[69] Indeed, we have found very small doubly degenerate real or imaginary frequencies (typically below 50 cm^{-1}) for the C_{3v} geometries of these AX_4 species. But as these stationary points fall just short of meeting the mathematical

(66) These findings do not agree with earlier work[27,61] which appears to be an artifact probably arising from the instability of the wave function. The reported MP2/DZP data[27,61] differs tremendously from our results, e.g., D_{4h} ClF_4^+ was claimed to be the global minimum (!), 16.2 kcal mol^{-1} lower in energy than the C_{2v} form, and C_{3v} ClF_4^+ was reported to be 65.3 kcal mol^{-1} higher in energy than the closely related C_s "lever" transition state! We found two apparent D_{4h} stationary points, one with a short and the other, low in energy, with a longer Cl−F distance at both MP2/6-311+G* and B3LYP/6-311+G*. Both D_{4h} forms were instable at both levels, and the C_{3v} form is stable.

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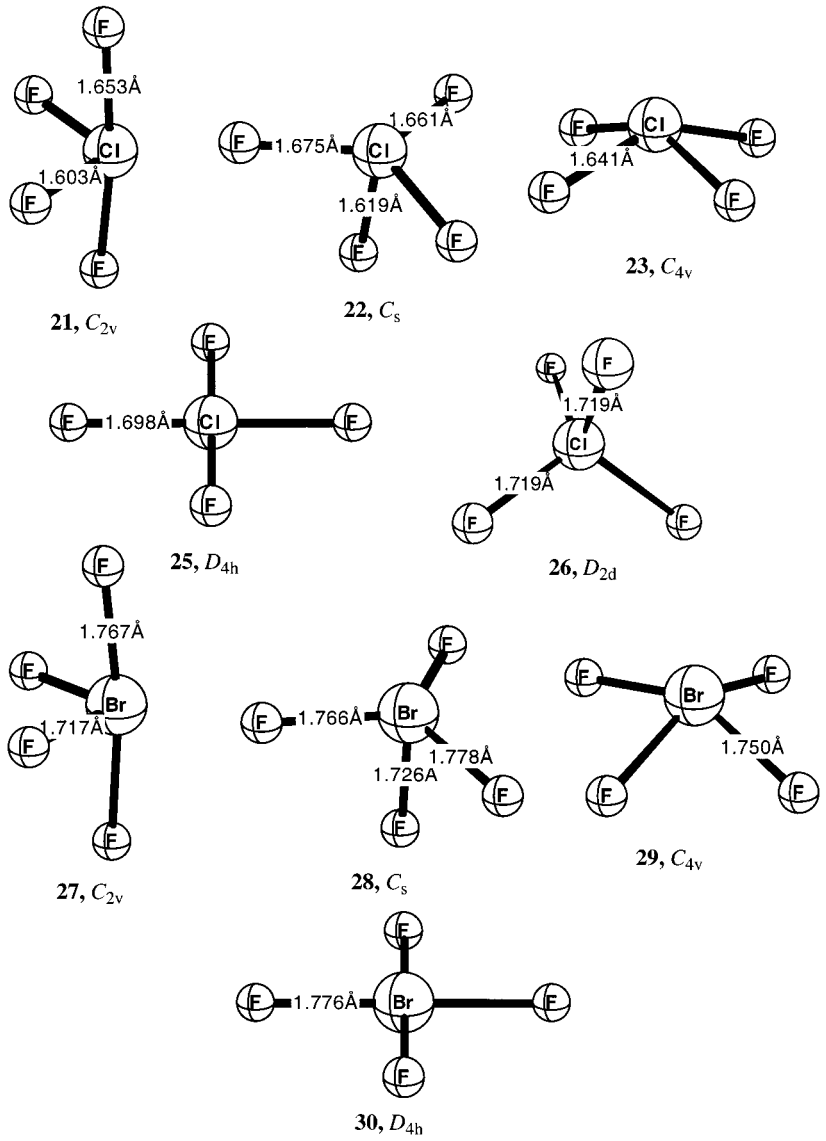

Figure 8. B3LYP/6-31+G* optimized structures of the stationary points on the ClF_4^+ and BrF_4^+ potential surfaces, related to the discussion of the lever process.

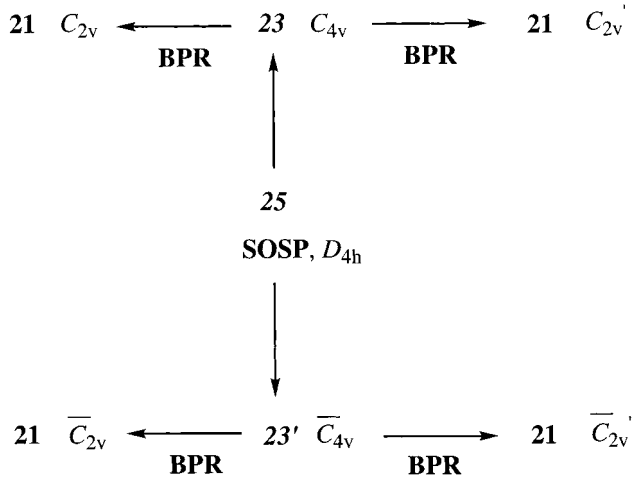

Figure 9. Gradient lines pertaining to the cuneal inversion of the C_{2v} minima in interhalogen cations (exemplified by ClF_4^+) and SF_4 via the D_{4h} structure. The second-order saddle point (SOSP) in the center connects to the two inverted forms of **23**, the Berry rotation TS's.

conditions for a "monkey saddle" (i.e., exactly zero frequencies), we prefer the term "effective monkey saddle point" to describe them. The "minimum energy paths" either encircle the effective monkey saddle point (Figure 12) or pass right through it, since, at least approximately, the reaction path branches there (Figure 13). An IRC run on the ClF_4^+ MP2/6-31G PES (with a C_{3v} minimum) approached the extremely shallow central "minimum", only 10^{-5} hartree lower in energy than the C_s "transition state".

The minimum energy path originating from one C_{2v} minimum (Figure 13) will proceed without any significant barrier toward either of the two other C_{2v} minima, once the branching point at the C_{3v} hilltop is passed. Hence, the C_{3v} form can be regarded as the "transition state" for the reaction, coinciding with a bifurcation.[69] A monkey saddle point apparently would violate the Murrell−Laidler theorem[70] and the McIver−Stanton rules.[71] The controversy about the existence of monkey saddle points in chemistry goes back to Murrell and Laidler's work in 1967,[70] which ruled out the possibility of "three valleys meeting at a hilltop" on the basis of the harmonic approximation.[70] This viewpoint was challenged in 1974 by Stanton and McIver by

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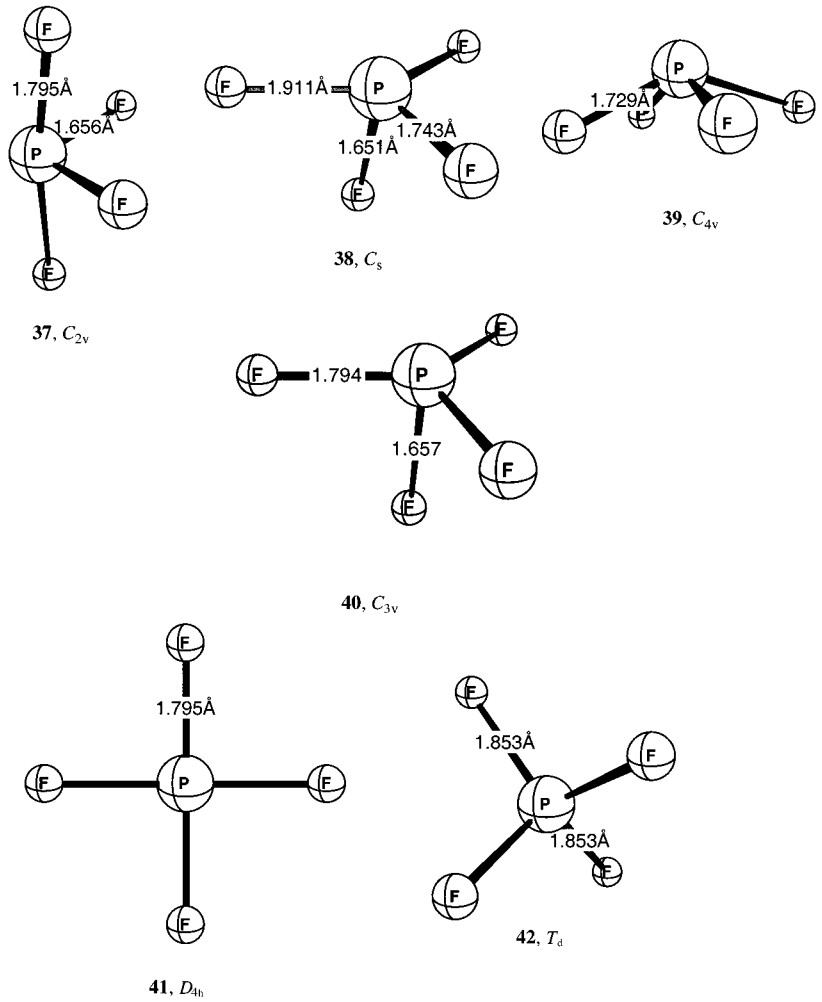

Figure 10. The B3LYP/6-31+G* optimized structures of the tetrafluorophosphate anion PF_4^-. Note the similarity to the isoelectronic forms of SF_4 and ClF_4^+.

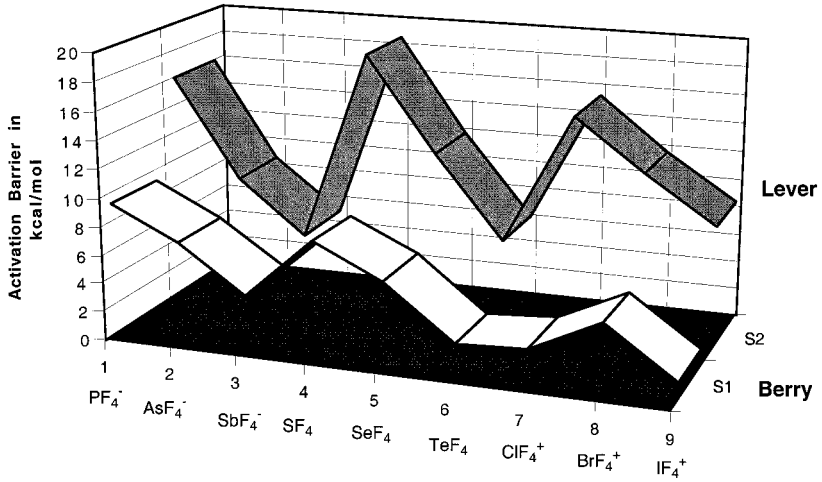

Figure 11. Trends in the activation energy barriers for the Berry (lighter ribbon) and lever (darker ribbon) mechanisms in AF_4 species.

taking cubic and higher order terms into account in describing the potential surface at a "monkey saddle".[71] They even considered "monkey saddles" with four valleys, in which case even the cubic, and not only the quadratic, terms vanish.[71] Stanton and McIver maintained that "it would be an unlikely numerical accident if an eigenvalue (of the Hessian) should be exactly zero at such a (stationary) point".[71] We argue that small changes in cases where an effective monkey saddle point already is present, e.g., by changing the basis set in a quantum-chemical computation, or by very small variations in the ligand groups, might allow such an "accident" to be approached very closely. The usual harmonic approximation for the calculation of vibrational frequencies is not appropriate for such systems, because quadratic terms are absent in the decription of the potential surface at the central point. Hence, small variations in the level of theory might change the nature of the C_{3v} structure from a minimum into a second-order saddle point, or vice versa. More recently, Wales and Berry[72] demonstrated that in high-

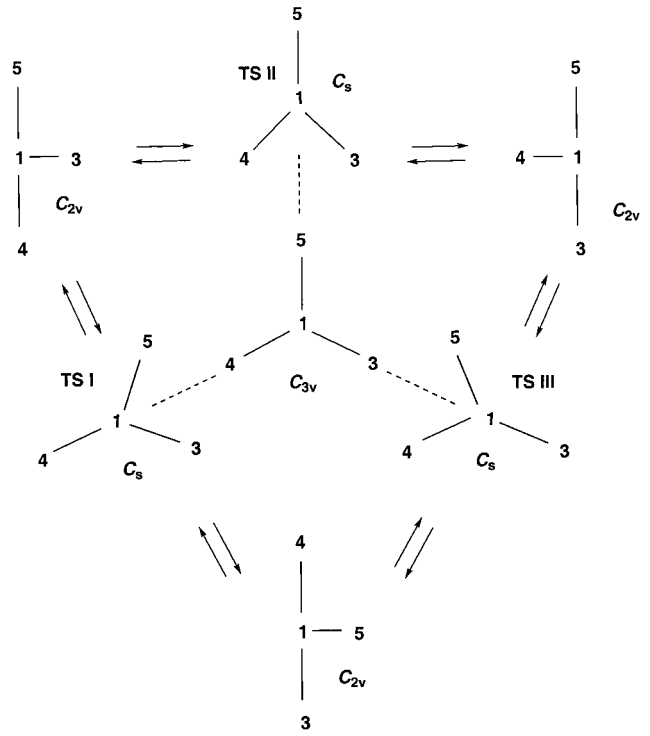

Figure 12. Schematic illustration of the "effective monkey saddle points" when the central C_{3v} structure has two imaginary frequencies (the bond to the fourth ligand 2 is perpendicular to the projection plane).

symmetry cases, such "*as second order Jahn-Teller points or transition states at points of three-fold or higher symmetry*", the "*effective potential energy function fails to satisfy the conditions required for the Murrell-Laidler theorem to hold.*" [72,73] They concluded that it is possible to find potential surfaces with transition states connecting three or more potential minima.[72]

Several examples of monkey saddle points have been proposed[74−77] involving "forbidden" [71] transition states that violate the Stanton−McIver symmetry rule; i.e., that "*no structure can serve as a transition state for a given reaction if a C_3 rotation or other odd degree symmetry operation associated with the structure converts reactants into products*".[71] In 1976, Pechukas deliberately ignored the "weird possibility" of a monkey saddle in extending Stanton and McIver's work to derive more stringent rules governing the allowed symmetries for transition states.[78] The most recent example is the 4-fold monkey saddle point described by Li and Houk.[77] This is involved in the syn dimerization of two cyclobutadienes which gives four equivalent products. The D_{4h} saddle point has two imaginary vibrational modes corresponding to two degenerate asynchronous concerted [4 + 2] cycloadditions, but the steepest descent is along four equivalent paths on the PES in the directions of the dimer minima. Cremer discussed a monkey saddle in 1993 on the barbaralyl cation ($C_9H_9^+$) PES, where a D_{3h} structure is connected by six equivalent downhill paths to six equivalent C_s minima.[76]

Because "effective monkey saddle points" are, for all practical purposes, the lowest maxima on the minimum energy paths

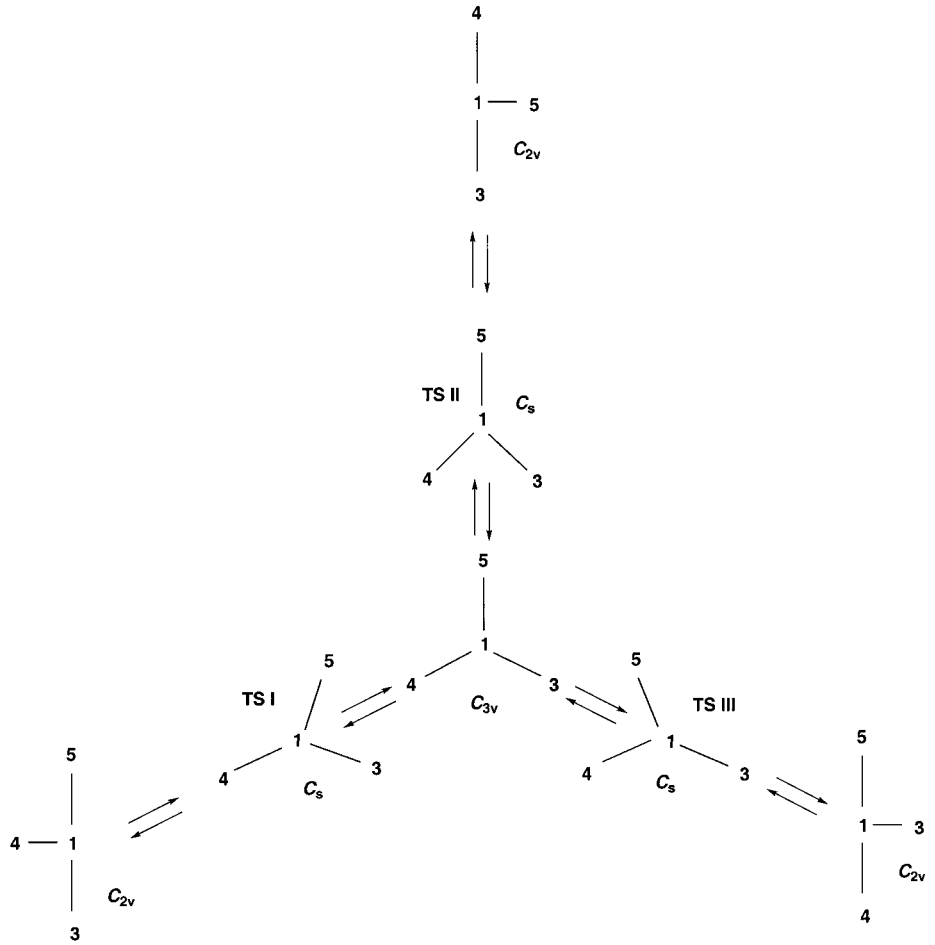

Figure 13. Schematic illustration of the minimum energy paths, connecting permutational isomers of AX_4 species, which pass through a central C_{3v} minimum, the "effective monkey saddle" branching point.

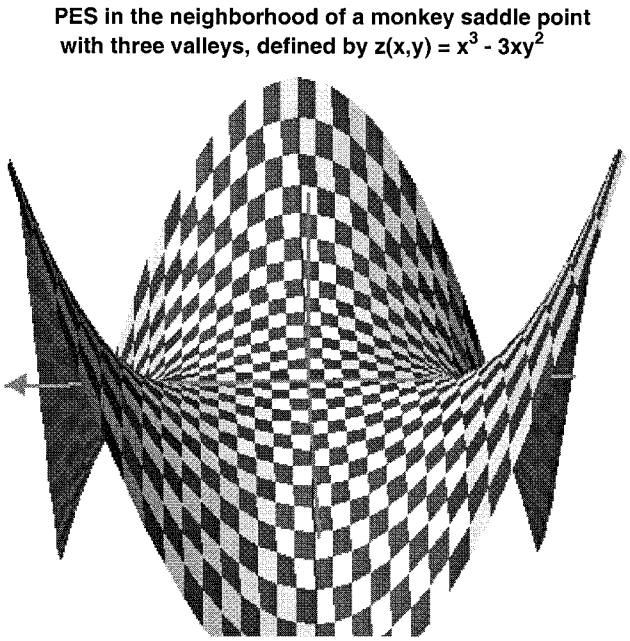

Figure 14. Perspective representation of the functional form of the ideal monkey saddle.

connecting reactants to products, we suggest a revision of the rules[71,78] for the allowed point group symmetries of transition states.

4. Conclusions

While the Berry mechanism is preferred in SF_4 and all isoelectronic AF_4 systems, the lever process is required for the enantiomerization of chiral isomers of SCl_2F_2. The lever mechanism provides the only means to exchange achiral $F_{ax}F_{ax}$ or $F_{eq}F_{eq}$ isomers with the chiral $F_{ax}F_{eq}$ forms. Interhalogen cations (Table 3, Figure 8) and the PF_4^- anion (Table 4, Figure 10) behave like SF_4 and SCl_2F_2 and have similar potential energy surface topographies.

Both Berry and lever activation barriers in AF_4 species (Figure 11) decrease down the group. The only AX_4 system which showed a strong preference for the lever mechanism is $SbCl_4^-$. Other ACl_4 systems also might favor the lever mechanism.

Chiral halosulfuranes such as **a**, **b**, and **c** in Scheme 1 or related systems, like chiral periodonium ions,[79] or chiral four-coordinated transition metal complexes with a "saw horse" structure, like $RuHClL_2$ ($L = P^iPr_3$),[80] are in principle capable of enantiomerization via a combination of a single Berry pseudorotation and two lever steps (Figure 5). The necessity of including lever steps in the enantiomerization mechanism explains the optical stability of chiral halosulfuranes where higher activation barries are involved.

Remarkably, the C_{3v} and the C_s (lever transition state) structures are almost isoenergetic for all AX_4 systems studied (Table 5). The C_{3v} forms have either (1) two very small degenerate imaginary or (2) real frequencies, the two lowest of which are very small. In the former case, the minimum energy lever path encircles a second-order saddle point in triangular fashion (Figure 12), while in the second case the C_{3v} structure lies in an extremely shallow potential well on the minimum energy path, connecting two equivalent global minima (Figure 13).

The corresponding potential surface topography, the "effective monkey saddle point", can be described as three valleys on a corrugated surface that meet at a hilltop. Both these cases approximate the topological monkey saddle, which is characterized by the absence of any negative curvature, but with two degenerate (exactly) zero eigenvalues of the Hessian (i.e., zero frequencies).[69]

According to the Stanton−McIver theorems,[71] monkey saddles such as those described in this work are precluded as transition states. Our findings suggest that an ideal monkey saddle can be approached to a high degree of approximation by an effective monkey saddle point adjusted by small variations in the chemistry, e.g., alterations in a ligand chain, that only will result in negligible deviations from the local symmetries at the central atom. As a consequence, the effective monkey saddle point becomes for all practical purposes the transition state of a chemical reaction. Hence, we suggest an amendment in the accepted rules extending the allowed symmetries of transition states.

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Supporting Information Available: Table A containing bond angle data of intermediate structures along the IRC path. This material is available free of charge via the Internet at http://pubs.acs.org.

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(73) One of the referees remarked that we might have overlooked "Jahn-Teller effects as the possible driving force behind the frequent occurrence of C_{3v} stationary points with degenerate imaginary frequencies". The referee suggested that the C_{3v} HOMOs might be half-filled degenerate molecular orbitals. This is not the case. Moreover, our wave function stability calculations on the C_{3v} forms of ClF_4^+ and SF_4 showed the absence of singlet or triplet instabilities for both closed-shell species. We cannot preclude that the structures discussed in our work as effective monkey saddles are second-order Jahn−Teller points involving closely lying MOs.[81]
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