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Structures of the 1,1-Difluoroethylene and Tetrafluoroethylene Anions

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The $CH_2CF_2^-$ and $CF_2CF_2^-$ anions were studied by using theoretical (DFT) B3LYP, MP2, and QCISD methods in conjunction with large basis sets. The standard split valence plus polarization basis sets augmented with diffuse functions on heavy atoms (B*n*+) are considered to be appropriate for these anions. Structures (anti, syn, planar, and perpendicular) of the two anions were studied based on B3LYP geometry optimization, frequency analysis, and intrinsic reaction coordinate (IRC) calculations. For $CF_2CF_2^-$, a new minimum-energy structure having C_2 symmetry was found in the IRC calculations. Anti structure is the most stable for each of the two anions. Syn structure of $CF_2CF_2^-$ is the transition state for the $C_2 \leftrightarrow C_2$ interconverting process, and syn structure of $CH_2CF_2^-$ does not exist. The planar structures of the two anions are the transition states for the anti ↔ anti interconverting processes. The isotropic hyperfine coupling constants (*hfcc*'s) in anti-$CH_2CF_2^-$ and anti-$CF_2CF_2^-$ were explicitly calculated using the B3LYP and MP2(full) methods, and the calculations with the 6-311+G(2d,p) basis set predict *hfcc* values in good agreement with experiment. Adiabatic and vertical electron affinity (AEA and VEA) values of the CH_2CF_2 and CF_2CF_2 molecules were calculated using the B3LYP and QCISD methods. The QCISD/6-311+G(2d,p) calculations for the two molecules predict the values of the VEAs associated with the π^* states ($^2B_1$ and $^2B_{2g}$, respectively) of the anions in quite good agreement with the experimental VEA(π^*) values. It is argued that the σ^* states of the two anions are the ground states at the molecular geometries and that the existence of the anti structures of the two anions is considered as a consequence of the pseudo-Jahn−Teller effect.

Introduction

Radical anions of fluorinated alkenes and aromatics are important species in spectroscopy and as reaction intermediates. Experimental and theoretical studies[1−6] on the radical anions of fluorinated ethylenes have focused upon whether these anions are formed by electron attachment to σ^* or π^* orbitals of the neutral molecules and whether the geometries of these anions are distorted from planarity. We have carried out theoretical study on the 1,1-difluoroethylene anion ($CH_2CF_2^-$) and tetrafluoroethylene anion ($CF_2CF_2^-$), and on the basis of the calculation results for the two anions, we explore the two focus problems for the radical anions of fluorinated ethylenes.

The $CH_2CF_2^-$ and $CF_2CF_2^-$ anions were detected in EPR experiments[1,2] more than 20 years ago. For $CH_2CF_2^-$ the isotropic hyperfine coupling constants (*hfcc*'s) on the H and F centers were reported to be 4.8 and 196.4 G[1], respectively, and for $CF_2CF_2^-$ the isotropic *hfcc*'s on ^{13}C and F were reported to be 48.7 and 94.3 G[2], respectively. The $CH_2CF_2^-$ and $CF_2CF_2^-$ anions were considered as temporary anions due to the negative vertical electron affinities (VEAs) (−2.39 and −3.00 eV[3], respectively) of their parent molecules, and both the two anions were detected as the π^* temporary anions by electron transmission spectroscopy (ETS).[3]

Based on information from their ESR experiments, Willianms et al.[1] suggested a perpendicular structure (C_{2v}) for $CH_2CF_2^-$ and Shiotani et al.[2] suggested a planar structure (D_{2h}) for $CF_2CF_2^-$. In the previous theoretical studies on the two anions[4−6] the researchers considered planar, perpendicular, syn (cis bent), and anti (trans bent) structures (see Figure 1). In 1981 Merry et al.[4] suggested that the most stable structure of $C_2F_4^-$ had anti form, on the basis of their UHF calculations with STO-3G and 3-21G basis sets. In 1982 Paddon-Row et al.[5] reported their theoretical study on geometries of the anions of fluorinated ethylenes. They performed UHF/3-21G calculations for planar, perpendicular, and anti structures of $CH_2CF_2^-$ and planar, syn, and anti structures of $CF_2CF_2^-$, and they concluded that anti structures of the two anions were the most stable, in contrast to the suggestions by the experimental groups.[1,2] The qualitative analysis on fluorination, nonplanar distortion, and stabilization for the anions of fluorinated ethylenes presented in the paper of Raddon-Row et al.[5] is instructive, but their calculations were carried out at a low HF level and apparently the frequency analysis calculations for structures were not carried out (not possible in early 1980s). In 1997 King et al.[6] performed calculations on anti structure of $CF_2CF_2^-$ by using DFT methods and a DZP basis set augmented with diffuse functions, and the anti structure was predicted to be a minimum-energy structure with a (C_{2h}) ^2A_g state. Their DFT calculations predicted VEA values of −0.69 to −1.27 eV for the CF_2CF_2 molecule, which were far different from the experimental value of −3.00 eV.[3] They realized that the anion computed at the neutral geometry had a (D_{2h}) ^2A_g ground state corresponding to a σ^* temporary anion, while the electron transmission spectroscopy[3] detected a π^* temporary anion.

We have carried out a computational study on the 1,1-difluoroethylene and tetrafluoroethylene anions by using DFT (density functional theory[7,8]) B3LYP (Becke's three-parameter hybrid function[9] with the nonlocal correlation of Lee−Yang−Parr[10]), MP2 (second-order Moller−Plesset perturbation

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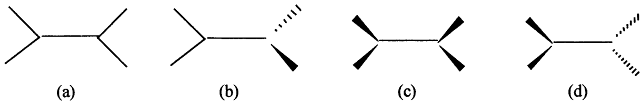

Figure 1. Planar (a), perpendicular (b), syn (c), and anti (d) structures of the 1,1-difluoroethylene and tetrafluoroethylene anions.

theory[11,12]), and QCISD (quadratic configuration interaction[13] with single and double substitutions) methods in conjunction with large basis sets. The structures of the two anions were considered as stationary points in the potential energy surfaces and studied by performing B3LYP geometry optimization, frequency analysis, and IRC (intrinsic reaction coordinate) calculations. For supporting the ESR and ETS experiments concerning the two anions, isotropic *hfcc*'s in the most stable structures of the two anions were explicitly calculated at the B3LYP and MP2 levels and electronic affinities of the 1,1-difluoroethylene and tetrafluoroethylene molecules were calculated at the B3LYP and QCISD levels. In the present paper we will report our calculation results, and we will also discuss the two focus problems on the basis of the calculation results and theoretical analysis.

Computational Methods

In Figure 1 shown are the planar, perpendicular, syn, and anti structures of the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions. The atom labels (X*n* representing dummy atoms) used for anti structures of the two anions and for the C_2 structure (see section of results and discussion) of $CF_2CF_2^-$ are given in Figure 2, and the C*n*−X*n* ($n = 1$ and 2) dashed lines are the bisectors of the H−C−H and F−C−F angles.

In the B3LYP, MP2, and QCISD calculations for $CH_2CF_2^-$ we used the following three groups of basis sets:[14] (1) 6-31G(d,p), 6-311G(d,p), and 6-311G(2d,p), denoted as B0, B1, and B2, respectively; (2) 6-31+G(d,p), 6-311+G(d,p), and 6-311+G(2d,p), denoted as B0+, B1+, and B2+, respectively; and (3) 6-31++G(d,p), 6-311++G(d,p), and 6-311++G(2d,p), denoted as B0++, B1++, and B2++, respectively. In the B3LYP, MP2, and QCISD calculations for $CF_2CF_2^-$ we used two groups of basis sets: (1) 6-31G(d), 6-311G(d), and 6-311G(2d); and (2) 6-31+G(d), 6-311+G(d), and 6-311+G(2d). These two groups of basis sets are also denoted as B*n* and B*n*+ ($n = 0-2$), respectively.

The B3LYP geometry optimization calculations were performed for locating structures of the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions, with different symmetry constraints for different structures. We studied planar (C_{2v}), perpendicular (C_{2v}), syn (C_s), and anti (C_s) structures of $CH_2CF_2^-$ and planar (D_{2h}), syn (C_{2v}), anti (C_{2h}), and C_2 structures of $CF_2CF_2^-$. The B3LYP frequency analysis calculations were performed for all the calculated structures in order to characterize the corresponding stationary points in the potential energy surfaces as minima or saddle points (first-order, second-order, or third-order saddle points). For finding possible "topological connections" between the stationary points, the B3LYP/B1+ IRC calculations were performed starting at geometries of all the first-order saddle points. In the IRC calculations one may find new minimum-energy structures.

At the B3LYP optimized geometries of the most stable structures of the $CH_2CF_2^-$ and $CF_2CF_2^-$ radical anions, hyperfine structure calculations were performed at the B3LYP and MP2(full) levels, and the isotropic *hfcc*'s on the H, ^{13}C, and F centers were explicitly calculated.

Electron affinities of the CH_2CF_2 and CF_2CF_2 molecules were first calculated at the B3LYP levels. The VEAs of the two molecules were evaluated as the differences between the B3LYP energies of the molecules in the ground states and the anions in specific states, and the B3LYP energies of both the molecules and anions were calculated at the B3LYP optimized geometries of the molecules. The adiabatic electron affinities (AEAs) of the two molecules were evaluated as the differences between the B3LYP energies of the molecules in the ground states and the anions in the ground states, and the B3LYP energies of the molecules and anions were calculated at their respective B3LYP optimized geometries. Since the VEA and AEA values calculated at the B3LYP levels were not satisfactory, we also calculated the VEA and AEA values at the QCISD (fc) level. In the QCISD VEA and AEA calculations, we used the B2+ basis and the B3LYP/B2+ optimized geometries of the molecules and anions.

The B3LYP, MP2, and QCISD calculations were carried out using the Gaussian 98W suit of programs,[15] and spin-unrestricted theory was used. The $<S^2>$ values in the (U)B3LYP, (U)MP2, and (U)QCISD calculations with the B*n*+ basis sets were smaller than 0.763, 0.798, and 0.798 (except in the QCISD/B2+ calculations for the $^2B_1$ state of $CH_2CF_2^-$, see below), respectively.

Results and Discussion

1. Structures of 1,1-Difluoroethylene Anion. Paddon-Row et al.[5] suggested that syn geometry of $CH_2CF_2^-$ was not a "minimum", on the basis of their UHF calculations. Our B3LYP calculations also indicate that syn structure of $CH_2CF_2^-$ does not correspond to a stationary point in the potential energy surface. In Table 1 given are the results of the B3LYP geometry optimization and frequency analysis calculations for anti, planar, and perpendicular structures of $CH_2CF_2^-$, including relative energies to anti structure, electronic states, and numbers of imaginary frequencies.

The materials presented in Table 1 also show difficulties in our B3LYP calculations for a temporary anion. With B*n*++ basis sets, the geometry optimization calculations for the planar structure were not successful since the calculated electronic structure described a system composed of the CH_2CF_2 neutral molecule plus a free electron (M + e). The failure is realized to be caused by the diffuse functions on hydrogens (the second " + ") in the B*n*++ basis sets, based on our and other people's

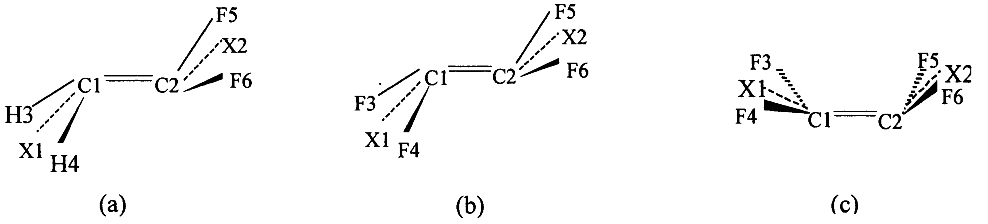

Figure 2. Notations and atom labelings in anti structures of the 1,1-difluoroethylene anion (a) and tetrafluoroethylene anion (b) and in the C_2 structure of tetrafluoroethylene anion (c) in which the two CF_2 groups are twisted. The C*n*−X*n* dashed lines are the bisectors of the HCH and FCF angles.

TABLE 1: Relative Energies (Δ*E*, in kcal/mol) for Anti, Planar, and Perpendicular Structures[a] of the 1,1-Difluoroethylene Anion Calculated Using the B3LYP Method with the Bn, B*n*+, and B*n*++ (*n* = 0−2) Basis Sets, together with the Calculated Electronic States and Numbers of Imaginary Frequencies (N)

	anti (C_s)			planar (C_{2v})			perpendicular (C_{2v})		
basis set	Δ*E*		*N*	Δ*E*		*N*	Δ*E*		*N*
B0	0.0 (−276.99008)[b]	$^2A'$	0	26.29	$^2B_1$	3	17.67	$^2B_1$	3
B1	0.0 (−277.09248)	$^2A'$	0	25.61	$^2B_1$	3	17.62	$^2B_1$	3
B2	0.0 (−277.09816)	$^2A'$	0	25.54	$^2B_1$	3	17.81	$^2B_1$	3
B0+	0.0 (−277.05437)	$^2A'$	0	13.54	$^2A_1$	1	20.58	$^2B_1$	3
B1+	0.0 (−277.12654)	$^2A'$	0	11.50	$^2A_1$	1	19.84	$^2B_1$	3
B2+	0.0 (−277.13121)	$^2A'$	0	9.97 [11.46][c]	$^2A_1$	1	19.70 [17.18]	$^2B_1$	3
B0++	0.0 (−277.05469)	$^2A'$	0				20.46	$^2B_1$	2
B1++	0.0 (−277.12693)	$^2A'$	0	(M + e)[d]			19.87	$^2B_1$	3
B2++	0.0 (−277.13164)	$^2A'$	0				19.77	$^2B_1$	3

[a] Syn structure of $CH_2CF_2^-$ was not found in the B3LYP geometry optimization calculations. [b] Values in parentheses are the total energies in a.u. [c] Values in square brackets are the relative energies with zero-point energy corrections. [d] B3LYP/B*n*++ calculations for planar structure of $CH_2CF_2^-$ failed to predict a stable anion (see text).

experiences in previous theoretical studies on hydrogencarbon anions.[16,17] The B3LYP/B*n*++ calculations predict that the perpendicular structure of $CH_2CF_2^-$ is about 20 kcal/mol higher in energy than anti structure. Therefore we have to give up all the B3LYP/B*n*++ results. The B3LYP/Bn calculations predict the planar structure to be in the $^2B_1$ state with three imaginary frequencies and to be higher in energy than the perpendicular one, while the B3LYP/B*n*+ calculations predict that it is in the $^2A_1$ state with one imaginary frequency and lower in energy than the perpendicular one. It is realized that the $^2B_1$ state predicted by the B3LYP/B*n* calculations is not the ground state at the planar geometry (we will come back to this point later). The Bn basis sets, in which no diffuse functions are included, are considered not to be appropriate for anions. We trust the B3LYP/B*n*+ results.

The B3LYP/B*n*+ (*n* = 0−2) calculations predict that anti (C_s), planar (C_{2v}), and perpendicular (C_{2v}) structures of $CH_2CF_2^-$ are in the $^2A'$, $^2A_1$, and $^2B_1$ states and represent an energy minimum (no imaginary frequency), a first-order saddle point (one imaginary frequency), and a third-order saddle point (three imaginary frequencies) in the potential energy surface, respectively. The B3LYP/B*n*+ (*n* = 0−2) calculations predict that planar and perpendicular structures are about 10 and 20 kcal/mol higher in energy than anti structure, and the B3LYP/B2+ relative energies (with zero-point energy (ZPE) corrections) of the planar and perpendicular structures to anti structure are predicted to be 11.46 and 17.18 kcal/mol, respectively.

The B3LYP/B1+ IRC calculations were performed starting at the geometry of the planar structure (a first-order saddle point). The IRC calculations indicate that the planar structure ($^2A_1$) is the transition state for the anti ($^2A'$) $\leftrightarrow$ anti interconverting process.

The previous UHF/3-21G calculations[5] predicted the planar structure of $CH_2CF_2^-$ to be higher in energy than the perpendicular structure, as our B3LYP/Bn calculations. By repeating the UHF/3-21G calculations and checking the relative energy value, we realize that the UHF/3-21G calculations for the planar structure predict a $^2B_1$ state, as our B3LYP/B*n* calculations.

The B3LYP optimized geometries for anti structure of $CH_2CF_2^-$, which has been predicted to be the most stable among the three structures by the B3LYP (/B*n*+) calculations, are given in Table 2. The ∠X1C1C2 and ∠X2C2C1 angle values describe the nonplanarity at the C1 (connecting with the two hydrogen atoms) and C2 (connecting with the two fluorine atoms) centers, respectively. At the B3LYP/B2+ level, the two angle values are predicted to be 146.0° and 134.3°, respectively.

The B3LYP/B2+ natural population analysis calculations indicate that negative charges on the C1-centers (connecting with the two hydrogens) in anti, planar, and perpendicular structures of $CH_2CF_2^-$ are large (−0.628*e*, −0.833*e*, and −0.489*e*, respectively). The charges on the H-centers are positive, but very small (less than 0.09 e).

2. Structures of Tetradifluoroethylene Anion. In our B3LYP IRC calculations (see below), we have found a minimum-energy structure of $C_2F_4^-$, which has C_2-symmetry. Therefore we studied a total of four structures for $CF_2CF_2^-$: anti, syn, planar, and C_2 structures. In Table 2 given are the results of the B3LYP geometry optimization and frequency analysis calculations with B*n* and B*n*+ (*n* = 0−2) basis sets for the four structures of $CF_2CF_2^-$, including relative energies to anti structure, electronic states, and numbers of imaginary frequencies.

We first examine the results of the B3LYP calculations with the different basis sets presented in Table 3. The B3LYP/B*n* (*n* = 0−2) calculations predict that the planar structure is in the $^2B_{2g}$ state with three imaginary frequencies. The B3LYP/B*n* relative energies for the planar structure in the $^2B_{2g}$ state are about 20 kcal/mol larger than the B3LYP/B*n*+ relative energies for the planar structure in the ^2A_g state. Apparently, the $^2B_{2g}$ state is not the ground state at the planar geometry (we will come back to this point later). We trust the B3LYP/B*n*+ results.

As shown in Table 2, the B3LYP/B*n*+ calculations predict similar results (relative energies, electronic states, and numbers of imaginary frequencies) for all the four structures of $CF_2CF_2^-$,

TABLE 2: Geometric Parameters for Anti Structure of 1,1-Difluoroethylene Anion Calculated Using the B3LYP Method with the B*n*, B*n*+, and B*n*++ (*n* = 0−2) Basis Sets[a]

basis set	R(C−C)	R(C−H)	R(C−F)	∠X1C1C2	∠X2C2C1	∠H3C1H4	∠F5C2F6
B0	1.4377	1.0976	1.4295	132.6	130.1	111.0	104.9
B1	1.4310	1.0930	1.4321	135.7	130.5	112.8	104.7
B2	1.4310	1.0931	1.4247	134.0	130.7	112.2	104.7
B0+	1.4144	1.0879	1.4252	147.1	133.4	116.2	105.4
B1+	1.4106	1.0859	1.4218	146.5	133.8	116.1	105.2
B2+	1.4084	1.0852	1.4161	146.0	134.3	115.9	105.5
B0++	1.4116	1.0870	1.4229	148.3	134.2	116.5	105.6
B1++	1.4078	1.0850	1.4196	147.8	134.5	116.4	105.4
B2++	1.4050	1.0841	1.4134	147.5	135.1	116.3	105.6

[a] For notations see Figure 2a; distances in angstroms and angles in degrees.

TABLE 3: Relative Energies (Δ*E*, in kcal/mol) for Anti, Syn, Planar, and C_2 Structures of the Tetrafluoroethylene Anion Calculated Using the B3LYP Method with the B*n* and B*n*+ (*n* = 0−2) Basis Sets, together with the Calculated Electronic States and Numbers of Imaginary Frequencies (*N*)

	anti(C_{2h})			syn (C_{2v})			planar (D_{2h})			C_2		
basis set	Δ*E*		*N*	Δ*E*		*N*	Δ*E*		*N*	Δ*E*		*N*
B0	0.0 (−475.46877)[a]	^2A_g	0	11.66	$^2B_2$	1	51.75	$^2B_{2g}$	3	9.64	^2B	0
B1	0.0 (−475.63344)	^2A_g	0	11.13	$^2B_2$	1	51.36	$^2B_{2g}$	3	8.95	^2B	0
B2	0.0 (−475.64449)	^2A_g	0	11.13	$^2B_2$	1	51.49	$^2B_{2g}$	3	9.03	^2B	0
B0+	0.0 (−475.54701)	^2A_g	0	11.35	$^2B_2$	1	32.36	^2A_g	1	9.14	^2B	0
B1+	0.0 (−475.67463)	^2A_g	0	10.96	$^2B_2$	1	30.85	^2A_g	1	8.58	^2B	0
B2+	0.0 (−475.68290)	^2A_g	0	10.87 [10.64][b]	$^2B_2$	1	28.75 [30.11]	^2A_g	1	8.63 [8.29]	^2B	0

[a] Values in parentheses are the total energies in au. [b] Values in square brackets are the relative energies with zero-point energy corrections.

TABLE 4: Geometric Parameters for Anti and C_2 Structures of the Tetrafluoroethylene Anion Calculated Using the B3LYP Method with the B*n* and B*n*+ (*n* = 0−2) Basis Sets[a]

	basis set	*R*(C−C)	*R*(C1−F3) (C2−F6)	*R*(C1−F4) (C2−F5)	∠X1C1C2	∠F3C1F4	∠X1C1C2X2
anti structure							
	B0	1.4908	1.4064		123.0	105.0	
	B1	1.4860	1.4055		123.6	104.8	
	B2	1.4839	1.4007		123.8	105.0	
	B0+	1.4793	1.4031		124.9	105.1	
	B1+	1.4734	1.3992		125.5	105.2	
	B2+	1.4697	1.3955		125.8	105.7	
C_2 structure							
	B0	1.3989	1.4347	1.3935	139.5	106.0	46.4
	B1	1.3952	1.4385	1.3913	139.4	105.6	45.3
	B2	1.3944	1.4332	1.3875	139.2	105.7	45.0
	B0+	1.4037	1.4361	1.3907	137.7	105.4	43.9
	B1+	1.3975	1.4355	1.3862	138.6	105.3	44.7
	B2+	1.3963	1.4315	1.3833	138.5	105.5	44.1

[a] For notations see Figure 2 (b) and (c); distances in Å and angles in degrees.

and we describe the B3LYP/B2+ results here. Anti structure (C_{2h}) is predicted to be in the ^2A_g state representing an energy minimum in the potential energy surface and to be the most stable among the four structures. The C_2 structure is predicted to be in the ^2B state representing an energy minimum and to be 8.29 kcal/mol (with ZPE corrections) less stable than anti structure. Syn (C_{2v}) and planar (D_{2h}) structures are predicted to be in the $^2B_2$ and ^2A_g states and to be 10.64 and 30.11 kcal/mol (with ZPE corrections) higher in energy than anti structure, respectively. Both syn and planar structures represent first-order saddle points.

The B3LYP/B1+ IRC calculations were performed starting at the geometries of syn and planar structures (first-order saddle points). The IRC calculations starting at the planar structure indicate that this structure (^2A_g) is the transition state for the anti (^2A_g) $\leftrightarrow$ anti interconverting process. The energy barrier (30.11 kcal/mol) for the anti $\leftrightarrow$ anti process of $CF_2CF_2^-$ is much higher than the barrier (11.46 kcal/mol) for the anti $\leftrightarrow$ anti process of $CH_2CF_2^-$ (the values in parentheses are the B3LYP/B2+ relative energies with ZPE corrections for the respective planar structures). In the IRC calculations starting at syn structure (∠X1C1C2X2 = 0°), we found a new minimum-energy structure of $CF_2CF_2^-$, which has C_2 symmetry with the ∠X1C1C2X2 dihedral angle of around 45°. Syn structure ($^2B_2$) is the transition state for the C_2 (^2B) $\leftrightarrow$ C_2 interconverting process, and the energy barrier for this process is very low (2.35 kcal/mol). Syn and C_2 structures are along one internal rotation potential energy curve, E(∠X1C1C2X2), but anti structure (^2A_g) (∠X1C1C2X2 = 180.0°) is not along the same curve as syn and C_2 structures. This can be understood by considering the symmetries of their electronic states.

The previous UHF calculations[5] predicted the planar structure of $CF_2CF_2^-$ to be higher in energy than the anti structure by 49.2 kcal/mol, which is comparative to the B3LYP/Bn relative energy values for the planar structure in the $^2B_{2g}$ state. By repeating the UHF/3-21G calculations and checking the relative energy value, we realize that the UHF/3-21G calculations for the planar structure predict the $^2B_{2g}$ state, which is not the ground state at the planar geometry.

The B3LYP optimized geometries for anti and C_2 structures of $CF_2CF_2^-$ are given in Table 4. At the B3LYP/B2+ level, the ∠X1C1C2X2 dihedral angle in C_2 structure is predicted to be 44.1°. At the same level, the ∠X1C1C2 angles (describing nonplanarity at the C-centers) in anti, C_2, and syn structures are predicted to be 125.8°, 138.5°, and 135.5° (not given in Table 4), respectively. King et al.[6] reported their B3LYP geometry of anti structure (^2A_g) of $CF_2CF_2^-$, and they used a DZP basis set augmented with diffuse functions. The basis sets was denoted as DZP++ in their paper, but it has a similar size to our B0+ basis. The B3LYP/DZP++ geometric parameter values[6] (the XCC angle is evaluated to be 125.1°) are close to the respective B3LYP/B*n*+ values except the C−C bond length, for which the B3LYP/DZP++ value is significantly (around 0.075 Å) smaller than the B3LYP/B*n*+ values.

The B3LYP/B2+ natural population analysis calculations indicate that the sums of negative charges on the four F-centers in anti, syn, planar, and C_2 structures of $CF_2CF_2^-$ are around −0.8 e.

TABLE 5: Isotropic Hyperfine Coupling Constants (in G) on the H, ^{13}C, and F Centers in Anti Structures of the 1,1-Difluoroethylene and Tetrafluoroethylene Radical Anions Calculated Using the B3LYP and MP2 (full) Methods with the B*n*, B*n*+, and B*n*++ (*n* = 0−2) Basis Sets

		$CH_2CF^-_2$ (anti)		$CF_2CF_2^-$ (anti)	
	basis set	H	F	^{13}C	F
B3LYP	B0	−2.6	128.2	72.4	67.5
	B1	−2.9	147.7	57.6	76.9
	B2	−1.3	146.7	57.8	78.5
MP2(full)[a]	B0	−3.8	131.9	68.5	67.1
	B1	−2.9	148.6	53.0	76.5
	B2	−2.2	147.0	53.9	76.9
B3LYP	B0+	−5.2	193.2	60.6	94.5
	B1+	−4.3	199.8	52.0	95.8
	B2+	−3.9	200.5	52.2	97.8
MP2(full)[a]	B0+	−4.5	186.3	57.5	86.1
	B1+	−3.2	192.9	46.4	89.8
	B2+	−3.0	193.0	47.4	90.7
B3LYP	B0++	−5.1	196.8		
	B1++	−4.5	203.4		
	B2++	−4.1	204.6		
MP2(full)[a]	B0++	−4.4	190.2		
	B1++	−3.4	196.8		
	B2++	−3.2	197.0		
exptl.		(−)4.8[b]	196.4[b]	48.7[c]	94.3[c]

[a] Calculated at the B3LYP optimized geometries. [b] Reference 1. [c] Reference 2.

3. Hyperfine Coupling Constants in 1,1-Difluoroethylene and Tetrafluoroethylene Anions. Isotropic hyperfine coupling constants (*hfcc*'s) in anti structures (the most stable minimum-energy structures) of $CH_2CF_2^-$ and $CF_2CF_2^-$ should correspond to the ESR experimentally observed couplings for the two anion radicals. The isotropic *hfcc*'s on H, ^{13}C, and F are denoted as *a*(H), *a*(C), and *a*(F), respectively. The *a*(H) and *a*(F) values in anti-$CH_2CF_2^-$ and the *a*(C) and *a*(F) values in anti-$CF_2CF_2^-$, calculated using the B3LYP and MP2(full) methods with the Bn, B*n*+, and B*n*++ basis sets, are listed in Table 5. The *a*(C) values in anti-$CH_2CF_2^-$ are not reported since the experimental values are not available. The MP2(full) calculations were performed at the B3LYP geometries optimized using the same basis sets.

At the B3LYP/Bn and MP2(full)/Bn//B3LYP/Bn levels the predicted *a*(F) values in anti-$CH_2CF_2^-$ and anti-$CF_2CF_2^-$ are significantly smaller than the experimental values (196.4 G[1] and 94.3 G[2], respectively), and the predicted *a*(C) values in anti-$CF_2CF_2^-$ are larger than the experimental value (48.7 G[2]). The B3LYP and MP2(full) calculations with the B*n*+ basis sets predict better *hfcc* results. At the MP2(full)/B2+//B3LYP/B2+ level the *a*(F) and *a*(H) values in anti-$CH_2CF_2^-$ are predicted to be 193.0 G and −3.0 G, which are close to the experimental values of 196.4 G and (−)4.8 G, respectively. At the same level, the *a*(C) and *a*(F) values in anti-$CF_2CF_2^-$ are predicted to be 47.4 and 90.7 G, which are also close to the experimental values of 48.7 and 94.3 G, respectively. The *a*(H), *a*(C), and *a*(F) values in anti structures of the two anions, calculated at the B3LYP/B2+ level, are also in good agreement with experiment (the B3LYP/B2+ *a*(F) and *a*(C) values are slightly larger than the respective experimental values). For anti-$CH_2CF_2^-$, the B3LYP and MP2(full) calculations with the B*n*++ basis sets predict *a*(F) and *a*(H) values similar to those calculated using the B*n*+ basis sets.

We will also report isotropic *hfcc* values in the other structures of the two anions, predicted by the B3LYP/B2+ calculations. For $CH_2CF_2^-$, the predicted *a*(H) values are −0.8 and 46.3 G and the *a*(F) values are 195.7 and 46.2 G for planar and perpendicular structures, respectively. For $CF_2CF_2^-$, the predicted *a*(C) values are 222.2 G, −1.1 G, and 194.7 G and the *a*(F) values are 125.1, 207.2, and 104.9 G for syn, planar, and C_2 structures, respectively. The *a*(F) value of 104.9 G for C_2 structure is an average of the values on the F3 (20.9 G) and F4 (188.9 G) centers, considering the low energy barrier for the $C_2 \leftrightarrow C_2$ interconverting process. Though the C_2 structure of $CF_2CF_2^-$ also represents an energy minimum, the B3LYP/B2+ *a*(C) and *a*(F) values (194.7 and 104.9 G, respectively) for C_2 structure are far different from the experimental couplings (48.7 and 94.3 G[2], respectively). The $CH_2CF_2^-$ and $CF_2CF_2^-$ anions detected by ESR experiments[1,2] are both in the most stable minimum-energy anti structures, which is supported by the agreements between the calculated (B3LYP/B2+ and MP2(full)/B2+) and experimental *hfcc* values.

Willianms et al.[1] argued that the $CH_2CF_2^-$ anion had a perpendicular structure. However the B3LYP/B2+ *a*(H) and *a*(F) values (see above) for perpendicular structure of $CH_2CF_2^-$ are far different from the experimental coupling values[1] (*a*(H) = (−)4.8 G and *a*(F) = 196.4 G). Shiotani et al.[2] suggested a planar structure for $CF_2CF_2^-$. However, the B3LYP/B2+ *a*(C) and *a*(F) values (see above) for planar structure of $CF_2CF_2^-$ are far different from the experimental coupling values[2] (*a*(C) = 48.7 G and *a*(F) = 94.3 G). Another fact, which does not support the suggestions of the two experimental groups,[1,2] is that the two structures are not minimum-energy structures, but represent saddle points.

4. Electron Affinities of 1,1-Difluoroethylene and Tetrafluoroethylene Molecules. In Table 6 given are the vertical and adiabatic electron affinity (VEA and AEA) values of 1,1-difluoroethylene and tetrafluoroethylene molecules, predicted by the B3LYP calculations with the B*n* and B*n*+ (*n* = 0−2) basis sets and by the QCISD calculations with the B2+ basis using the B3LYP/B2+ geometries of the molecules and anions. The details of calculation for VEAs and AEAs are described in section of computational methods.

Geometries of the two molecules optimized at the B3LYP/Bn and B3LYP/B*n*+ levels are given in Table 6 (for CH_2CF_2 we only report the optimized values for the C−C and C−F bond lengths and the FCF bond angle). The B3LYP/Bn and B3LYP/B*n*+ calculations predict very similar molecular geometries for each of the molecules. We did not calculated the VEAs of CH_2CF_2 at the B3LYP/B*n*++ levels due to the failure of the B3LYP/B*n*++ calculations for $CH_2CF_2^-$ at the molecular geometry, and in Table 6 we do not report the B3LYP/B*n*++ geometries for CH_2CF_2, which are almost identical to the B3LYP/B*n*+ geometries. At the B3LYP/B2+ level, the C−C and C−F bond lengths and the FCF and HCH bond angles in the CH_2CF_2 molecule are predicted to be 1.3151 Å, 1.3247 Å, 109.5°, and 120.4° (not given in Table 6), which are in agreement with the experimental values[18] of 1.315 Å, 1.323 Å, 109.1°, and 121.8°, respectively. At the same level, the C−C and C−F bond lengths and the FCF angle in the CF_2CF_2 molecule are predicted to be 1.3204 Å, 1.3196 Å, and 113.3°, which are in agreement with the experimental values[19] of 1.313 Å, 1.319 Å, and 112.5°, respectively. In the QCISD/B2+ VEA and AEA calculations we used the B3LYP/B2+ geometries of the molecules and anions.

Experimental AEA values of the CH_2CF_2 and CF_2CF_2 molecules are not available. The most stable structures of the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions are the anti structures (the geometries are given in Tables 2 and 4) and the ground states are $^2A_1$ and ^2A_g, respectively. For CH_2CF_2, the AEA values predicted by the B3LYP/Bn, B3LYP/B*n*+, and QCISD/B2+//

TABLE 6: Vertical Electron Affinities (VEAs) and Adiabatic Electron Affinities (AEAs) (in eV) of the 1,1-Difluorethylene and Tetrafluoroethylene Molecules Predicted by the B3LYP Calculations with the B*n* and B*n*+ ($n = 0-2$) Basis Sets[a] and by the QCISD Calculations with the B2+ Basis at the B3LYP/B2+ Geometries

			molecular geometry[b]						
	method	basis set	R(C−C)	R(C−F)	∠FCF	AEA[c]	VEA (σ*)[d]	VEA (π*)[e]	exptl (VEA(π*))[f]
CH_2CF_2									
(C_{2v})	B3LYP	B0	1.3220	1.3262	109.9	−1.95		−3.65	
		B1	1.3176	1.3245	109.7	−1.48		−3.14	
		B2	1.3154	1.3223	109.7	−1.54		−3.20	
		B0+	1.3222	1.3322	109.5	−0.79	−1.39		
		B1+	1.3174	1.3266	109.5	−0.80	−1.31		
		B2+	1.3151	1.3247	109.5	−0.87 (−0.74)[g]	−1.31		
	QCISD	B2+				−1.24	−2.11	−2.37	−2.39
CF_2CF_2									
(D_{2h})	B3LYP	B0	1.3256	1.3243	113.7	−0.84		−3.83	
		B1	1.3220	1.3212	113.3	−0.40		−3.40	
		B2	1.3206	1.3196	113.4	−0.49		−3.49	
		B0+	1.3261	1.3267	113.3	0.29	−1.13		
		B1+	1.3224	1.3209	113.2	0.24	−1.11		
		B2+	1.3204	1.3196	113.3	0.12 (0.23)	−1.14		
	QCISD	B2+				−0.26	−1.48	−3.25	−3.0

[a] No results from the calculations with the B*n*++ basis sets are given since B3LYP/B*n*++ calculations for $CH_2CF_2^-$ at the molecular geometries were not successful. [b] The B3LYP optimized molecular geometries are in agreement with experiment (see text for details), and only three of the geometric parameters are listed. [c] The $CH_2CF_2^-$ and $CF_2CF_2^-$ anions are in the most stable anti structures with the ground states of $^2A'$ and ^2A_g, respectively; and the optimized geometries are given in Tables 2 and 4. [d] The states of $CH_2CF_2^-$ and $CF_2CF_2^-$ are $^2A_1$ and ^2A_g, respectively; for the B3LYP/Bn VEA(σ*) calculations, see text. [e] The states of $CH_2CF_2^-$ and $CF_2CF_2^-$ are $^2B_1$ and $^2B_{2g}$, respectively; the B3LYP/B*n*+ calculations for VEA (π*) were not successful. [f] Reference 5. [g] Values in parentheses are the AEAs with zero-point energy corrections.

B3LYP/B2+ calculations are all negative. The B3LYP/B2+ AEA values with and without ZPE corrections are −0.74 eV and −0.87 eV, respectively. The QCISD/B2+// B3LYP/B2+ calculations predict an AEA value of −1.24 eV. For CF_2CF_2, the B3LYP/B*n* AEA values are negative, while the B3LYP/B*n*+ AEA values are positive. The B3LYP/B2+ AEA values with and without ZPE corrections are 0.23 and 0.12 eV, respectively. However, these positive B3LYP/B*n*+ AEA values are very small in magnitude, and the QCISD/B2+//B3LYP/B2+ AEA value for CF_2CF_2 is a small negative value (−0.26 eV).

We also calculated the vertical ionization potentials (VIPs) (=vertical detachment energies (VDEs)) of anti-$CH_2CF_2^-$ and anti-$CF_2CF_2^-$ at the B3LYP/B*n*+ ($n = 0-2$) levels. The VIP (VDE) was evaluated as the difference between the B3LYP/B*n*+ energies of the neutral and anion calculated at the B3LYP/B*n*+ geometries of the anion in anti-form. The calculated VIPs are 0.58−0.66 eV for anti-$CH_2CF_2^-$ and 2.13−2.26 eV for anti-$CF_2CF_2^-$. The positive VIP (VDE) values imply that the two anions might be kinetically stable in their anti-forms. For anti-$CF_2CF_2^-$, our calculated VIP values are close to the previously reported VDE value of 2.28 eV[6] calculated at the B3LYP/DZP++ level.

ETS experiments provide another kind of information (VEAs) concerning temporary anions. The VEAs associated with the anions formed by electron attachment to π* and σ* orbital are denoted as VEA(π*) and VEA(σ*), respectively. The gas-phase ETS[3] detected the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions arising from occupation of π* orbitals of the CH_2CF_2 and CF_2CF_2 molecules, and the VEA(π*) values were reported to be −2.39 and −3.00 eV, respectively. Accurate theoretical prediction of VEAs concerning temporary anions has been a difficult task, and researchers have tested many theoretical methods (approaches) and many kinds of basis sets (see ref 20 and references therein). In the case of fluorinated ethylenes, we realize that we have one more difficult problem: that is, to determine the ground states of the anions at the molecular geometries (π* states (electron attachment to π* orbitals) or σ* states (electron attachment to σ* orbitals)).

For CH_2CF_2, the B3LYP/Bn calculations predict VEA values of −3.20 ∼ −3.65 eV, which are the values of the VEA(π*) associated with the anion state of $^2B_1$, and the B3LYP/B*n*+ calculations predict VEA values of −1.31 to −1.39 eV, which are the values of the VEA(σ*) associated with the anion state of $^2A_1$. For CF_2CF_2, the B3LYP/Bn calculations predict VEA values of −3.49 ∼ −3.83 eV, which are the values of the VEA(π*) associated with the anion state of $^2B_{2g}$, and the B3LYP/B*n*+ calculations predict VEA values of −1.1 to −1.14 eV, which are the values of the VEA(σ*) associated with the anion state of ^2A_g. We failed to calculate the VEA(π*) values associated with the $^2B_1$ and $^2B_{2g}$ states of the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions, respectively, at the B3LYP/B*n*+ levels. As reported above, the B3LYP/Bn calculations predicted the π* states ($^2B_1$ and $^2B_{2g}$, respectively) for planar structures of the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions, respectively, and the predicted relative energies (to anti structures) of the planar structures in these states are very large (around 26 and 51 kcal/mol, respectively), compared to the relative energies of the planar structures in the σ* states predicted by the B3LYP/B*n*+ calculations. We were able to calculate the $^2A_1$ state of the $CH_2CF_2^-$ anion at the molecular geometry at the B3LYP/B1 and B3LYP/B2 levels, and the $^2A_1$ state was predicted to lie above the $^2B_1$ state (the predicted VEA(σ*) values (not given in Table 6) being more negative than the VEA(π*) values). We believe that lack of diffuse functions in the Bn basis sets causes that the π* states of the two anions were by error predicted to be the ground states at the molecular geometries and for planar structures.

We believe that the σ* states of the two anions are the ground states at the molecular geometries and the π* states lie above the σ* states. The previous DFT/DZP++(DZP+) calculations performed by King et al.[6] indicated that the ground state of $CF_2CF_2^-$ at the neutral geometry be the (σ*) ^2A_g state, and their B3LYP/DZP++ VEA value of −1.03 eV is close to our B3LYP/B*n*+ VEA(σ*) values. Our QCISD/B2+ calculations indicate that the π* states of the two anions lie above the σ* states (see below). We also performed MRSDCI (multireference single- and double-excitation configuration interaction) calculations with a D95+(d) basis using the program system MELD[21] for the anion states at the B3LYP/B2+ optimized molecular geometries, and the MRSDCI/D95+(d) calculations indicate that for $CH_2CF_2^-$ the $^2B_1$ state lies above $^2A_1$ and for $CF_2CF_2^-$ the $^2B_{2g}$ state lies above ^2A_g.

The QCISD/B2+//B3LYP/B2+ calculations for CH_2CF_2 predict a VEA(σ*) value of −2.11 eV and a VEA(π*) value of −2.37 eV, and the later value is close to the experimental VEA(π*) value of −2.39 eV. Our QCISD/B2+//B3LYP/B2+ calculations for CF_2CF_2 predict a value of −3.25 eV for the VEA(π*) associated with the anion state of $^2B_{2g}$, which is quite close to the experimental VEA(π*) value of −3.00 eV, while the calculated VEA(σ*) value (−1.48 eV) is significantly smaller in magnitude than the experimental VEA(π*) value. It seems that the QCISD/B2+ calculations predict the VEA(π*) values of the two molecules in quite good agreement with experiment. However our QCISD/B2+ VEA calculations were not so satisfactory: the $\langle S^2 \rangle$ value obtained in the QCISD/B2+ calculations (computed for the reference wave function) for the $^2B_1$ state (π* state) of $CH_2CF_2^-$ was large (0.862).

5. Pseudo-Jahn−Teller Effect. Paddon-Row et al. mentioned in their paper[5] that distortions in the anions of fluorinated ethylenes could be interpreted as arising from a mixing of the π* and σ* orbitals (in their molecular orbital pictures the σ* orbitals lay above the π* orbitals) and that the situation was similar to that for the acetylene anion which distorts due to $\sigma^*-\pi^*$ mixing. Recently we studied structures and hyperfine structure of the acetylene anion (another temporary anion).[16] The existence of the trans-bent structure of the anion has been considered as consequence of the Renner−Teller effect, and the analysis based on the calculations for the Renner−Teller splitting parterns was clear and simple.[16] The distortions from planar to anti form for the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions seem “ similar ” to the distortion from linear to trans-bent form for the acetylene anion. The applicability of the Renner−Teller theory to the acetylene anion is based on the fact that the ground electronic state of the anion at the molecular geometry (linear) is a degenerate $^2\Pi_g$ state, and both Jahn−Teller and Renner−Teller phenomena are related to degenerate electronic states at undistorted geometries. However, the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions will never have degenerate states at the molecular geometries which have symmetries of C_{2v} and D_{2h}, respectively.

Now we present our analysis for the cause of the distortions in the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions from the planar geometries (the molecular geometries) to the anti geometries (the equilibrium geometries of the anions) in terms of the pseudo-Jahn−Teller (pseudo-JT) theory.[22] We should first emphasize that the σ* states ($^2A_1$ and ^2A_g, respectively) of the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions are the ground states at the molecular geometries and the π* states ($^2B_1$ and $^2B_{2g}$, respectively; not $^2\Pi$!) lie above the σ* states, which has been argued in the last subsection. The pseudo-JT theory tells us that the σ* ground states of the two anions at the planar molecular geometries can mix with the low-lying π* excited states by distortions with specific symmetries. According to the theory, the $^2A_1$ ground state of $CH_2CF_2^-$ can mix with the $^2B_1$ state by a distortion with b_1 symmetry ($a_1 \times b_1 \times b_1 = a_1$), and the ^2A_g ground state of $CF_2CF_2^-$ can mix with the $^2B_{2g}$ state by a distortion with b_{2g} symmetry ($a_g \times b_{2g} \times b_{2g} = a_g$). The b_1 and b_{2g} modes of distortion are in line with the distortions from the planar to anti geometries for the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions, respectively.

The pseudo-JT theory expects the involved excited state(s) to be close to the ground state in energy. Based on the QCISD/B2+ VEA(σ*) and VEA(π*) values listed in Table 6, the energy separation between the $^2B_1$ and $^2A_1$ states of $CH_2CF_2^-$ is only 0.26 eV, while the separation between the $^2B_{2g}$ and ^2A_g states of $CF_2CF_2^-$ is 1.77 eV, which is quite large. We would suspect that the QCISD/B2+ VEA values for CF_2CF_2 be not so accurate (the VEA(π*) value of CF_2CF_2 is apparently overestimated by the QCISD/B2+ calculations, see Table 6).

As reported above, our B3LYP/B*n*+ calculations for the planar structures of $CH_2CF_2^-$ and $CF_2CF_2^-$ predict that they are in the σ* states ($^2A_1$ and ^2A_g, respectively) and represent saddle points with unique imaginary frequencies, and on the basis of these facts we expected the anti ($^2A'$ and ^2A_g, respectively) ↔ anti interconverting processes with the planar structures as transition states, which were confirmed by the B3LYP/B1+ IRC calculations. By checking the outputs of the calculations, we have found that the optimized geometries (not reported) of the planar structures of the $CH_2CF_2^-$ and $CF_2CF_2^-$ anions are similar to their respective molecular geometries and the unique imaginary frequencies are just in the b_1 and b_{2g} modes, respectively. The pseudo-JT distortion from the planar molecular geometries and the interconverting processes with the planar structures of the anions as transition states seem to be theoretically related to each other in our cases.

Conclusions

The $CH_2CF_2^-$ and $CF_2CF_2^-$ anions were studied by performed B3LYP calculations with the Bn, B*n*+, and B*n*++ basis sets. Besides geometry optimization calculations, frequency analysis calculations were performed for characterizing the stationary points in the potential energy surfaces associated with the structures and the IRC technique was used for finding possible “connections” between structures and searching new minimum-energy structures. Anti structures were predicted to be the most stable for the two molecular anions. For $CF_2CF_2^-$, a new minimum-energy structure having C_2 symmetry was found and it is about 9 kcal/mol less stable than the anti structure. Syn structure of $CF_2CF_2^-$ is the transition state for the $C_2 \leftrightarrow C_2$ interconverting process, while syn structure of $CH_2CF_2^-$ does not exist. The planar structures of the two anions are the transition states for the anti ↔ anti interconverting processes. The B*n*+ basis sets (standard split valence plus polarization basis sets augmented with diffuse functions on heavy atoms) are considered to be appropriate for these anions. The B3LYP/B*n* calculations and the previous UHF/3-21G calculations[5] predicted wrong ground states for the planar structures of the two anions.

The isotropic hyperfine coupling constants (*hfcc*’s) in anti-$CH_2CF_2^-$ and anti-$CF_2CF_2^-$ were explicitly calculated using the B3LYP and MP2(full) methods, and the calculations with the B2+ (6-311+G(2d,p)) basis sets predict *hfcc* values in good agreement with experiment, which further confirms that the two anions detected in the ESR experiments are in their anti forms. The calculated *hfcc* values in the previously suggested structures (perpendicular and planar structures for $CH_2CF_2^-$ and $CF_2CF_2^-$, respectively) are far different from the experimental coupling values.

Accurate theoretical predictions for electron affinities associated with temporary molecular anions seem to be difficult. For CH_2CF_2, the B3LYP/B*n*+ and QCISD/B2+ calculations predict negative AEA values. For CF_2CF_2, the B3LYP/B*n*+ calculations predict small positive AEA values, while the QCISD/B2+ calculations predict a small negative AEA value. The B3LYP/B*n*+ calculations for the VEA(π*)’s of CH_2CF_2 and CF_2CF_2 were not successful. At the QCISD/B2+ level, we calculated the VEA(π*)'s of CH_2CF_2 and CF_2CF_2 which are associated with the anion states of $^2B_1$ and $^2B_{2g}$, respectively, and the calculated values are in quite good agreement with the experimental VEA(π*) values. It is argued that the σ* states of the two anions are the ground states at the molecular geometries and the π* states lie above the σ* states and that the existence of the anti structures of the two anions is considered as a consequence of the pseudo-Jahn−Teller effect.

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