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Substitution Effects on the Properties of Unsaturated Carbenes: Fluorovinylidene (HFC=C:)

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Abstract: Ab initio molecular electronic structure theory has been used to study the fluorovinylidene–fluoroacetylene isomerization reaction on the C_2HF singlet ground-state potential energy surface. The $\tilde{X}\ {}^2A'$ ground state of the fluorovinylidene anion and the two lowest triplet states (${}^3A'$ and ${}^3A''$) of neutral fluorovinylidene have also been investigated. The effects of electron correlation were included via configuration interaction and coupled-cluster methods. The *classical* barrier for 1,2-hydrogen migration in $\tilde{X}\ {}^1A'$ fluorovinylidene is predicted to be 2.4 kcal mol^{-1}. After correction for zero-point vibrational energies, an activation energy of ~0.8 kcal mol^{-1} is obtained. The ΔE for isomerization to fluoroacetylene is ~44 kcal mol^{-1}. The adiabatic electron affinity of ground-state fluorovinylidene is predicted to be 1.62 eV. The ${}^3A'$ and ${}^3A''$ states of neutral fluorovinylidene are predicted to lie very close together in energy ($\Delta T_0 = 0.12$ eV). In general, the theoretical results reported here are in excellent agreement with negative ion photodetachment spectroscopy results reported in the preceding paper by Gilles, Lineberger, and Ervin. However, our best results indicate that the ${}^3A'$ state may be the lowest triplet state for fluorovinylidene ($T_0 = 1.30$ eV).

Introduction

Vinylidene ($H_2C{=}C{:}$), the simplest unsaturated carbene, has attracted considerable interest during the past decade. Its isomerization to acetylene on the C_2H_2 singlet ground-state potential energy hypersurface via a 1,2-hydrogen shift has been the subject of several theoretical investigations[1-4] as a model for similar rearrangements in other molecules. The most recent and most reliable ab initio results to date have shown that $\tilde{X}\ {}^1A_1$ vinylidene is an extremely shallow minimum with a well depth of ~3 kcal mol^{-1} and a zero-point vibrational energy (ZPVE) corrected barrier of ~1.6 kcal mol^{-1} for 1,2-hydrogen migration.[4] Previously, Møller–Plesset perturbation theory results had prompted tentative speculation that the vinylidene stationary point was merely a transition state.[2] On the basis of a classical barrier of 2–4 kcal mol^{-1}, a lifetime against isomerization of about 1 ps has been predicted theoretically for ground-state vinylidene.[3] Because of the extremely brief lifetime of singlet vinylidene, experimental evidence for its presence is usually indirect. For example, it has been proposed as a reactive intermediate[5,6] and a short-lived product[7,8] in various reactions.

A substantially higher barrier (~54 kcal mol^{-1}) has been predicted for 1,2-hydrogen migration in the case of $\tilde{a}\ {}^3B_2$ vinylidene.[9,10] The lifetime of this excited triplet state is therefore expected to be significantly longer than that of the singlet ground state. An absorption spectrum observed at 137 nm following vacuum-UV photolysis of acetylene[11] and acrylonitrile[12] was assigned to long-lived $\tilde{a}\ {}^3B_2$ vinylidene by Laufer and co-workers as early as 1980. A stable C_2H_2 species with a lifetime ≥ 0.4 μs, presumably this excited triplet state, has recently been observed by mass spectrometry.[13]

The vinylidene anion $H_2C{=}C{:}^-$ is also relatively stable with respect to 1,2-hydrogen migration. Abstraction of H_2^+ from ethylene by O^- in the gas phase produces a long-lived $C_2H_2^-$ species.[14] Deuterium labeling experiments[14] and the reaction[15] of $C_2H_2^-$ with isotopically labeled ${}^{14}N^{15}NO$ clearly indicate a vinylidene-like structure for the anion produced by this ion–molecule reaction. The results of several theoretical studies[16-18] of the $C_2H_2^-$ potential energy surface support these experimental findings regarding the stability of $\tilde{X}\ {}^2B_2$ vinylidene anion. As with $\tilde{a}\ {}^3B_2$ neutral vinylidene, the barrier for a 1,2-hydrogen shift in the vinylidene anion is predicted to be very high (~45 kcal mol^{-1}).[18]

The first direct observation of $\tilde{X}\ {}^1A_1$ vinylidene was reported by Burnett, Stevens, Feigerle, and Lineberger[19] in 1983 as vibrational structure in the 488-nm photoelectron spectra of $H_2C{=}C{:}^-$ and $D_2C{=}C{:}^-$. In a much more recent and detailed study, Ervin, Ho, and Lineberger[20] observed vibrational structure in the 351-nm photoelectron spectra of $H_2C{=}C{:}^-$, $HDC{=}C{:}^-$, and $D_2C{=}C{:}^-$ due to the $\tilde{X}\ {}^1A_1$ ground state and the low-lying $\tilde{a}\ {}^3B_2$ and $\tilde{b}\ {}^3A_2$ excited states of neutral vinylidene. Their results clearly showed that vinylidene was a minimum on the C_2H_2 singlet ground-state potential energy surface with a well at least as deep as the observed $2 \leftarrow 0$ CH_2 rock transition (450 cm^{-1}, or 1.3 kcal mol^{-1}). They estimated that the lifetime of $\tilde{X}\ {}^1A_1$ vinylidene against rearrangement to acetylene was 0.04–0.2 ps.

Negative ion photodetachment spectroscopy has recently been used by Gilles, Lineberger, and Ervin[21] to make the first direct

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observation of fluorovinylidene ($\mathrm{HFC{=}C}$:). Previous experimental evidence for the existence of fluorovinylidene has been rather tenuous. For example, it has been proposed that the triplet mercury photosensitized decomposition of *cis*- and *trans*-1,2-difluoroethylene proceeds by $\alpha\alpha$-elimination of molecular HF, thus yielding fluorovinylidene.[22] The observation of *fluoroacetylene* and HF as products was explained in terms of the extremely short lifetime expected for singlet fluorovinylidene against 1,2-hydrogen migration. A later study[23] of the distribution of vibrationally excited HF molecules produced by this decomposition reaction appeared to cast doubt upon the hypothesis that fluorovinylidene was a short-lived product because surprisingly large amounts of vibrational energy were present in HF.

Several theoretical studies[24,25] of the C_2HF singlet ground-state potential energy hypersurface have appeared in the chemical literature. Isomerization of fluorovinylidene to fluoroacetylene can follow two different pathways: a 1,2-hydrogen shift or a 1,2-fluorine shift. Using relatively low levels of theory and modest-sized basis sets by today's standards, it was predicted[24,25] in 1981 that the barrier for hydrogen migration was significantly lower (20–30 kcal mol^{-1}) than the barrier for fluorine migration. In fact, Frisch, Krishnan, Pople, and Schleyer[24] predicted that the zero-point corrected energy of the fluorovinylidene minimum is actually ***higher*** than the zero-point corrected energy of the 1,2-hydrogen shift transition state. They concluded that $\mathrm{HFC{=}C}$: should rearrange to fluoroacetylene via hydrogen migration ***without a barrier***. Goddard,[25] on the other hand, found that a small barrier against hydrogen migration existed even after a correction for ZPVE had been made. Over a decade later, this controversy remains unresolved.

Fluoroacetylene, the global minimum on the C_2HF singlet ground-state potential energy surface, has been studied in great detail experimentally. In 1963, its structure was accurately determined[26] by microwave spectroscopy using the method of isotopic substitution. More recently, Holland, Newnham, and Mills[27] have reported a detailed analysis of high-resolution IR and near-IR spectra for fluoroacetylene.

The fluorovinylidene anion has also been studied experimentally. A stable C_2HF^- species (presumably vinylidene-like in structure) is formed by dissociative electron attachment to *cis*- and *trans*-1,2-difluoroethylene.[28] In addition, Dawson and Jennings[29] have reported that the gas-phase reaction of O^- with vinyl fluoride yields predominantly the fluorovinylidene anion.

In this paper, we report the results of an ab initio study of singlet ground-state fluorovinylidene–fluoroacetylene isomerization. As noted above, the existence or absence of a ZPVE corrected barrier for 1,2-hydrogen migration has not yet been firmly established.[24,25] Lack of optimized structures and harmonic frequencies determined at correlated levels of theory for relevant stationary points is a serious shortcoming of previous theoretical studies. Larger basis sets and significantly higher levels of theory have been employed here in an attempt to resolve this issue.

Previous theoretical studies[24,25] have indicated that the 1,2-fluorine migration pathway is extremely unfavorable energetically compared to 1,2-hydrogen migration for isomerization of ground-state fluorovinylidene to fluoroacetylene. Geometry optimizations performed at correlated levels of theory were not expected to qualitatively change this aspect of the C_2HF ground-state potential energy surface. This proved to be the case. Preliminary results obtained using configuration interaction (CI) and couple-cluster (CC) methods merely confirmed predictions made by Goddard[25] and Frisch et al.[24] regarding the high relative energy of the 1,2-fluorine shift transition state. Our study therefore focused upon the much more energetically favorable 1,2-hydrogen migration process, and the transition state for fluorine migration was not investigated in greater detail.

Theoretical results for the optimized structures, harmonic vibrational frequencies, and relative energies of the fluorovinylidene anion and low-lying excited states of neutral fluorovinylidene are conspicuously absent from the chemical literature. Therefore, we also report the results of our study of $\tilde{X}\ {}^2A'$ $\mathrm{HFC{=}C}:^-$ and two low-lying excited states of $\mathrm{HFC{=}C}$: (the ${}^3A'$ and ${}^3A''$ states that correspond to the $\tilde{a}\ {}^3B_2$ and $\tilde{b}\ {}^3A_2$ states of vinylidene, respectively). This information is particularly useful because hot bands and vibrational structure from at least one excited state of neutral fluorovinylidene have been observed in the 351-nm negative ion photodetachment spectrum of $\mathrm{HFC{=}C}:^-$ (see the preceding paper[21]). In addition, these theoretical results permit a broader comparison with past results for vinylidene in an effort to understand the effects of fluorination.

Theoretical Methods

Four different basis sets were used in this research. The double-ζ plus polarization basis, denoted DZP, is a standard Huzinaga–Dunning[30,31] double-ζ set of contracted Gaussian functions augmented by a set of six Cartesian d-like polarization functions on carbon [$\alpha_d(C) = 0.75$] and fluorine [$\alpha_d(F) = 1.00$] and a set of p-type polarization functions on hydrogen [$\alpha_p(H) = 0.75$]. The contraction scheme for the DZP basis is thus

$$\mathrm{C,\ F\ (9s5p1d/4s2p1d);\ H\ (4s1p/2s1p)}$$

The triple-ζ plus double polarization basis, denoted TZ2P, adds two sets of polarization functions per atom [$\alpha_d(C) = 1.5, 0.375$; $\alpha_d(F) = 2.0, 0.5$; $\alpha_p(H) = 1.5, 0.375$] to a standard Huzinaga–Dunning[30,32] set of contracted Gaussian functions that is triple-ζ in the valence region. The contraction scheme for the TZ2P basis is as follows

$$\mathrm{C,\ F\ (10s6p2d/5s3p2d);\ H\ (5s2p/3s2p)}$$

It has been shown[33] that a basis set that includes diffuse functions must be used for molecular anions in order to accurately determine many of their properties. Therefore, two additional basis sets designated DZP+diff and TZ2P+diff were utilized in the study of the fluorovinylidene anion. The DZP+diff basis was constructed by adding diffuse functions [$\alpha_s(C) = 0.043$, $\alpha_p(C) = 0.0363$; $\alpha_s(F) = 0.1049$, $\alpha_p(F) = 0.0826$; and $\alpha_s(H) = 0.0441$] to the DZP basis. The diffuse function exponents were determined as even-tempered extensions of the respective primitive sets using the method suggested by Lee and Schaefer.[33] In a similar manner, the TZ2P+diff basis was formed by adding diffuse functions [$\alpha_s(C) = 0.0481$, $\alpha_p(C) = 0.03389$; $\alpha_s(F) = 0.1164$, $\alpha_p(F) = 0.0716$; and $\alpha_s(H) = 0.0302$] to the TZ2P basis.

The restricted Hartree–Fock (RHF) self-consistent-field (SCF) method was initially employed in this study. The effects of electron correlation were taken into account using the method of configuration interaction including all single and double excitations from an SCF reference wave function (CISD), the coupled-cluster method including all single and double excitations (CCSD), and the CCSD method with the effect of connected triple excitations included perturbatively [CCSD(T)]. Only the valence electrons have been explicitly correlated; the three lowest (carbon and fluorine 1s-like) SCF molecular orbitals were constrained to be doubly-occupied. In addition, the three highest (carbon and fluorine 1s*-like) virtual orbitals were deleted from the correlation procedure. With the TZ2P basis, this resulted in a total of 46 977 configurations for singlet fluoroacetylene (using C_{2v} symmetry), 89 755 configurations for singlet fluorovinylidene and the transition state for 1,2-hydrogen migration (C_s symmetry), 264 595 configurations for ${}^3A'$ fluorovinylidene (C_s symmetry), and 271 334 configurations for ${}^3A''$ fluorovinylidene (C_s symmetry). Using the TZ2P+diff basis resulted in a total of 156 966 configurations for $\tilde{X}\ {}^2A'$ fluorovinylidene anion and 124 877 configurations for $\bar{X}\ {}^1A'$ fluorovinylidene (both C_s symmetry).

The structures of ground-state fluorovinylidene, fluoroacetylene, and the transition state connecting them via a 1,2-hydrogen shift were fully optimized using closed-shell analytic gradient techniques at the SCF,[34–36]

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Table I. Total Energies (hartrees) and Optimized Geometries for the Fluorovinylidene, 1,2-Hydrogen Shift Transition State, and Fluoroacetylene Isomers of Singlet Ground-State C_2HF^a

	SCF	CISD		CCSD		CCSD(T)	
	TZ2P	DZP	TZ2P	DZP	TZ2P	DZP	TZ2P
Fluorovinylidene							
E_{total}	−175.657 72	−176.007 23	−176.098 03	−176.050 13	−176.149 43	−176.063 11	−176.168 55
$r_e(C_1C_2)$	1.3066	1.3337	1.3154	1.3458	1.3269	1.3501	1.3319
$r_e(C_1F_3)$	1.3112	1.3324	1.3262	1.3421	1.3366	1.3439	1.3409
$r_e(C_1H_4)$	1.0757	1.0904	1.0803	1.0954	1.0857	1.0983	1.0893
$\theta_e(F_3C_1C_2)$	126.2	128.3	128.0	128.0	127.9	129.1	129.0
$\theta_e(H_4C_1C_2)$	117.0	115.0	114.8	115.5	115.1	114.3	113.9
Transition State							
E_{total}	−175.638 98	−176.000 19	−176.090 89	−176.043 74	−176.142 88	−176.059 29	−176.164 74
$r_e(C_1C_2)$	1.2362	1.2797	1.2638	1.2943	1.2768	1.3075	1.2903
$r_e(C_1F_3)$	1.2604	1.2953	1.2880	1.3071	1.2992	1.3145	1.3085
$r_e(C_1H_4)$	1.2815	1.1842	1.1761	1.1807	1.1802	1.1615	1.1637
$r_e(C_2H_4)$	1.2643	1.4343	1.4324	1.4718	1.4527	1.5610	1.5312
$\theta_e(F_3C_1C_2)$	174.3	165.6	164.3	164.2	163.8	159.8	160.0
$\theta_e(H_4C_1C_2)$	60.3	71.1	71.8	72.8	72.4	78.2	77.0
Fluoroacetylene[b]							
E_{total}	−175.714 76	−176.073 63	−176.167 63	−176.116 33	−176.218 27	−176.131 25	−176.239 71
$r_e(C_1C_2)$	1.1714	1.1993	1.1846	1.2102	1.1949	1.2161	1.2017
$r_e(C_1F_3)$	1.2598	1.2818	1.2753	1.2911	1.2853	1.2933	1.2896
$r_e(C_2H_4)$	1.0519	1.0641	1.0542	1.0690	1.0595	1.0702	1.0612

[a] Bond lengths in angstroms and bond angles in degrees. [b] Experimental r_s structure for fluoroacetylene, ref 26: $r_s(C_1C_2) = 1.198$ Å; $r_s(C_1F_3) = 1.279$ Å; $r_s(C_2H_4) = 1.053$ Å.

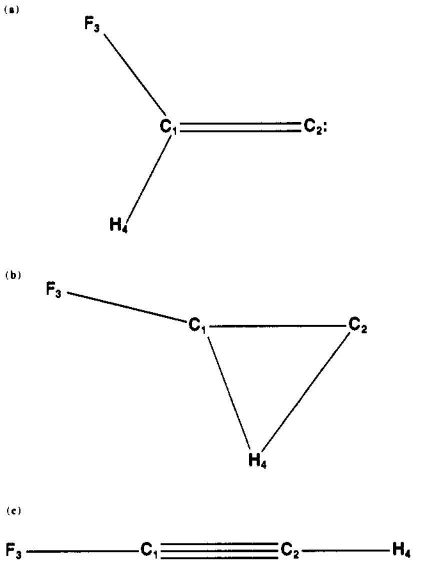

Figure 1. Numbering scheme for atomic nuclei used in the definition of geometric parameters for (a) fluorovinylidene, (b) 1,2-hydrogen shift transition state, and (c) fluoroacetylene.

Table II. Harmonic Vibrational Frequencies (cm^{-1}) for the Fluorovinylidene, 1,2-Hydrogen Shift Transition State, and Fluoroacetylene Isomers of Singlet Ground-State C_2HF

	SCF	CISD		CCSD		CCSD(T)	
	TZ2P	DZP	TZ2P	DZP	TZ2P	DZP	Exptl
Fluorovinylidene							
CH stretch	3330	3258	3243	3197	3171	3162	
CC stretch	1871	1784	1786	1716	1713	1687	1680[a]
HCC bend	1288	1222	1217	1193	1183	1178	
CF stretch	1151	1068	1064	1033	1024	1007	960[a]
FCC bend	410	336	333	321	314	296	205[a]
C_2 oop bend	874	756	778	713	732	683	
Transition State							
CH stretch	2511	2647	2596	2638	2538	2706	
CC stretch	2225	2081	2068	1992	1981	1920	
CF stretch	1126	1089	1094	1049	1046	1054	
FCC bend	686	845	841	809	792	825	
H_4 migration	527*i*	346*i*	402*i*	369*i*	414*i*	344*i*	
F_3 oop bend	426	416	441	392	408	406	
Fluoroacetylene							
CH stretch	3634	3580	3561	3514	3484	3496	3500[b]
CC stretch	2485	2394	2375	2316	2295	2275	2284[b]
CF stretch	1161	1108	1100	1068	1059	1055	1076[b]
HCC linear bend	746	633	634	580	573	550	597[b]
FCC linear bend	503	410	427	349	366	308	375[b]

[a] Fundamental frequency, ref 21. [b] Harmonic frequency, ref 27.

CISD,[37-39] CCSD,[40] and CCSD(T)[41] levels of theory. The structure of the fluorovinylidene anion and the two lowest triplet states of neutral fluorovinylidene were fully optimized using open-shell analytic gradient techniques at the SCF and CISD levels of theory. In all cases, the residual Cartesian and internal coordinate gradients were less than 10^{-6} atomic units. At the CCSD and CCSD(T) levels of theory, the anion's structure was determined from total energies[42] since no analytic gradient procedure is presently available for open-shell systems with these methods. Harmonic vibrational frequencies were obtained using analytic SCF second-derivative techniques[43-45] and central finite differences of analytic CISD, CCSD, and CCSD(T) gradients.

Relative energies designated CISD+Q were obtained for the various isomers studied here by adding the Davidson correction[46] for unlinked quadruple excitations to the CISD energy. Improved predictions of the relative energies for the fluorovinylidene anion and the two excited triplet states of neutral fluorovinylidene were determined using open-shell coupled-cluster methods[42] at the CISD optimized geometries. The notation used to designate these single-point energies is fairly standard: a TZ2P CCSD(T) energy that was evaluated at the TZ2P CISD optimized ge-

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Table III. Barrier Height (kcal mol^{-1}) for 1,2-Hydrogen Migration in $\tilde{X}\ ^1A'$ Fluorovinylidene

method	classical barrier[a]	ZPVE correction	corrected barrier
		DZP	
SCF	12.3	−2.8	9.5
CISD	4.4	−1.9	2.5
CCSD	4.0	−1.8	2.2
CCSD(T)	2.4	−1.6	0.8
		TZ2P	
SCF	11.8	−2.8	9.0
CISD	4.5	−2.0	2.5
CCSD	4.1	−1.9	2.2
CCSD(T)	2.4	~−1.6[b]	~0.8

[a] Reference 21, D_e = 2.0 kcal mol^{-1} from Franck–Condon simulations of the observed photoelectron spectrum. [b] ZPVE correction estimated from DZP CCSD(T) harmonic vibrational frequencies.

Table IV. ΔE (kcal mol^{-1}) for Ground-State Fluorovinylidene–Fluoroacetylene Isomerization

method	classical ΔE	ZPVE correction	corrected ΔE
		DZP	
SCF	−35.2	+1.2	−34.0
CISD	−41.7	+1.1	−40.6
CCSD	−41.5	+0.8	−40.7
CCSD(T)	−42.8	+0.8	−42.0
		TZ2P	
SCF	−35.8	+1.2	−34.6
CISD	−43.7	+1.1	−42.6
CCSD	−43.2	+0.8	−42.4
CCSD(T)	−44.7	~+0.8[a]	~−43.9

[a] ZPVE correction estimated from DZP CCSD(T) harmonic vibrational frequencies.

ometry has been labeled TZ2P/CCSD(T)//TZ2P/CISD.

Results

Figure 1 illustrates the basic structure of the three stationary points studied for singlet ground-state C_2HF. The optimized geometries and total energies determined for these three structures at the SCF, CISD, CCSD, and CCSD(T) levels of theory appear in Table I. The corresponding harmonic vibrational frequencies are listed in Table II. DZP SCF results are not listed in Tables I and II, but they are available upon request. Harmonic vibrational frequencies were not obtained for singlet C_2HF isomers at the TZ2P CCSD(T) level of theory because of the great computational expense involved. Surprisingly, virtually no change in CCSD frequencies was observed upon switching to the larger TZ2P basis. It was therefore expected that our DZP CCSD(T) harmonic vibrational frequencies would provide a reasonable estimate of the corresponding TZ2P CCSD(T) values. The energetics of ground-state fluorovinylidene–fluoroacetylene isomerization are summarized in Tables III and IV. The classical and ZPVE corrected barrier for 1,2-hydrogen migration predicted at the SCF, CISD, CCSD, and CCSD(T) levels of theory using both the DZP and TZ2P basis sets are listed in Table III. Table IV gives corresponding values for the classical and ZPVE corrected ΔE for isomerization.

Figure 1a illustrates the basic arrangement of nuclei (not necessarily the *bonding*) for the fluorovinylidene anion and the $^3A'$ and $^3A''$ excited states of neutral fluorovinylidene. Optimized geometries and total energies for HFC=C:$^-$ determined at the SCF and CISD levels of theory using the DZP, DZP+diff, TZ2P, and TZ2P+diff basis sets are listed in Table V, and the corresponding harmonic frequencies are listed in Table VI. Table V also contains the DZP CCSD and DZP CCSD(T) optimized geometries and total energies for the fluorovinylidene anion. Adiabatic electron affinities [EA(HFC=C:)] predicted for $\tilde{X}\ ^1A'$ fluorovinylidene at various levels of theory are presented in Table VII, including results from single-point energies determined using open-shell coupled-cluster methods at CISD optimized geometries. The structure of $\tilde{X}\ ^1A'$ neutral fluorovinylidene was optimized at the SCF and CISD levels of theory using the DZP+diff and TZ2P+diff basis sets in order to obtain the corresponding EA values listed in Table VII. Harmonic vibrational frequencies for ground-state HFC=C: were also determined at similar levels of theory using the DZP+diff and TZ2P+diff basis sets in order to obtain consistent zero-point vibrational energies. The DZP+diff and TZ2P+diff vibrational frequencies and optimized structures for ground-state fluorovinylidene are not listed in this paper, but they are available upon request.

Total energies and optimized geometries for the $^3A'$ and $^3A''$ excited states of neutral fluorovinylidene determined at the SCF and CISD levels of theory with the DZP and TZ2P basis sets are given in Table VIII. Corresponding harmonic vibrational frequencies are listed in Table IX. Predictions for the relative energies of these two triplet states, including results from single-point energies determined using open-shell coupled-cluster methods at CISD optimized geometries, are presented in Table X.

Finally, Table XI compares harmonic vibrational frequencies for the fluorovinylidene anion and the $^3A'$, $^3A''$, and $\tilde{X}\ ^1A'$ states of neutral fluorovinylidene with similar frequencies for the corresponding isotopically-substituted *d*-fluorovinylidenes. The best possible set of frequencies obtained at a comparable level of theory (TZ2P CISD) for each of the four electronic states has been used in this comparison.

Discussion

Fluoroacetylene. Written in terms of C_{2v} symmetry orbitals, the electronic configuration of ground-state fluoroacetylene becomes

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 5a_1^2\ 6a_1^2\ [1b_1^2\ 1b_2^2]\ 7a_1^2[2b_1^2\ 2b_2^2]$$

The two pairs of molecular orbitals (MOs) enclosed by brackets

Table V. Total Energies (hartrees) and Optimized Geometries for $\tilde{X}\ ^2A'$ Fluorovinylidene Anion[a]

method	E_{total}	$r_e(C_1C_2)$	$r_e(C_1F_3)$	$r_e(C_1H_4)$	$\theta_e(F_3C_1C_2)$	$\theta_e(H_4C_1C_2)$
			DZP			
SCF	−175.654 02	1.3262	1.4153	1.0849	124.6	129.2
CISD	−176.042 19	1.3350	1.4427	1.0930	125.2	129.5
CCSD	−176.087 45	1.3442	1.4608	1.0987	125.4	129.8
CCSD(T)	−176.101 24	1.3487	1.4697	1.1007	125.6	129.9
			DZP+diff			
SCF	−175.667 75	1.3231	1.4082	1.0847	124.3	128.7
CISD	−176.062 72	1.3305	1.4370	1.0927	124.7	129.2
			TZ2P			
SCF	−175.686 38	1.3111	1.4105	1.0773	124.4	129.0
CISD	−176.144 56	1.3137	1.4396	1.0799	124.6	129.8
			TZ2P+diff			
SCF	−175.690 18	1.3113	1.4074	1.0777	124.3	128.8
CISD	−176.149 72	1.3136	1.4365	1.0804	124.5	129.6

[a] Bond lengths in angstroms and bond angles in degrees.

Table VI. Harmonic Vibrational Frequencies (cm^{-1}) for $\tilde{X}$ $^2A'$ Fluorovinylidene Anion

method	CH str	CC str	HCC bend	CF str	FCC bend	C_2 oop
			SCF			
DZP	3266	1654	1371	916	556	765
DZP+diff	3262	1656	1363	918	560	760
TZ2P	3252	1665	1370	896	564	785
TZ2P+diff	3253	1661	1366	898	564	773
			CISD			
DZP	3185	1592	1297	842	509	716
DZP+diff	3182	1602	1283	833	512	697
TZ2P	3191	1610	1294	811	517	737
exptl				710[a]	485[a]	

[a] Fundamental frequency, ref 21.

Table VII. Adiabatic Electron Affinities (eV) for $\tilde{X}$ $^1A'$ Fluorovinylidene[a]

method	EA(HFC=C:)[b]
DZP SCF	0.66 (0.68)
DZP CISD	0.95 (0.97)
DZP CISD+Q	0.99 (1.00)
DZP CCSD	1.02 (1.03)
DZP CCSD(T)	1.04 (1.05)
TZ2P SCF	0.78 (0.80)
TZ2P CISD	1.27 (1.28)
TZ2P CISD+Q	1.36 (1.38)
DZP+diff SCF	0.92 (0.95)
DZP+diff CISD	1.30 (1.32)
DZP+diff CISD+Q	1.37 (1.39)
TZ2P+diff SCF	0.86 (0.89)
TZ2P+diff CISD	1.37 (1.38)
TZ2P+diff CISD+Q	1.47 (1.49)
TZ2P+diff/CCSD//TZ2P+diff/CISD	1.53 (1.54)
TZ2P+diff/CCSD(T)//TZ2P+diff/CISD	1.60 (1.62)

[a] Numbers in parentheses include ZPVE corrections. With the exception of the TZ2P+diff basis (where TZ2P CISD ZPVEs have been used), CISD ZPVE corrections from the same basis set have been used for CISD+Q, CCSD, and CCSD(T) results. [b] Experimental value from photoelectron spectroscopy is EA(HFC=C:) = 1.718 eV, ref 21.

Table VIII. Total Energies (hartrees) and Optimized Geometries for the Low-Lying $^3A'$ and $^3A''$ States of Neutral Fluorovinylidene[a]

	SCF		CISD	
	DZP	TZ2P	DZP	TZ2P
		$^3A'$ State		
E_{total}	−175.602 61	−175.628 57	−175.965 85	−176.054 96
$r_e(C_1C_2)$	1.2989	1.2886	1.3156	1.2986
$r_e(C_1F_3)$	1.3292	1.3268	1.3479	1.3451
$r_e(C_1H_4)$	1.0773	1.0704	1.0850	1.0737
$\theta_e(F_3C_1C_2)$	122.9	122.8	122.9	122.6
$\theta_e(H_4C_1C_2)$	124.5	124.7	124.4	124.8
		$^3A''$ State		
E_{total}	−175.603 86	−175.630 75	−175.963 49	−176.053 75
$r_e(C_1C_2)$	1.4122	1.3985	1.4219	1.4038
$r_e(C_1F_3)$	1.3084	1.3021	1.3242	1.3169
$r_e(C_1H_4)$	1.0814	1.0751	1.0906	1.0790
$\theta_e(F_3C_1C_2)$	122.0	122.1	122.2	122.1
$\theta_e(H_4C_1C_2)$	126.4	126.1	126.9	126.8

[a] Bond lengths in angstroms and bond angles in degrees.

Table IX. Harmonic Vibrational Frequencies (cm^{-1}) for the Low-Lying $^3A'$ and $^3A''$ States of Neutral Fluorovinylidene

	SCF		CISD		
	DZP	TZ2P	DZP	TZ2P	Exptl
		$^3A'$ State			
CH stretch	3389	3373	3306	3299	
CC stretch	1833	1823	1720	1719	
HCC bend	1428	1433	1355	1358	
CF stretch	1196	1176	1128	1104	1100[a]
FCC bend	638	643	599	606	600[a]
C_2 oop bend	845	875	632	713	
		$^3A''$ State			
CH stretch	3349	3327	3257	3248	
CC stretch	1571	1563	1490	1481	
HCC bend	1372	1369	1304	1301	
CF stretch	1149	1149	1109	1104	
FCC bend	555	566	516	528	
C_2 oop bend	803	844	728	774	

[a] Fundamental frequency, ref 21.

Table X. Relative Energies (eV) of Low-Lying $^3A'$ and $^3A''$ States of Neutral Fluorovinylidene[a]

method	$T(^3A')$	$T(^3A'')$	$\Delta T(^3A'' - {}^3A')$
DZP SCF	0.74 (0.77)	0.71 (0.70)	−0.03 (−0.07)
DZP CISD	1.13 (1.15)	1.19 (1.19)	+0.06 (+0.04)
DZP CISD+Q	1.20 (1.22)	1.32 (1.32)	+0.12 (+0.10)
DZP/CCSD// DZP/CISD	1.19 (1.21)	1.35 (1.35)	+0.16 (+0.14)
DZP/CCSD(T)// DZP/CISD	1.20 (1.22)	1.40 (1.40)	+0.20 (+0.18)
TZ2P SCF	0.79 (0.82)	0.73 (0.73)	−0.06 (−0.09)
TZ2P CISD	1.17 (1.20)	1.20 (1.21)	+0.03 (+0.01)
TZ2P CISD+Q	1.26 (1.28)	1.33 (1.33)	+0.07 (+0.05)
TZ2P/CCSD// TZ2P/CISD	1.26 (1.28)	1.36 (1.36)	+0.10 (+0.08)
TZ2P/CCSD(T)// TZ2P/CISD	1.28 (1.30)	1.42 (1.42)	+0.14 (+0.12)
experimental[b]	(1.358)	(1.320)	(−0.038)

[a] Numbers in parentheses (T_0 values) include ZPVE corrections. Note that CISD ZPVE corrections from the same basis set were used with CISD+Q, CCSD, and CCSD(T) results. [b] Experimental T_0 results, ref 21.

Table XI. TZ2P CISD Harmonic Vibrational Frequencies (cm^{-1}) for Various Anionic and Neutral Electronic States of the HFCC (Fluorovinylidene) and DFCC (*d*-Fluorovinylidene) Isotopomers

	CH str	CC str	HCC bend	CF str	FCC bend	C_2 oop
			$\tilde{X}$ $^2A'$ Anion			
HFCC	3191	1610	1294	811	517	737
DFCC	2360	1578	949	806	512	619
			$\tilde{X}$ $^1A'$ Neutral			
HFCC	3243	1786	1217	1064	333	778
DFCC	2387	1759	1100	875	328	662
			$^3A'$ Neutral			
HFCC	3299	1719	1358	1104	606	713
DFCC	2439	1697	992	1097	599	600
			$^3A''$ Neutral			
HFCC	3248	1481	1301	1104	528	774
DFCC	2394	1423	1099	979	521	648

correspond to the two π_u orbitals. In other words, the $2b_1$ and the $2b_2$ (C_{2v} symmetry) MOs together form the doubly-degenerate $2\pi_u$ ($C_{\infty v}$ symmetry) MO.

Tyler and Sheridan[26] estimate that their r_s values for bond lengths should be within 0.002 Å of the equilibrium values. Candidly, we suspect that such small differences between r_s and r_e structures are, in general, overly optimistic. The TZ2P CCSD(T) optimized geometry reported in Table I represents our best prediction for the equilibrium structure of fluoroacetylene. It is in good agreement with the experimentally determined structure. At this level of theory, the $r_e(C_1C_2)$, $r_e(C_1F_3)$, and $r_e(C_2H_4)$ bond distances are predicted to be longer than the corresponding r_s values by 0.004, 0.011, and 0.008 Å, respectively. The agreement is poorest for the CF bond distance; however, determination of the experimental r_s value for the CF bond distance required special considerations[26] due to the lack of a second fluorine isotope. Our best equilibrium structure for fluoroacetylene is actually in better agreement with an alternate structure determined by Tyler and Sheridan using the second difference method [$r_s(C_1C_2)$ = 1.203 Å, $r_s(C_1F_3)$ = 1.284 Å, and $r_s(C_2H_4)$ = 1.058 Å]. A comparison of TZ2P CCSD(T) bond lengths with those predicted at the DZP CCSD(T) and TZ2P CCSD levels of theory shows that the CF bond distance is perhaps less sensitive to improvements in basis set and treatment of electron correlation than the CC and CH bond distances.

Theoretical and experimental[27] harmonic vibrational frequencies for fluoroacetylene show very good agreement. Although not listed in Table II, the following TZ2P CCSD(T) harmonic frequencies have been predicted as part of a separate, systematic study[47] of the CCSD(T) method: 3460 (CH stretch), 2244 (CC stretch), 1038 (CF stretch), 539 (HCC linear bend), and 320 $\mathrm{cm^{-1}}$ (FCC linear bend). As suggested above, these values are quite similar to the DZP CCSD(T) values in Table II. It should be noted that TZ2P results for the fluoroacetylene CC, CF, and CH stretches are all slightly smaller than the corresponding DZP values at a given level of theory. The predicted values for the two linear bending modes, however, *increase* in magnitude when switching to the larger TZ2P basis.

All of the predicted CCSD(T) frequencies for fluoroacetylene are smaller than the respective experimental values. Typically, ab initio results approach experimental values from above as progressively larger basis sets and more sophisticated correlated methods are employed.[48] The percentage errors for the TZ2P CCSD(T) values of the HCC and FCC linear bends are particularly large (−9.7% and −14.7%, respectively) compared to the CH stretch (−1.1%), the CC stretch (−1.8%), and the CF stretch (−3.5%). Theoretical harmonic frequencies for HCC linear bends in acetylene[48,49] show similar behavior. It has been reported elsewhere[49,50] that addition of higher-order polarization functions to a TZ2P basis (f-type functions on heavy atoms and perhaps d-type functions on hydrogen atoms) will bring theoretically predicted linear bend frequencies for π-bonded molecules into better agreement with experimental harmonic frequencies. In addition, including the carbon and fluorine core electrons and all SCF virtual MOs in the correlation procedure causes a slight increase (more pronounced for the HCC and FCC linear bends)[48] in the CCSD and CCSD(T) frequencies predicted for fluoroacetylene, thus giving better agreement with experiment.

Fluorovinylidene. $\tilde{X}\ ^1A'$ fluorovinylidene has the following electronic configuration

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 1a''^2\ 8a'^2\ 9a'^2\ 2a''^2$$

The highest occupied molecular orbital (HOMO) is the 2a″ π-orbital. It has a single node between the fluorine atom and the carbon atoms. Along with the 5a′ σ-bonding MO, the 2a″ HOMO forms the expected CC double bond. The second-highest occupied molecular orbital (SHOMO) is the 9a′ lone pair of the terminal (carbene) carbon. The 10a′ MO is the lowest unoccupied molecular orbital (LUMO).

The TZ2P CCSD(T) optimized geometry reported in Table I is presumably the best equilibrium structure for this unsaturated carbene. The theoretically predicted CF bond distance for ground-state fluorovinylidene [$r_e(\mathrm{C_1F_3})$ = 1.3409 Å at the TZ2P CCSD(T) level of theory], perhaps not surprisingly, proves to be very similar to an experimental CF bond distance [$r_0(\mathrm{CF})$ = 1.338 Å] reported for monofluoroformaldehyde.[51]

It should be noted that fluorination usually causes a *shortening* of the other bonds in a molecule.[52] In the case of fluoroacetylene, this certainly holds true. For example, comparison of the DZP CISD structure for fluoroacetylene found in Table I with comparable DZP CISD results [$r_e(\mathrm{CC})$ = 1.2131 Å and $r_e(\mathrm{CH})$ = 1.0691 Å] reported previously[4] for acetylene shows that fluorination shortens the CC triple bond by 0.014 Å and shortens the CH single bond slightly by 0.005 Å. In the case of the unsaturated carbene isomers, however, the *opposite* trend is observed for theoretical bond lengths. A similar comparison of the DZP CISD structure for fluorovinylidene with comparable DZP CISD results reported for vinylidene[4] [$r_e(\mathrm{CC})$ = 1.3159 Å, $r_e(\mathrm{CH})$ = 1.0879 Å, $\theta_e(\mathrm{HCC})$ = 120.2°] shows that fluorination causes an unexpected and significant *lengthening* of the CC bond distance by 0.018 Å. The CH bond distance in fluorovinylidene is almost unchanged (+0.003 Å). The predicted values of $\theta_e(\mathrm{H_4C_1C_2})$ and $\theta_e(\mathrm{F_3C_1C_2})$ for fluorovinylidene are about 5° smaller and about 8° larger, respectively, than the value of $\theta_e(\mathrm{HCC})$ predicted for vinylidene.

The smallest harmonic vibrational frequency for $\tilde{X}\ ^1A'$ fluorovinylidene (~300 $\mathrm{cm^{-1}}$) corresponds to the reaction coordinate for 1,2-hydrogen migration. It has been assigned as the FCC bend in Table II. Isotopic shifts for fluorovinylidene frequencies upon deuteration (see Table XI) and potential energy distributions (PEDs) in terms of internal coordinates for theoretical harmonic frequencies both clearly indicate that this frequency has been properly assigned as the FCC bend. It might be expected that the reaction coordinate for hydrogen migration should be the HCC bend. In fact, the so-called FCC bend *does* involve motion of the hydrogen atom. The plotted results of our normal coordinate analyses of analytic SCF second derivatives include FCC bend and HCC bend normal modes that are essentially identical to those appearing in the preceding paper.[21] The key difference between these two vibrational modes is that only the FCC bend permits the simultaneous motion of the hydrogen atom toward a bridging position between the two carbon atoms *and* bending of the FCC bond angle toward linearity. Thus, the FCC bend is clearly the fluorovinylidene analog of the vinylidene $\mathrm{CH_2}$ rock, while the HCC bend is analogous to the vinylidene $\mathrm{CH_2}$ scissors.

The agreement between experimentally observed fluorovinylidene fundamental frequencies and theoretically predicted harmonic frequencies is good. The DZP CCSD(T) frequencies presented in Table II are expected to be the most reliable for $\tilde{X}\ ^1A'$ fluorovinylidene. Although the value of 296 $\mathrm{cm^{-1}}$ predicted for the FCC bend at this level of theory appears quite large compared to the value of 205 $\mathrm{cm^{-1}}$ obtained from negative ion photodetachment spectroscopy by Gilles et al.[21] (the percentage error is +44.4%), it should be kept in mind that this vibrational mode is expected to be extremely anharmonic due to the shallowness of the potential energy well. Therefore, it is not surprising or cause for alarm that a theoretical *harmonic* frequency for the FCC bend may deviate from the experimental *fundamental* frequency by such a large margin. A similar situation exists in the case of vinylidene, where the best harmonic frequency (386 $\mathrm{cm^{-1}}$ at the TZ2P CCSD level of theory) predicted by Gallo et al.[4] for the extremely anharmonic $\mathrm{CH_2}$ rock exceeded the observed 320 $\mathrm{cm^{-1}}$ fundamental[20] by 21%. A proper anharmonic quantum mechanical study of the lowest vibrational levels of vinylidene and fluorovinylidene would be quite useful in this regard.

Although the predicted value of the FCC bend frequency decreases with the use of more sophisticated theoretical methods and the larger TZ2P basis set, it shows no sign of becoming imaginary. Therefore, we conclude that the fluorovinylidene stationary point is a shallow minimum on the $\mathrm{C_2HF}$ singlet ground-state potential energy surface.

Fluorovinylidene–Fluoroacetylene Isomerization. The transition state for unimolecular fluorovinylidene–fluoroacetylene isomerization via 1,2-hydrogen migration belongs to the C_s point group. It therefore has the same MO occupation scheme as $\tilde{X}\ ^1A'$ fluorovinylidene.

A close examination of the structures presented in Table I reveals that improved treatment of electron correlation leads to the prediction of a progressively "earlier" transition state for isomerization of fluorovinylidene to fluoroacetylene. In other words, as increasingly sophisticated correlated methods are employed, the geometric parameters of the transition state for 1,2-hydrogen migration become closer to those of fluorovinylidene and less like those of fluoroacetylene. The redundant geometric parameter $r_e(\mathrm{C_2H_4})$ has been included in Table I for the transition

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[47] DeLeeuw, B. J., unpublished results.

[48] Thomas, J. R.; DeLeeuw, B. J.; Vacek, G.; Crawford, T. D.; Yamaguchi, Y.; Schaefer, H. F., to be published.

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state to more clearly illustrate this trend. Note that $\theta_e(F_3C_1C_2)$ in the transition state is essentially linear (~175°) at the SCF level of theory. The CCSD(T) method, on the other hand, predicts a value of about 160° for $\theta_e(F_3C_1C_2)$. Similarly, the SCF method predicts a value of $r_e(C_1C_2)$ for the transition state that is slightly closer to the fluoroacetylene CC triple bond distance than to the fluorovinylidene CC double bond distance. At the CCSD(T) level of theory, however, the $r_e(C_1C_2)$ bond distance for the transition state has lengthened considerably and is much closer to that of fluorovinylidene. In the case of vinylidene ($H_2C{=}C$:), results reported previously by Gallo et al.[4] show similar changes in the structure of the 1,2-hydrogen shift transition state at progressively higher levels of theory.

Tables III and IV show that isomerization of fluorovinylidene to fluoroacetylene is an exothermic process with a very small barrier for 1,2-hydrogen migration. At the CCSD(T) level of theory, a classical barrier of 2.4 kcal mol^{-1} is predicted with both the DZP and TZ2P basis sets. The apparent insensitivity of this barrier height to basis set improvements contrasts with the basis set dependence observed for that of vinylidene ($H_2C{=}C$:), the parent carbene. For example, the classical barrier heights predicted for vinylidene–acetylene isomerization at the TZ2P CISD and TZ2P CCSD levels of theory decreased by 0.5 kcal mol^{-1} relative to the corresponding DZP values.[4]

Gilles et al.[21] have modeled the FCC bend as a Morse oscillator in Franck–Condon simulations of their observed negative ion photoelectron spectrum and report a well depth (D_e) of 0.09 eV, or 2.0 kcal mol^{-1}. Classical barriers of 1.6–2.3 kcal mol^{-1} all gave reasonable fits to their observed spectrum. These results are thus in excellent agreement with our best theoretical prediction.

The ZPVE correction used in Table III omits the single imaginary frequency of the 1,2-hydrogen migration transition state. We predict a value of −1.6 kcal mol^{-1} for the ZPVE correction to the barrier height based upon DZP CCSD(T) harmonic frequencies. In conjunction with the TZ2P CCSD(T) value for the classical barrier height, this gives a ZPVE corrected barrier of only 0.8 kcal mol^{-1} for hydrogen migration. Although this barrier is almost negligible, the results presented in Table III seem to imply that neither the classical nor the ZPVE corrected barrier will ever disappear entirely. This statement might be greeted with some skepticism. It is conceivable that the use of still larger basis sets might alter the predicted classical barrier height. It should be noted, however, that use of the larger TZ2P basis slightly *raises* the CISD and CCSD classical barriers. Because Table III shows so little difference between DZP and TZ2P results at correlated levels of theory, it is expected that switching to a QZ3P basis set would probably not significantly alter our results. The effect of adding higher angular momentum polarization functions might be significant and could be tested using a TZ2P+f basis. In our opinion, however, it is not necessary to go to this extreme at the present time. On the basis of Franck–Condon simulations, Gilles et al.[4] have assigned some vibrational structure as transitions to excited vibrational levels of the FCC bend (perhaps as high as $v = 4$) in $\tilde{X}\ ^1A'$ fluorovinylidene. Such assignments, if correct, clearly indicate the presence of a ZPVE corrected barrier for hydrogen migration and render discussion of basis set effects a less significant point.

The results listed in Table IV show that the value of ΔE predicted for fluorovinylidene–fluoroacetylene isomerization tends to increase with improvements in the basis set and the theoretical method employed. The SCF results are noticeably smaller than those determined at correlated levels of theory. Our best estimate for ΔE (~43.9 kcal mol^{-1}) is based upon TZ2P CCSD(T) total energies and a ZPVE correction estimated from the DZP CCSD(T) harmonic vibrational frequencies for fluorovinylidene and fluoroacetylene.

A comparison of Tables III and IV with comparable results reported for vinylidene[4] ($H_2C{=}C$:) reveals the effect of fluorination upon the energetics of the isomerization process. Our best prediction of ~2.4 kcal mol^{-1} for the barrier height against hydrogen migration in fluorovinylidene (HFC=C:) is slightly lower than the value of ~3 kcal mol^{-1} reported[4] for vinylidene ($H_2C{=}C$:). The effect of fluorination upon ΔE also appears to be small, increasing the value for fluorovinylidene–fluoroacetylene isomerization by about 1 kcal mol^{-1} relative to the value reported for C_2H_2.

Fluorovinylidene Anion. The electronic configuration of $\tilde{X}\ ^2A'$ fluorovinylidene anion differs from that of neutral $\tilde{X}\ ^1A'$ fluorovinylidene by the addition of a single electron to the 10a′ LUMO

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 1a''^2\ 8a'^2\ 9a'^2\ 2a''^2\ 10a'$$

In neutral $\tilde{X}\ ^1A'$ fluorovinylidene, the 10a′ LUMO is essentially a 2p-like orbital perpendicular to the CC bond axis and centered on the carbene carbon; however, some antibonding character exists between this 2p portion and the hydrogen and fluorine atoms. A comparison of equilibrium structures (see Tables I and V) shows a lengthening of the CF bond by about 0.12 Å and an increase of the HCC bond angle by about 15.0° in the anion relative to the neutral ground state. The increased CF bond distance and HCC bond angle in the anion are apparently due to antibonding interactions that result when an electron is added to the 10a′ MO. The longer CF bond distance predicted for the anion is accompanied by a CF stretch frequency that is about 240 cm^{-1} less than the corresponding value in the neutral ground state. The HCC bending frequency increases in the anion by roughly 80 cm^{-1}. Note that the CC stretching frequency decreases by about 200 cm^{-1}, even though the CC bond distance has also decreased slightly.

Note that the fluorovinylidene anion's FCC bend frequency increases by 160 cm^{-1} relative to neutral $\tilde{X}\ ^1A'$ fluorovinylidene. This is perhaps indicative of an increase in the barrier against hydrogen migration; however, this upward shift is much smaller than the ~520-cm^{-1} increase predicted[18] for the CH_2 rock in $\tilde{X}\ ^2B_2$ vinylidene anion. A more complete theoretical study of the C_2HF^- potential energy surface to determine the barrier heights for hydrogen (and perhaps fluorine) migration might be of interest.

The agreement of theoretical harmonic frequencies with the available experimental fundamental frequencies is reasonable. The TZ2P CISD values for the CF stretch (811 cm^{-1}) and FCC bend (517 cm^{-1}) differ from experimental results by +14.2% and +6.6%, respectively. Both of these errors are higher than is usually expected for the TZ2P CISD methodology,[48] but not greatly so. No TZ2P+diff CISD harmonic frequencies were determined for the anion. The effect of adding diffuse functions to the less flexible DZP basis sets is expected to be greater than the effect of adding diffuse functions to the larger TZ2P basis,[33] and there is little difference between the DZP CISD and DZP+diff CISD vibrational frequencies in Table VI. The TZ2P CISD frequencies for the fluorovinylidene anion are therefore considered to be reasonably accurate predictions.

Adiabatic Electron Affinity of Ground-State Fluorovinylidene. As noted above, the use of basis sets with added diffuse functions produced surprisingly little change in the structure or frequencies predicted for the fluorovinylidene anion. This is not necessarily true of other properties. In particular, Table VII clearly shows that an accurate value for the adiabatic electron affinity cannot be obtained without basis sets containing diffuse functions. Electron correlation effects are obviously very important as well. The SCF results found in Table VII are all quite poor. Even with the TZ2P+diff basis, SCF theory produces an adiabatic electron affinity that is too small by a factor of 2. Use of the CISD method gives greatly improved values for EA(HFC=C:). The Davidson-corrected CISD+Q results represent a further slight improvement. Even with the TZ2P+diff basis, however, CISD+Q energies give a value (1.47 eV) that is smaller than the experimentally observed value[21] [EA(HFC=C:) = 1.718 eV] by 14%.

At the TZ2P+diff/CCSD(T)//TZ2P+diff/CISD level of theory, we obtain a "best" equilibrium value of 1.60 eV for EA(HFC=C:). The effect of using CISD optimized geometries for the anion and the neutral ground state is expected to be quite small. Using available TZ2P CISD harmonic frequencies (see Tables II and VI), we obtain a small ZPVE correction of about +0.02 eV. Therefore, our best estimate of EA(HFC=C:) is 1.62 eV. This result deviates from the experimental value by less than 0.1 eV, or about 6%. This represents outstanding agreement for a theoretically predicted electron affinity.[53] Accurately predicting EA(HFC=C:) appears to be a much more straightforward problem than determining the corresponding value for vinylidene. Even when basis sets containing diffuse functions are employed, SCF values for EA(H_2C=C:) are often *qualitatively* incorrect.[16-18]

The use of CCSD and CCSD(T) single-point energies gives values of EA(HFC=C:) that are significantly better than CISD or CISD+Q results. This can probably be explained by the fact that CCSD wave functions include contributions from unlinked higher-order excitations that are excluded from the corresponding CISD expansion.[40] It should be noted that truncated coupled-cluster methods are not variational, so the CCSD and CCSD(T) total energies are *not* guaranteed to be upper bounds to the true energy. This should not be a serious drawback for determination of a relative energy such as EA(HFC=C:), because relative energies are nonvariational irrespective of the theoretical method employed.

Low-Lying Triplet States of Fluorovinylidene. The $^3A'$ state of fluorovinylidene analogous to $\tilde{a}\ ^3B_2$ vinylidene has the following electronic configuration

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 1a''^2\ 8a'^2\ 9a'\ 2a''^2\ 10a'$$

It differs from that of $\tilde{X}\ ^1A'$ fluorovinylidene by excitation of an electron from the 9a′ SHOMO to the 10a′ LUMO. This $^3A'$ excited state of neutral fluorovinylidene is expected to be quite low-lying in energy and is considered to have a CC double bond.

As noted above, the 10a′ MO is essentially a 2p-like orbital perpendicular to the CC bond axis and centered on the carbene carbon that has antibonding interactions with the hydrogen and fluorine atoms. TZ2P CISD results (see Tables I and VIII) show that $r_e(C_1F_3)$ has lengthened by 0.019 Å in the $^3A'$ state relative to the ground state. This is much less than the lengthening of the CF bond in the fluorovinylidene anion due to the singly-occupied 10a′ MO. In addition, $\theta_e(H_4C_1C_2)$ increases by 10°, $\theta_e(F_3C_1C_2)$ decreases by 5.4°, $r_e(C_1H_4)$ shortens by 0.007 Å, and $r_e(C_1C_2)$ shortens by 0.017 Å.

The TZ2P CISD harmonic frequency for the FCC bend is 606 cm^{-1}. Note that it has increased by 273 cm^{-1} relative to the value of 333 cm^{-1} predicted for the FCC bend in the ground state at the same level of theory. In the preceding paper,[21] Gilles et al. report observation of vibrational structure due to this $^3A'$ state of fluorovinylidene in the 351-nm negative ion photoelectron spectrum of HFC=C:⁻. Although the harmonic 1104-cm^{-1} CF stretching and 606-cm^{-1} FCC bending frequencies predicted at the TZ2P CISD level of theory for the $^3A'$ state appear a bit small compared to the experimentally observed[21] 1100-cm^{-1} (CF stretch) and 600-cm^{-1} (FCC bend) fundamentals, the agreement still seems to be fairly good.

The $^3A''$ state of fluorovinylidene that corresponds to the $\tilde{b}\ ^3A_2$ state of vinylidene has the following electronic configuration

$$1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 6a'^2\ 7a'^2\ 1a''^2\ 8a'^2\ 9a'^2\ 2a''\ 10a'$$

It differs from that of $\tilde{X}\ ^1A'$ fluorovinylidene by excitation of an electron from the 2a″ HOMO to the 10a′ LUMO. This $^3A'$ excited state of neutral fluorovinylidene is also expected to be quite low-lying. Because the 2a″ HOMO is only singly-occupied, the CC bond is expected to have a bond order of $^3/_2$.

As discussed above, singly-occupying the 10a′ LUMO is expected to favor an increase in the $r_e(C_1F_3)$ bond length and the $\theta_e(H_4C_1C_2)$ bond angle relative to the ground-state structure. However, the 2a″ HOMO is a π-orbital delocalized over the fluorine and carbon atoms with a single node between F_3 and C_1. Therefore, it is expected that removal of an electron from the 2a″ HOMO will tend to cause the $r_e(C_1F_3)$ bond length to decrease and the $r_e(C_1C_2)$ bond length to increase relative to the ground-state structure. In fact, comparison of TZ2P CISD structures for the ground state and the $^3A''$ state of fluorovinylidene (see Tables I and VIII) shows that $r_e(C_1F_3)$ actually shortens slightly by about 0.01 Å and $r_e(C_1C_2)$ lengthens by about 0.09 Å. In addition, $\theta_e(H_4C_1C_2)$ increases by about 12°, $\theta_e(F_3C_1C_2)$ decreases by 6°, and $r_e(C_1H_4)$ shortens very slightly. With the exception of the CC stretch, the harmonic vibrational frequencies predicted for the $^3A''$ state of fluorovinylidene are very similar to those predicted for the $^3A'$ state. Removal of an electron from the 2a″ orbital weakens the C_1C_2 π-bond. Therefore, the frequency for the CC stretch is ~240 cm^{-1} lower in the $^3A''$ state than in the $^3A'$ state.

Singlet–Triplet Splittings. Theoretically predicted values for the relative energies of the $^3A'$ and $^3A''$ states of fluorovinylidene are listed in Table X. In the case of vinylidene, negative ion photodetachment spectroscopy[20] has shown that the analogous $\tilde{a}\ ^3B_2$ (T_0 = 2.065 eV) and $\tilde{b}\ ^3A_2$ (T_0 = 2.754 eV) states are separated by about 0.7 eV. The results in Table X clearly show that fluorination has *decreased* the splitting between the ground state and the two lowest excited states. Furthermore, the $^3A'$ and $^3A''$ states of fluorovinylidene are predicted to lie *much* closer together in energy than the corresponding triplet states of vinylidene. At the TZ2P/CCSD(T)//TZ2P/CISD level of theory, we have predicted T_e = 1.276 eV for the $^3A'$ state, T_e = 1.422 eV for the $^3A''$ state, and $\Delta T_e(^3A'' - {}^3A')$ = +0.146 eV. If the TZ2P CISD harmonic frequencies reported in Tables II and IX are used to estimate differences in zero-point vibrational energies, corrections of +0.023 eV for the $^3A'$ state and +0.001 eV for the $^3A''$ state are obtained. Therefore, our best estimates for the relative energies of these two states are T_0 = 1.30 eV for the $^3A'$ state, T_0 = 1.42 eV for the $^3A''$ state, and $\Delta T_0(^3A'' - {}^3A')$ = +0.12 eV.

In the preceding paper,[21] Gilles et al. have reported the *opposite* ordering of states on the basis of the results of negative ion photodetachment spectroscopy. Specifically, they report experimental values of T_0 = 1.358 eV for the $^3A'$ state, T_0 = 1.320 eV for the $^3A''$ state, $\Delta T_0(^3A'' - {}^3A')$ = −0.038 eV. The assignment of the $^3A'$ origin made by Gilles et al. is strongly supported by measurements of the asymmetry parameter for that peak. Our value of T_0 for the $^3A'$ state is in excellent agreement with the experimentally determined value. A very low intensity peak has been assigned[21] as the $^3A''$ origin. Assuming that this assignment is correct, it will be a truly formidable task for ab initio methods to correctly predict the ordering of the $^3A'$ and $^3A''$ states of fluorovinylidene with an experimental triplet–triplet splitting of only 0.038 eV.

Interestingly, our best estimate of $\Delta T_0(^3A'' - {}^3A')$ would place the origin for the $^3A''$ state almost directly *beneath* the $^3A'$ state $1 \leftarrow 0$ CF stretch peak.[21] Assuming that vibrational structure due to the $^3A''$ state is considerably less intense than peaks due to the $^3A'$ state, the $^3A''$ state origin and other features from the $^3A''$ state *might* be hidden by stronger $^3A'$ state peaks. This alternate interpretation of the negative ion photoelectron spectrum appears to be incomplete in that it can offer no explanation for the peak assigned by Gilles et al.[21] as the $^3A''$ origin.

It should be noted that SCF theory finds that the $^3A''$ state is lower in energy than the $^3A'$ state. When correlated methods are employed, however, the predicted ordering of these two states *reverses*. Improved treatment of electron correlation effects steadily lowers the $^3A'$ state relative to the $^3A''$ state. This tends to support our finding that the lowest triplet state is the $^3A'$ state. Improving the basis set quality from DZP to TZ2P lowers the $^3A''$ state relative to the $^3A'$ state. Optimizing the structures of these two triplet states at the CCSD and CCSD(T) levels of theory, a tedious process without analytic gradients, is not expected to give relative energies that differ greatly from our single-point energy results. Since the triplet–triplet splitting is extremely small (~0.1 eV), we cannot unequivocally rule out the possibility that optimizing the geometries of the $^3A''$ and $^3A'$ states of fluorovinylidene using more sophisticated theoretical methods in conjunction with a TZ2P+f (or larger) basis set would reverse the ordering of states predicted here.

Concluding Remarks

Optimized geometries, harmonic vibrational frequencies, and relative energies have been predicted for several isomers of singlet

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ground-state C_2HF. Fluorination appears to have little effect upon the predicted ΔE for isomerization from unsaturated carbene to alkyne. The ZPVE corrected value of $\Delta E = \sim 44$ kcal mol^{-1} for C_2HF is about 1 kcal mol^{-1} larger than the value reported for the unfluorinated system. Stabilization of the transition state for 1,2-hydrogen migration by fluorination is apparent in a slight (~ 1 kcal mol^{-1}) lowering of the classical barrier height to 2.4 kcal mol^{-1}. A very small activation energy for hydrogen migration (~ 0.8 kcal mol^{-1}) is predicted after a correction for differences in zero-point vibrational energies has been made.

Optimized geometries, harmonic vibrational frequencies, and relative energies have also been predicted for $\tilde{X}\ ^2A'$ fluorovinylidene anion and two low-lying excited states ($^3A'$ and $^3A''$) of neutral fluorovinylidene. The 10a′ MO is singly-occupied in each of these three states. The adiabatic electron affinity of fluorovinylidene predicted here [EA($HFC{=}C$:) = 1.62 eV] is in excellent agreement with the experimentally reported[21] value of EA($HFC{=}C$:) = 1.718 eV. Note that EA($HFC{=}C$:) is more than 1.2 eV *larger* than the experimentally reported[20] value for vinylidene [EA($H_2C{=}C$:) = 0.49 eV]. This indicates that fluorination has stabilized the anion relative to the neutral ground state. Furthermore, the $^3A'$ and $^3A''$ excited states of neutral fluorovinylidene are much lower-lying (~ 0.8 eV) than the corresponding $\tilde{a}\ ^3B_2$ and $\tilde{b}\ ^3A_2$ excited states of vinylidene.[21] A close examination of SCF molecular orbital eigenvalues for $\tilde{X}\ ^1A'$ fluorovinylidene and $\tilde{X}\ ^1A_1$ vinylidene reveals that the $HFC{=}C$: 10a′ LUMO lies lower in energy than the corresponding $H_2C{=}C$: 2b$_2$ LUMO. This suggests that electronic states of fluorovinylidene with the 10a′ MO singly-occupied should lie lower in energy than the corresponding states of vinylidene with the 2b$_2$ MO singly-occupied.

The $^3A'$ and $^3A''$ excited states of fluorovinylidene are predicted to be nearly isoenergetic [$\Delta T_0(^3A'' - {}^3A') = +0.12$ eV]. Recall that the $^3A'$ state arises from the LUMO ← SHOMO excitation and the $^3A''$ state arises from the LUMO ← HOMO excitation. The SCF molecular orbital eigenvalues for the fluorovinylidene 2a″ HOMO and the vinylidene 1b$_1$ HOMO show that fluorination does not significantly alter the energy of the CC π-bonding orbital. However, the 9a′ $HFC{=}C$: carbene lone-pair SHOMO lies *lower* in energy than the analogous 5a$_1$ $H_2C{=}C$: carbene lone-pair SHOMO. This suggests that the $^3A'$ and $^3A''$ states of fluorovinylidene should lie *closer* in energy than the corresponding $\tilde{a}$ $^3B_2$ and $\tilde{b}\ ^3A_2$ states of vinylidene because fluorination has made the LUMO ← SHOMO excitation less favorable.

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Bonding and Dynamics of the $ThCr_2Si_2$ and $CaBe_2Ge_2$ Type Main Group Solids: A Monte Carlo Simulation Study

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Abstract: A Monte Carlo simulation study based on the extended-Hückel tight-binding method was carried out to examine the thermodynamic properties of the $ThCr_2Si_2$ and $CaBe_2Ge_2$ type main group solids. At room temperature, the $ThCr_2Si_2$ structure is more stable owing to a less dispersed filled band and a lower Fermi level. Weaker bonding also counts for the larger atomic thermal motion in layers D of the $CaBe_2Ge_2$ structure. At higher temperatures, the entropic contribution will become more important and thus can favor the $CaBe_2Ge_2$ type. The free-energy difference at room temperature between these structures was calculated using the free-energy perturbation technique. The calculations indicate that the $ThCr_2Si_2$ type has not only lower energy, but also lower free energy. At high temperatures, however, the $CaBe_2Ge_2$ type can be the more stable structure.

Introduction

The $ThCr_2Si_2$ type family comprises more than 400 compounds.[1] It has attracted much attention because many of the solids show a variety of novel physical properties, such as superconductivity,[2] unique magnetic behavior, valence fluctuation, and heavy fermion phenomenon.[3] Some of these members also have intriguing chemical and structural properties. For example, they can transform from the $ThCr_2Si_2$ type to the closely related $CaBe_2Ge_2$ structure at a temperature range of 1000–1700 °C.

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