of the interannular proton-transfer rate constants.[7,17,29]

By contrast, the time resolution of the radiolytic technique has extended the range of measurable rate constants up to at least 10^8 s^{-1}. Even more importantly the processes investigated are truly thermal reactions, occurring at a defined temperature and obeying standard thermal kinetics. This not only allows evaluation of Arrhenius activation parameters but also confers the results with a much higher degree of generality, making them legitimately comparable with the corresponding processes occurring in solution.

As a closing remark, it is worth noting that the radiolytic results fully support the conclusions of a recent mass spectrometric study pointing to the formation of stable ion–neutral complexes in the reaction of Me$_3$C$^+$ with α,ω-diphenylalkanes.[14a]

(29) A rate $\gg 10^6$ s^{-1} follows from the complete equilibration of 16 or even 21 protons in protonated oligophenylalkanes: Kuck, D.; Fastabeud, U. *Adv. Mass Spectrom.* **1989**, *11A*, 904.

Photoelectron Spectroscopy of the Monofluorovinylidene and Difluorovinylidene Anions: The Monofluorovinylidene–Fluoroacetylene Rearrangement

Mary K. Gilles,† W. C. Lineberger,*,† and Kent M. Ervin‡

Contribution from the Joint Institute for Laboratory Astrophysics of the University of Colorado and National Institute of Standards and Technology, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440, and Department of Chemistry and Chemical Physics Program, University of Nevada, Reno, Nevada 89557. Received August 21, 1992

Abstract: The 351.1-nm photoelectron spectra of HFC=C:$^-$ and F$_2$C=C:$^-$ are reported. Transitions from the anion ground state to the neutral singlet ground state and low-lying triplet states are observed. The electron affinity of difluorovinylidene is 2.255 (6) eV, and the triplet term energy is $T_0(\tilde{a}\ ^3A_2\ F_2CC) = 0.924$ (9) eV. In the singlet state of F$_2$C=C:, vibrational progressions are observed at 510 (25), 905 (25), and 1670 (25) cm^{-1}. Vibrational frequencies of 505 (25) and 800 (35) cm^{-1} are observed in the difluorovinylidene anion. The adiabatic electron affinity of monofluorovinylidene is 1.718 (6) eV, and the triplet term energies are $T_0(\tilde{a}\ ^3A''\ \text{HFCC}) = 1.320$ (9) eV and $T_0(\tilde{b}\ ^3A'\ \text{HFCC}) = 1.358$ (9) eV. Vibrational fundamentals are observed at 205 (30), 960 (30), and 1680 (30) cm^{-1} in the $\tilde{X}\ ^1A'$ state of HFC=C:, at 600 (50) and 1100 (100) cm^{-1} in the $\tilde{b}\ ^3A'$ state, and at 485 (30) and 710 (35) cm^{-1} in the negative ion ($\tilde{X}\ ^2A'$). Ab initio calculations indicate that the normal mode primarily involved in the hydrogen migration to form fluoroacetylene from monofluorovinylidene is the CCF bending mode. By modeling the observed CCF bending mode as an anharmonic oscillator, we estimate the hydrogen isomerization barrier height to be 2 ± 1 kcal/mol.

Introduction

Negative ion photodetachment spectroscopy has been used in several ways to probe transition states and unstable species. The transition states of the hydrogen abstraction reactions X + HY (X = F, Cl, Br, Y = Cl, Br, I) have been probed by photodetachment of XHY$^-$ species by Bradforth et al.[1] and Metz et al.[2] Moylan et al.[3] measured the photodetachment threshold of several ROHY species (R = C$_6$H$_5$CH$_2$ and CH$_3$, Y = F$^-$ and OCH$_3^-$) to determine the well depth for proton transfer between RO$^-$ and HY using a thermochemical cycle. An early study of the vinylidene anion revealed vibrational structure in the photoelectron spectrum of singlet vinylidene, which readily isomerizes to acetylene.[4] In a more recent study from this laboratory,[5] photodetachment of the vinylidene anion accessed the very shallow well of the ground neutral state of vinylidene, and information about the rearrangement barrier was obtained from the analysis of the vibrational structure in the spectrum. The lifetime of the $\tilde{X}\ ^1A_1$ state of vinylidene against rearrangement was found to be 0.04–0.2 ps.

In this study the photodetachment spectra of monofluorovinylidene (HFC=C:$^-$) and difluorovinylidene (F$_2$C=C:$^-$) anions are reported. Figure 1 shows schematic molecular orbital diagrams for the electronic states of the vinylidenes with symmetry labels.

Since difluorovinylidene and vinylidene are both C_{2v}, they have the same symmetry labels; the symmetry labels for monofluorovinylidene (C_s) are slightly different. The singlet states arise from detachment of an electron from the in-plane terminal carbon p (b$_2$) orbital of the anions. There are two low-lying triplet states. The $^3B_2$ ($^3A'$) states arise from photodetachment from the carbon lone-pair (a$_1$) orbital of the anion. The $^3A_2$ ($^3A''$) triplet arises from photodetachment of an electron from the C–C π-bond of the anion or from the singlet neutral ground state via a b$_1$ (π) → b$_2$ (p) excitation. In vinylidene the $\tilde{a}\ ^3B_2$ state is the lowest energy triplet. The ordering of the triplet states in monofluorovinylidene and difluorovinylidene are determined in this work.

There are several recent calculations on the fluorovinylidene species. New high-level calculations on monofluorovinylidene by DeLeeuw et al.[6] include geometry and frequency optimization on the ground-state singlet and anion. The transition-state geometry

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* Author to whom correspondence should be addressed.
† University of Colorado.
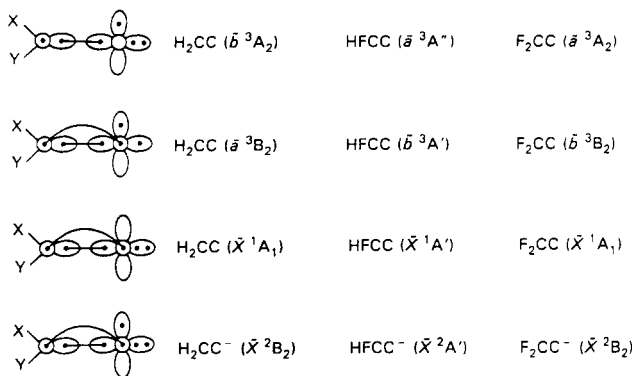‡ University of Nevada.

Figure 1. Schematic molecular orbital diagrams for vinylidene. Also shown are the analogous state symmetry assignments for monofluorovinylidene and difluorovinylidene.

Table I. Electron Affinities (eV)

species	electron affinity
H_2C=C:	0.490 (6)[a]
HFC=C:	1.718 (6)
F_2C=C:	2.255 (6)

[a] Reference 5.

and energy for the hydrogen migration and vibrational frequencies were also calculated. The frequencies and geometry of singlet difluorovinylidene have also been reported.[7-9]

Monofluorovinylidene and difluorovinylidene each have singlet ground states that can isomerize to fluoroacetylenes. For monofluorovinylidene there are two pathways for isomerization, via hydrogen migration or via fluorine migration. Estimates of the classical hydrogen isomerization barrier (2.4–12.3 kcal/mol)[6] are strongly dependent upon the level of calculation. The barrier for fluorine migration is expected to lie around 35 kcal/mol.[10-12] The antiaromatic character of the cyclic 4π transition state during fluorine migration may be responsible for the large barriers involved in fluorine migration.[10,11] For difluorovinylidene, the only pathway for rearrangement is fluorine migration, predicted to have a barrier large enough ($\sim$30–35 kcal/mol) that the F_2C=C: species is expected to be long lived, with the consequence that rearrangement has never been implicated in difluorovinylidene chemistry.[10-15]

Because monofluorovinylidene undergoes facile rearrangement to fluoroacetylene and is highly reactive, this species has not been directly observed. Triplet mercury photosensitized decompositions of 1,1- and *cis*- and *trans*-1,2-difluoroethylenes are thought to produce monofluoroacetylene as the principal product.[15] Difluorovinylidene has been proposed as an intermediate in several studies, but the evidence for the existence of F_2C=C: has been indirect. In these experiments,[14,16,17] carbene insertion reactions with the parent molecules are quite common, indicating the presence of F_2C=C:. The 1,2 fluorine migration product FCCF has not been observed in these experiments. Difluoroacetylene has only recently been observed from irradiation of difluorocyclopropenone in an argon matrix.[18] In the mercury photosensitization of trifluoroethylene,[16] energy transfer which promotes the olefin to its lowest triplet state is followed by geminal molecular elimination of HF. This results in formation of difluorovinylidene in its singlet ground state, which can add across the double bond of a parent olefin, producing trifluoroallene and CF_2. Stachnik and Pimentel[17] showed that similar trifluoroethylene chemistry occurred after multiphoton excitation. In the photolysis of F_2C=CHCl the primary product is C_2F_4; however, when H_2S is

present the principal product[14] is $F_2C_2H_2$, supporting the existence of F_2C=C: as an intermediate. A recent attempt at direct observation of difluorovinylidene from irradiation of difluoropropadienone in argon and nitrogen matrices was unsuccessful,[7] but the production of difluorodiazoethene in the nitrogen matrix supports the presence of difluorovinylidene. Bürger et al.[19] report an unassigned absorption feature at 1247 cm^{-1} in the neon matrix spectra of difluoroacetylene and suggest the possibility that this feature is the calculated[8] strong asymmetric C–F stretch in difluorovinylidene. The totally symmetric difluorovinylidene vibrations observed in this work lend support to the calculations and suggest that the tentative assignment of Bürger et al.[19] was correct.

Although the neutral monofluorovinylidenes are difficult to observe experimentally, several gas-phase experiments report production of the monofluorovinylidene and difluorovinylidene anions. C_2HF^- was observed from dissociative electron attachment to *cis*- and *trans*-1,2-difluoroethylene.[20] The difluorovinylidene anion is produced by dissociative electron attachment[20] to trifluoroethylene and by electron bombardment (10-eV electrons) of trifluoroacetaldehyde.[21] Abstraction of H_2^+ by O^- on ethylene and difluoroethylene[5,22] produces H_2C=C:$^-$ and F_2C=C:$^-$, respectively. A similar reaction[22] with vinyl fluoride produces the monofluorovinylidene anion HFC=C:$^-$.

This paper presents the 351-nm photoelectron spectra of the monofluorovinylidene and difluorovinylidene anions. First a brief overview of the experimental methods is presented. The discussion section begins with electron affinities and continues with the analysis of the singlet state of HFC=C:, including a discussion of the reaction coordinate for the monofluorovinylidene → fluoroacetylene isomerization. This is followed by the analysis of the singlet state of difluorovinylidene. Finally, the triplet-state symmetries and excitation energies are discussed.

Experimental Methods

The negative ion photoelectron spectrometer is described in detail elsewhere[5,23] and in a recent review article;[24] only a brief introduction is given here. The negative ions HFC=C:$^-$ and F_2C=C:$^-$ are produced[22] in a flowing afterglow source from vinyl fluoride and 1,1-difluoroethene, respectively, using O^- to abstract H_2^+. The ions are accelerated, focused into an ion beam, mass selected with a Wien velocity filter, and crossed by a continuous laser beam of fixed photon energy ($h\nu$ = 3.531 eV). Photodetached electrons are collected perpendicularly to the ion and laser beams and energy analyzed with an electrostatic analyzer. Photoelectron spectra are obtained by measuring the kinetic energy (eKE) of photodetached electrons from the process

$$A^-(v'') + h\nu \rightarrow A(v') + e^-(eKE)$$

where v'' and v' denote the vibrational states of the anionic and neutral species. In the present case, a$^-$ is either HFC=C:$^-$ or F_2C=C:$^-$. Conservation of energy requires that the transition energy from the anion initial state to the neutral final state plus the kinetic energy of the photoelectron be equal to the photon energy. Determination of the electron

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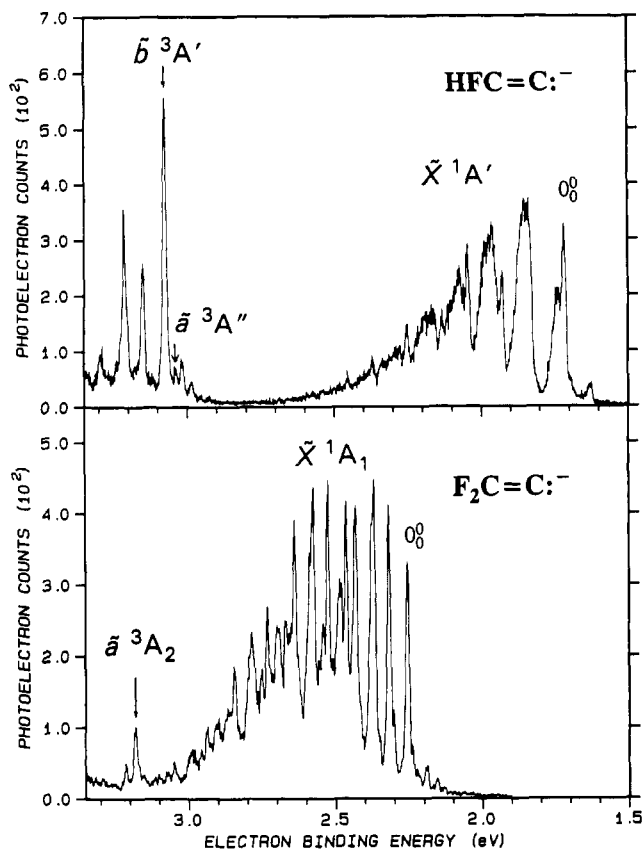
Figure 2. Photoelectron spectra of monofluorovinylidene anion (HFC=C:⁻) and the difluorovinylidene anion (F₂C=C:⁻) taken at 351 nm. Transitions to the ground state (at lower binding energies) and to the first excited triplet states are seen. The peaks which correspond to the electron affinity are indicated 0_0^0, and triplet-state origins are designated by an arrow. See text for a discussion and symmetry assignments of these transitions.

kinetic energy provides a vibrational and electronic spectrum of the transitions between the anion and neutral. Since electron kinetic energy depends upon the photon energy used, the spectra shown in this paper are converted into electron binding energy (eBE = $h\nu$ - eKE), which is the transition energy and is independent of the photon energy. All of the photoelectron spectra displayed in this paper were taken with the laser polarization at the "magic" angle.[25] Spectra taken at this angle give a photodetachment signal proportional to the total photodetachment cross section.

Results and Discussion

Photoelectron spectra of $\tilde{X}$ ²A′ HFC=C:⁻ and $\tilde{X}$ ²B₂ F₂C=C:⁻ are displayed in Figure 2; both exhibit extensive vibrational strucutre in the ground-state neutral and show two or more electronic states. In the spectrum of HFC=C:⁻, transitions to the ground-state singlet ($\tilde{X}$ ¹A′) and two triplet states ($\tilde{a}$ ³A″ and $\tilde{b}$ ³A′) are observed. In the spectrum of F₂C=C:⁻, transitions to the $\tilde{X}$ ¹A₁ state and the $\tilde{a}$ ³A₂ state are observed. The justification for the assignments of the triplet states will be explained below following an analysis of the singlets.

Electron Affinities. The peaks designated 0_0^0 in each of the spectra correspond to the transition from $v = 0$ in the anion to $v = 0$ in the ground-state neutral. The adiabatic electron affinities (EA) of the radicals are determined from the binding energy of these transitions. The electron affinities are 1.718 (6) eV for monofluorovinylidene and 2.255 (6) eV for difluorovinylidene. For comparison, the electron affinity of vinylidene[5] is included with these in Table I. The resulting trend is EA(H₂C=C:) < EA(HFC=C:) < EA(F₂C=C:). The substitution of a single hydrogen by fluorine increases the electron affinity by 1.2 eV, while the second fluorine adds another 0.5 eV. The fluorine

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substituent results in notable stabilization of the negative ion. The only previous estimates of the electron affinities relied upon appearance potentials for HFC=C:⁻ and F₂C=C:⁻, the heats of formation of the acetylenic forms, and calculated rearrangement barriers.[20] This procedure gave EA(HFC=C:) ≥ 2.2 ± 0.9 eV and EA(F₂C=C:) ≥ 2.2 ± 0.4 eV, much less precise but in agreement with our experimental results.

Vibrational Structure. In photoelectron spectra, uncomplicated by autodetachment resonances, the intensity of a transition is determined simply by the Franck–Condon principle. Qualitatively, if there is a large change in the equilibrium geometry between the anion and the neutral species, then a long progression of vibrational peaks is observed. The most intense peaks in the spectrum correspond to a nearly vertical transition. In Figure 2, transitions to the ground-state fluorovinylidenes each extend over a range of 1 eV. Without any other knowledge, it is apparent that there is a large change in geometry between the two states involved in this transition.

In the harmonic approximation the Franck–Condon principle leads to symmetry selection rules. For the ground-state singlet of HFC=C: (C_s symmetry) there are six normal coordinates, which we label as the CCF bend (a′), the out-of-plane bend (a″), the C—F stretch (a′), the CCH bend (a′), the C=C stretch (a′), and the C—H stretch (a′). For the singlet state of F₂C=C: (C_{2v}) the totally symmetric modes are the C=C stretch (a₁), the C—F symmetric stretch (a₁), and the CF₂ scissors (a₁). The remaining normal modes are the C—F asymmetric stretch (b₁), the CF₂ out-of-plane wag (b₂), and the CF₂ in-plane rock (b₁). Changes of $\Delta v = 0, \pm1, \pm2, ...$ are allowed for each of the totally symmetric modes, labeled a′ for HFC=C: and a₁ for F₂C=C:, while only even changes in quantum number ($\Delta v = 0, \pm2, \pm4, ...$) of the non-totally symmetric modes are allowed. Although five vibrational modes are symmetry allowed for HFC=C:, only three vibrational modes are distinctly observed. This is the same number of vibrational modes observed in the spectrum of F₂C=C:; the congestion in the photoelectron spectrum of HFC=C:⁻ compared to that of F₂C=C:⁻ is not simply due to a larger number of active vibrational modes.

To obtain more quantitative information from the photoelectron spectra, Franck–Condon simulations of the spectra were performed. Parameters in the simulation are the vibrational potentials (harmonic or Morse oscillator), vibrational frequencies, normal coordinate displacements, anion vibrational temperature, and vibrational origin position. With the exception of the CCF bend in monofluorovinylidene, discussed below, vibrational potentials for all of the neutral and anionic states were modeled as harmonic oscillators. Vibrational frequencies for the neutral species were obtained directly from clearly resolved peaks in the photoelectron spectrum. Hot bands, transitions originating from excited vibrational levels in the anion, provided anion vibrational frequencies and gave an estimate of the anion vibrational temperature (300–400 K). Franck–Condon factors were calculated by integrating the overlap between the trial wave functions of the neutral with the trial wave functions of the anion. Normal coordinate displacements were varied until the best fit was obtained. Since this experiment does not have rotational resolution, the vibrational peaks are fit with a Gaussian line shape with a fwhm set to that of the origin peak (18 meV for HFC=C: and 15 meV for F₂C=C:). For both monofluorovinylidene and difluorovinylidene the vibrational origin assignments were unambiguous, due to the intensity profiles and the differences between neutral and anion vibrational frequencies.

Singlet HFC=C:. The photoelectron spectrum of the ground state of HFC=C:, shown in the upper portion of Figure 3, is quite congested. Although five vibrational modes of HFC=C: are symmetry allowed, only three are observed—those corresponding to the change in geometry between the anion and singlet state. Four different vibrational frequencies are observed in the envelope of transitions terminating in the ground electronic state—three belong to the singlet neutral ground state and one to the anion. The observed frequencies are 205 (30), 960 (30), 1680 (30), and 710 (35) cm⁻¹. On the basis of the calculated frequencies of
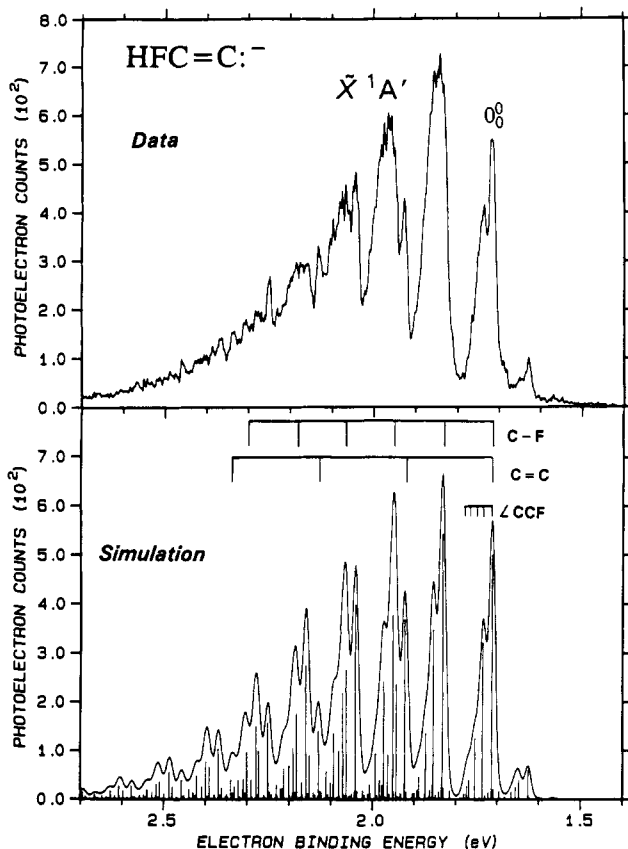
Figure 3. Photoelectron spectrum (351 nm) of the monofluorovinylidene anion showing the ground-state singlet (upper portion). The peak corresponding to the adiabatic electron affinity is indicated 0_0^0. The lower part shows the Franck–Condon simulation of the data. The spectrum was fit using three vibrational modes, the CCF bend, the C—F stretch, and the C=C stretch.

Table II. Experimental and Calculated Vibrational Frequencies for Monofluorovinylidene (cm^{-1})

species	CCF bend	C—F stretch	C=C stretch	source
$\tilde{X}$ ^{2}A′ HFCC$^-$	485 (30)	710 (35)		this work
	517	811	1610	theory[6]
$\tilde{X}$ ^{1}A′ HFCC	205 (30)	960 (30)	1680 (30)	this work
	296	1007	1687	theory[6]
$\tilde{b}$ ^{3}A′ HFCC	600 (50)	1100 (100)		this work
	606	1104		theory[6]

DeLeeuw et al.,[6] these are assigned in Table II as the neutral CCF bend, C—F stretch, C=C stretch, and the anion C—F stretch, respectively. The Franck–Condon simulation is shown beneath the experimental data in Figure 3, and the neutral fundamental progressions are indicated. Combination bands, consisting of the CCF bending progression on each of the fundamentals, are responsible for much of the spectral congestion. The intense progressions in the C—F stretch and C=C stretch indicate a large change in geometry in this transition. The C—F bond length is calculated to be substantially shorter in the neutral than in the anion.[6] Although there are several places where the simulated intensities do not match the experimental data, the overall fit is quite good, considering the simplicity of the models employed for the simulation and the complexity of the molecule. Experimental vibrational frequencies for each of the electronic states of monofluorovinylidene are summarized in Table II.

Reaction Coordinate for the Monofluorovinylidene → Fluoroacetylene Isomerization. To obtain information about the potential energy surface for the isomerization, we need to identify the vibrational coordinate of the singlet vinylidene species that is most closely identified with the reaction coordinate for isomerization. In our study[5] of H_2C=C:, we found that the CH$_2$ rock normal
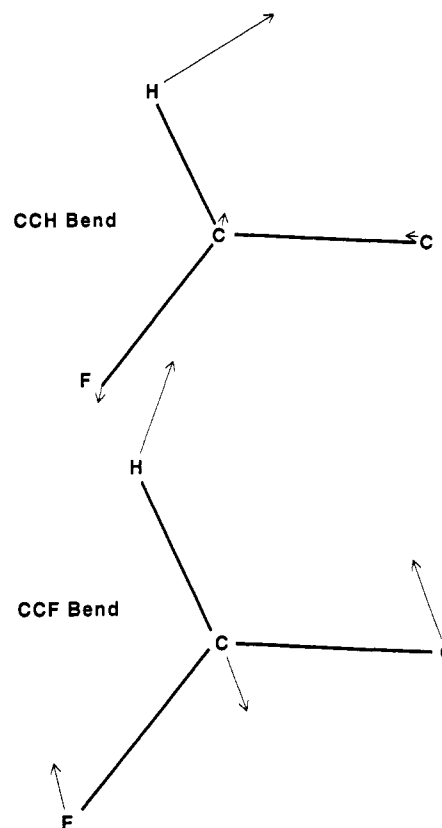

Figure 4. Drawings of the CCF and CCH bending modes calculated using a 6-31+G(d,p) basis set in Gaussian 90.[26] The motion of the fluorine into a nearly linear configuration with the carbons is an important step in the isomerization to fluoroacetylene. The magnitude of the hydrogen motion in the CCF bend is clearly seen in this drawing. The CCF bending frequency (314 cm^{-1}) has also been calculated to be much lower than the CCH bending mode (1183 cm^{-1}).[6]

coordinate leads most directly from the vinylidene local minimum on the potential energy surface toward the isomerization transition-state geometry. The CH$_2$ rock mode also has the lowest frequency in H_2C=C:, which corresponds to the shallow well leading to the isomerization barrier. An analysis of the vibrational energy levels and Franck–Condon intensities for the CH$_2$ rock mode allowed an estimate of the well depth of the vibrational potential energy along that coordinate and thus the isomerization barrier height. The true reaction coordinate cannot, in general, be described by a single normal coordinate at the vinylidene geometry, so this procedure necessarily gives an approximate value for the barrier height. Nevertheless, in the case of H_2C=C: we obtained an estimate which closely agreed with the best ab initio calculations.

In the case of HFC=C:, one might anticipate that the normal coordinate most related to the isomerization reaction coordinate, transferring the hydrogen from one carbon center to the other, would be the CCH bending mode. On the other hand, the lowest frequency mode in HFC=C: according to the calculations of DeLeeuw et al.[6] is the CCF bend at 314 cm^{-1}, compared to the CCH bend at 1183 cm^{-1}. We compare these two normal modes in Figure 4, which shows the normal coordinate vectors calculated at the Hartree–Fock level using a 6-31+G(d,p) basis set.[26] While both normal coordinates involve substantial hydrogen atom motion, only the CCF bend also leads to a straightening of the FCC bond angle, which must occur to go to the isomerization transition state, for which ∠FCC is predicted[6] to be about 176°. Thus, we make the preliminary conclusion that the CCF bending normal coor-

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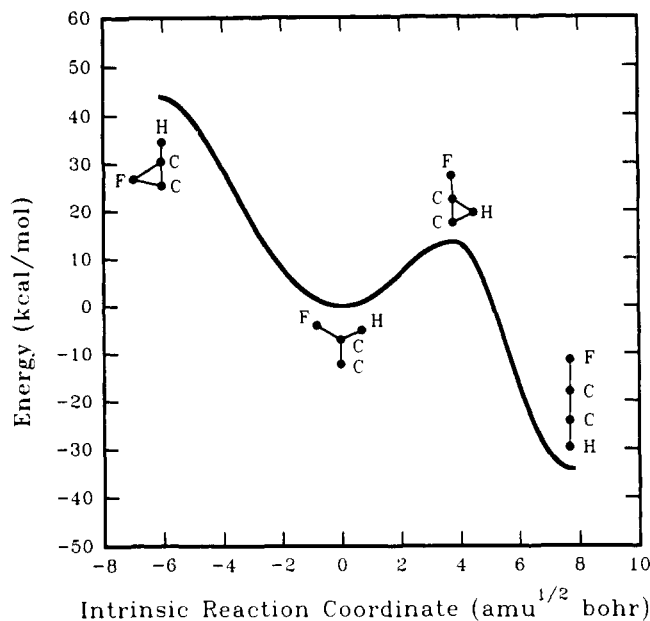
Figure 5. Potential energies for HFC=C: along the intrinsic reaction coordinate (RC) calculated at the HF/6-31+G(d,p) level. The IRC is expressed in mass-weighted internal coordinates relative to the monofluorovinylidene local minimum. Calculated molecular geometries are shown to scale at each extremum of the potential energy curve.

dinate is most related to the isomerization coordinate for HFC=C:.

To explicate the reaction coordinate further, we have performed intrinsic reaction coordinate (IRC)[27,28] calculations on HFC=C: at the Hartree–Fock level with a 6-31+G(d,p) basis set. The IRC or "reaction path" is the path of steepest descent in mass-weighted coordinates from the transition state to reactants or products, which the system would follow classically if the reaction were damped to proceed infinitely slowly.[26,28] Figure 5 shows the calculated potential energy surface along the IRC, from the monofluorovinylidene local minimum over the hydrogen atom transfer isomerization barrier to the FCCH acetylene geometry. Since the calculations do not include electron correlation effects, the barrier height is greatly overestimated (13.4 kcal/mol vs 2.4 kcal/mol calculated by DeLeeuw et al.[6]). For comparison, the path in the reverse direction to the much higher fluorine atom isomerization barrier is also shown in Figure 5.

We also calculated force constants (second derivatives of the potential energy surface) at points along the IRC for the isomerization process. Diagonalization of the force constant matrix yields the vibrational normal mode coordinates in directions along and orthogonal to the reaction path and the corresponding harmonic frequencies.[28] The five frequencies in directions orthogonal to the reaction path represent the curvature of the walls of the multidimensional valley along the IRC, while the remaining frequency represents the curvature of the potential energy with respect to the IRC itself (imaginary frequencies correspond to negative curvature at the saddle point). The calculated frequencies are presented in Figure 6. It is clear from this figure that the frequency of the CCF bending mode in monofluorovinylidene correlates with the imaginary frequency of the reaction coordinate for the transition state, confirming our initial conclusion. This mode then leads to one of the degenerate CCF bending coordinates in fluoroacetylene (the other CCF bend correlates with a rotation of the nonlinear species). In contrast, the frequency of the CCH bending mode of monofluorovinylidene varies little over the course of the reaction path, indicating that it is largely uninvolved in the isomerization dynamics, and correlates with the CF stretch of

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Table III. Experimental and Calculated Frequencies for Difluorovinylidene (cm^{-1})

species	CF$_2$ scissor	C–F sym stretch	C=C stretch	source
$\tilde{X}$ $^2B_2$ F$_2$CC$^-$	505 (25)	800 (35)		this work
$\tilde{X}$ $^1A_1$ F$_2$CC	510 (25)	905 (25)	1670 (25)	this work
	~485	~890	~1640	theory^a

^{a} Reference 8 with 5% correction.

fluoroacetylene. Apparently, the crucial geometry change for reaching the transition state is the straightening of the FCC bond angle, which allows a change of the central carbon atom to substantial sp character and partial conversion of the lone-pair electrons to an acetylenic π-bond.

Crossings between the frequency curves in Figure 6, with the same vibrational symmetry in C_s symmetry (all except the out-of-plane mode), are not allowed. There are several interesting avoided crossings, such as that between the CH stretch and CC stretch. The CF stretch in C_s symmetry correlates with the CCH bend in the linear molecule, while the CCH bend correlates to the CF stretch. This mode "reversal" probably arises from a curve crossing near the transition state where the two modes are strongly coupled. The details of the curves may well change at higher levels of calculation, but the overall vibrational correlations and trends of the frequency curves in Figure 6 are expected to be reliable.

Now that we have identified the CCF bending coordinate of HFC=C: as correlating with the reaction coordinate, we can analyze the vibrational structure of this mode in the photoelectron spectrum with a view toward inferring information about the reaction coordinate. Figure 7 exhibits an enlargement of the HFC=C: $\tilde{X}$ $^1A'$-state photoelectron spectrum including the origin and first peak in the vibrational progression assigned to the CCF bending mode (ν_6) vibration. Inspection of this vibrational transition at 205 (30) cm^{-1} reveals that this peak is at least three times wider than the vibrational origin 0_0^0, which suggests that it is broadened by additional transitions. We assign these to overtones of the CCF bend, transitions which have substantial intensities because of the large change in frequency between the anion and the singlet states (485 (30) cm^{-1} vs 205(30) cm^{-1}) as well as because of the large anharmonicity in the singlet state due to the low isomerization barrier. A Franck–Condon simulation of this progression was obtained using a Morse potential, for which the repulsive part corresponds to the potential energy curve (Figure 5) in the F-atom migration direction and the dissociative part corresponds to the H-atom isomerization barrier. The anion potential was taken as harmonic in the simulation. The best fit, shown in Figure 7, was obtained with ω_e = 205 (30) cm^{-1} and $\omega_e x_e$ = 14 cm^{-1} for the singlet Morse parameters. The resulting well depth is D_e = 0.09 eV (2 kcal/mol). Varying both ω_e and $\omega_e x_e$, well depths over the range of D_e = 0.07–0.1 eV all give reasonable fits to the data. This indicates only 4–7 bound vibrational levels in this vibrational mode. Taking the Morse well depth as an approximation of the barrier height for isomerization to the acetylenic form gives a barrier of 1.6–2.3 kcal/mol. This is in excellent agreement with the recent calculations by DeLeeuw et al.,[6] which give a classical barrier of 2.4 kcal/mol; inclusion of zero-point energy corrections[6] lowers the barrier height to under 1 kcal/mol. Because the photoelectron spectrum of monofluorovinylidene is severely congested, estimates of the lifetime from line broadening (as was done for vinylidene) were not possible.

Singlet F$_2$C=C:. The portion of the photoelectron spectrum showing transitions terminating in the $\tilde{X}$ $^1A_1$ state of F$_2$C=C: is shown in the upper portion of Figure 8. Neutral vibrational frequencies (Table III) observed at 510 (25), 905 (25), and 1670 (25) cm^{-1} are assigned to the CF$_2$ scissors, the C—F stretch, and the C=C stretch. These vibrational assignments were based upon the calculated frequencies of Gallo and Schaefer,[8] which are also given in Table III. The agreement between the experimental and calculated frequencies of the totally symmetric modes is quite good and suggests that the calculated C—F asymmetric frequency is also accurate. This agreement makes it likely that Bürger et al.[19]
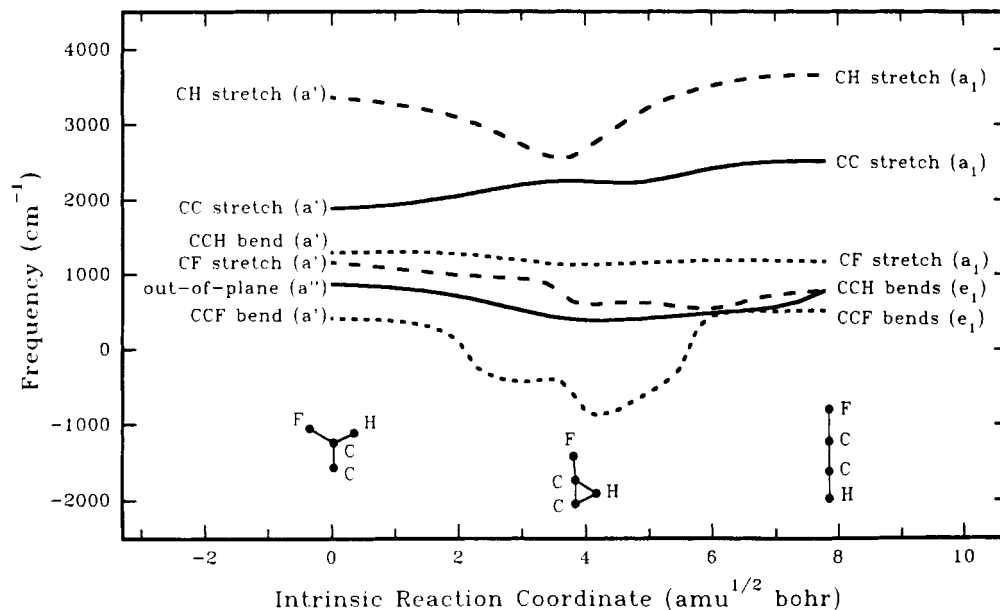
Figure 6. Variation of the calculated frequencies along the intrinsic reaction coordinate (IRC) for the HFC=C: → FCCH isomerization. The curves are labeled for HFC=C: and FCCH according to the normal coordinate descriptions. "Negative" frequency values correspond to imaginary frequencies or negative curvature of the potential energy curve along the IRC at and near the transition state. The molecular geometries along the reaction path are depicted in the lower part of the graph. The saddle point of the transition state lies at 3.8 amu$^{1/2}$ bohr.
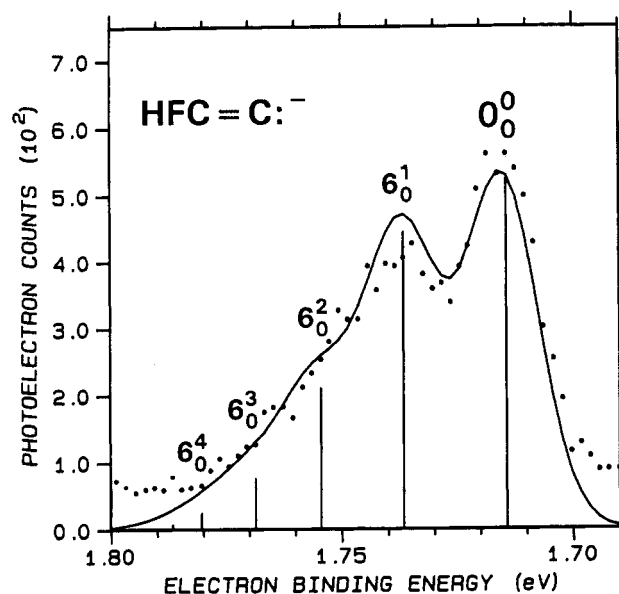

Figure 7. Photoelectron spectrum of the ground-state monofluorovinylidene displaying only the vibrational origin and the first neutral vibrational progression (ν_6). The Franck–Condon simulation, shown by the solid line, of the CCF bending mode employed a Morse potential. The best fit was obtained with $\omega_e = 205$ cm^{-1} and $\omega_e x_e = 14$ cm^{-1}. The resulting well depth is $D_e = 0.09$ eV. Taking this as an approximation to the barrier height for the hydrogen isomerization barrier to form fluoroacetylene gives a barrier height of 2 ± 1 kcal/mol.

did observe the F$_2$C=C: asymmetric stretch with difluoroacetylene in a Ne matrix.

Shown in the lower part of Figure 8 is the Franck–Condon simulation of the data with the fundamental modes indicated above the simulation. The two anion frequencies observed at 505 (25) and 800 (25) cm^{-1} were assigned to the CF$_2$ scissors and the C—F stretch, respectively. The anion C=C stretching mode was not observed, consistent with the anion temperature, and was constrained to the frequency of the neutral singlet. Normal coordinate displacements used for the simulation are 0.40 for the CF$_2$ wag, 0.29 Å (g/mol)$^{1/2}$ for the C—F stretch, and 0.21 Å (g/mol)$^{1/2}$ for the C=C stretch.

Triplet-State Analysis and Excitation Energies. Vinylidene possesses two low-lying triplet states. In vinylidene the ã ^{3}B$_2$ state
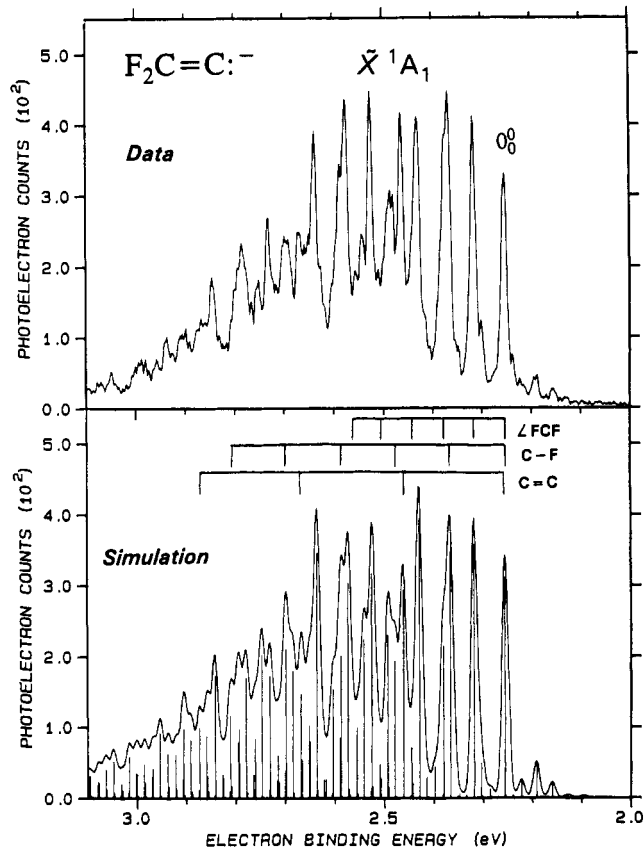

Figure 8. Photoelectron spectrum of difluorovinylidene (F$_2$C=C) ground state (upper trace) and the Franck–Condon simulation (lower trace). Vibrational modes active in the singlet were observed at 510 (25), 905 (25), and 1670 (25) cm^{-1}. The fundamentals of these three modes are indicated on the figure.

lies 0.689 eV lower than the b̃ ^{3}A$_2$ state.[5] The ^{3}A$_2$ state of difluorovinylidene is thought to be the lowest triplet state, but there has been no prior experimental confirmation of this prediction. The symmetry of the lowest triplet state (^{3}A'' or ^{3}A') of monofluorovinylidene has been unknown. For monofluorovinylidene the ^{3}A'' results from photodetachment from the carbon–carbon π-bond and the ^{3}A' state arises from photodetachment of an
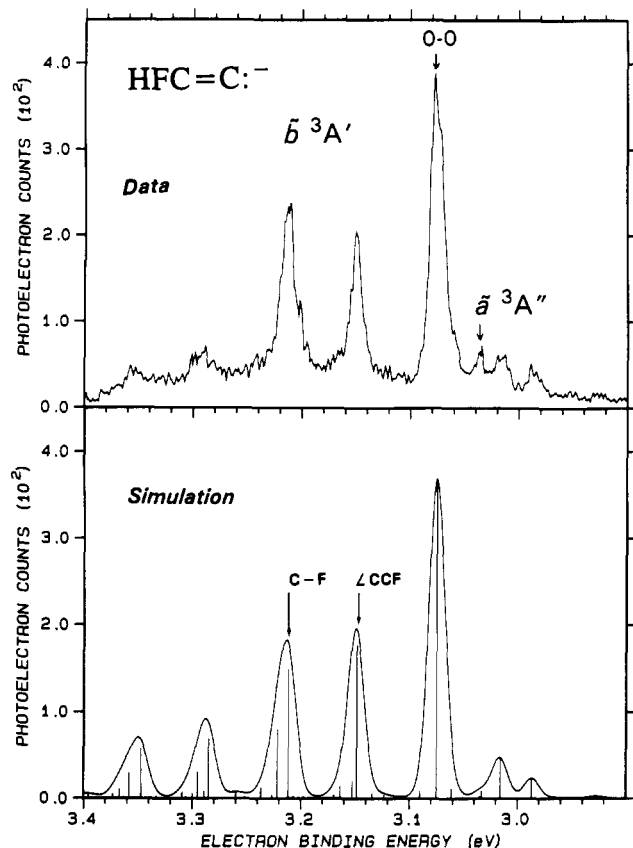
Figure 9. The upper portion displays the photoelectron spectrum of the ã ³A″ and the b̃ ³A′ states of monofluorovinylidene. State symmetry assignments are discussed in the text. The lower part displays the Franck–Condon simulation using the 0–0 peak as the origin. Active vibrational modes are the CCF bend and the C–F stretch.

Table IV. Triplet-State Excitation Energies and Electron Affinities (eV)

species	ΔS – T	triplet EA
H_2C=C:[a]	2.065 (6) (ã ³B₂)	2.555 (6)
	2.754 (20) (b̃ ³A₂)	3.244 (20)
HFC=C:	1.320 (9) (ã ³A″)	3.038 (6)
	1.358 (9) (b̃ ³A′)	3.076 (6)
F_2C=C:	0.924 (9) (ã ³A₂)	3.179 (6)

[a] Reference 5.

0–0 peak as an origin for this electronic state should give an intense peak at an electron binding energy of 3.24–3.28 eV, assuming a frequency of 1300–1650 cm⁻¹ for the CC stretch. Although detection of an electron at this energy approaches the limits of our apparatus, we are confident that we would have detected such a feature had it been present. There was no peak apparent at this energy. This finding suggests strongly that this progression does not arise from electron detachment to form the ³A″ state.

Each of the triplet states in the fluorovinylidenes and vinylidene are observed at electron energies quite close to threshold. Near threshold, photodetachment from a carbon lone-pair orbital has a larger cross section than detachment from a π-orbital. In the photoelectron spectrum of vinylidene anion⁵ the cross section for detachment from the lone-pair orbital to form the ³B₂ state is ~20 times larger than that for detachment from the π-bond to form the ³A₂ state. In monofluorovinylidene the peak marked 0–0 is ~7 times more intense than the peak indicated ã ³A″. This indicates that the 0–0 peak belongs to the ³A′ state and the peak immediately to the right in Figure 9 belongs to the ³A″ state. Since the origin for the ³A″ state is so weak, the CC stretch may not be observable and would lie underneath the peak marked C–F in Figure 9.

These three properties, the similarity of the measured asymmetry parameter of the 0–0 peak to that measured in vinylidene for the analogous state, the lack of a strong CC stretch expected for the ³A″ transition, and the intensity ratio of the 0–0 peak to the peak indicated ã ³A″, all support the assignment of peak 0–0 to the ³A′ state. Our inability to attribute the peak at 3.038 eV to mass contamination and the similarity in intensity to the vinylidene b̃ ³A₂ state are strong evidence that this peak belongs to the ³A″ state. This must also be the vibrational origin of this state, since little else was observed in the photoelectron spectrum of the vinylidene b̃ ³A₂ state.⁵ The calculations of DeLeeuw et al.⁶ suggest that the origin of this state actually lies some 0.12 eV higher, at an eKE where such a weak feature might be obscured by the stronger transitions to the other triplet. This possibility is very remote, however, since it would leave the peak we identify as the origin of the ³A″ state unidentified. The measured excitation energies to each of triplet states are summarized in Table IV.

In the b̃ ³A′ state of monofluorovinylidene shown in Figure 9, two vibrational modes are observed. DeLeeuw et al.⁶ calculated that the three lowest vibrational modes for the anion and singlet ground state are the CCF bend (a′), the out-of-plane bend (a″), and the C–F stretch (a′). Since single quanta of the out-of-plane mode are not symmetry allowed, the observed frequencies in the excited state belong to the CCF bend and the C–F stretch. The Franck–Condon simulation of the photoelectron spectrum, using the 0–0 peak as the origin, is shown in the lower part of Figure 9. Normal coordinate displacements used in the Franck–Condon simulation are 0.29 Å (g/mol)^{1/2} for the CCF bend and 0.25 Å (g/mol)^{1/2} for the C–F stretch.

In the photoelectron spectrum of F_2C=C: shown in Figure 2, very little vibrational structure is observed in the excited (ã ³A₂) state, where the origin is indicated with an arrow. The triplet excitation energy for this state is given in Table IV. A distinct vibrational spacing of 250 (25) cm⁻¹ is observed. Since this is much lower than any vibrational frequency expected for difluorovinylidene, we assume that this belongs to a sequence band. A transition to the b ³B₂ excited triplet state of difluorovinylidene is not observed. By comparison to H_2CC and HFCC, we would expect this transition to have a strong intensity. Its absence implies

electron in the carbon lone-pair orbital. Following is a discussion on our assignment of the observed triplet-state symmetries of monofluorovinylidene.

In Figure 9 we present a comparison between the photoelectron spectrum of the excited states of monofluorovinylidene (upper) and a Franck–Condon simulation (lower) for a single state (described later in this section). The peak labeled ã ³A″ in Figure 9 is not accounted for by the Franck–Condon simulation. Sequence band assignments will not fit this peak, and the peak is much too close to the origin (300 cm⁻¹) to be a fundamental mode in the anion. Shifting the Wien filter to slightly higher and lower masses to check for mass contamination did not eliminate this peak from the spectrum. In spectra taken years apart under varying conditions, the intensity ratio of the peak at 3.076 eV (b̃ ³A′ vibrational origin) to the ã ³A″ peak remains constant, which suggests it is not a hot band. This feature must arise from photodetachment of HFC=C:⁻, but it cannot be a part of the analyzed spectrum and must belong to a separate electronic state.

Since we have determined that there are two states present, we now need to assign the state symmetries. An attempt to measure²⁹ the asymmetry parameter for the peak labeled ã ³A″ was inconclusive due to low signal level. Because of the greater intensity of the peak labeled 0–0, we were able to measure the asymmetry parameter for this peak. The asymmetry parameter²⁵ β = +1.1 (2) is quite similar to the value measured⁵ for photodetachment to the ã ³B₂ of vinylidene (β = +1.45 (5)) and supports our assignment of this peak to the analogous ³A′ state of monofluorovinylidene. If the peak labeled 0–0 belonged to the ³A″ state of monofluorovinylidene, we would expect to observe a very strong vibrational progression belonging to the CC stretch, which would be active because the carbon–carbon bond length increases upon the removal of an electron in the π-bond. In Figure 9, using the

(29) Gilles, M. K.; Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1992**, *96*, 1130.
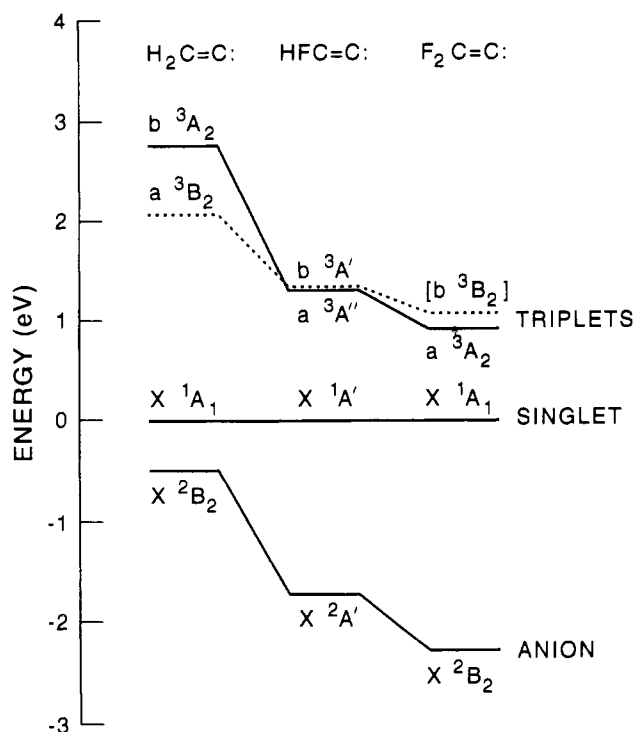
Figure 10. Schematic energy levels depicting trends in electron affinities and the binding energies to each of the triplet states. The energy origins have been fixed to the singlet state for each species, and the energy separations are from this experiment (HFCC and F_2CC) and from ref 5 (H_2CC). Since the energy of the b $^3B_2$ state of F_2CC is a lower limit from this experiment, it is placed in brackets. The fluorine substitution increases the singlet- (ground-) state electron affinity substantially, with the result that the singlet–triplet splitting decreases with fluorine substitution.

that the state is beyond our experimental energy range, giving T_0(b $^3B_2$) $\geq$ 1.09 eV.

Single–Triplet Splitting. Investigation of vinylidene, monofluorovinylidene, and difluorovinylidene enables us to obtain an overview of the effects of fluorine substitution on electron affinities, singlet–triplet splittings, and other state separations. These are summarized in Figure 10, where the energy origin has been fixed to the singlet state for each species. Fluorine substitution causes a substantial lowering of the energies of the anion and both triplet states relative to the singlet state. The singlet–triplet splitting decreases in the order (H_2C=C:) > (HFC=C:) > (F_2C=C:). The electron affinities increase nearly a factor of 5 from H_2C=C: (0.490eV) to F_2C=C: (2.255eV) with fluorine substitution. This situation is quite different from what has been reported on the simple one-carbon halocarbenes.[29,30]

(30) Murray, K. K.; Leopold, D. G.; Miller, T. M.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *89*, 5442.

The electron binding energy of the $^3B_2$ ($^3A'$) state, which is the energy required to remove an electron from the carbon lone pair on the anion, is nearly the same for H_2CC:, HFCC:, and F_2CC:. That indicates that the lone pair orbital is largely unaffected by fluorine substitution at the other carbon. The electronic feature that distinguishes the singlet from the anions or either triplet state is that the in-plane p-orbital on the terminal carbon atom is empty for the singlet but is singly occupied for the other states. In singlet vinylidene, there is a favorable mixing between the occupied CH bonding orbital and the empty C p–orbital ("hyperconjugation"). This interaction lowers the energy of the CH orbital and raises the energy of the carbon p-orbital. Since the anion and the two triplet states have an electron in the carbon p-orbital, their energies are raised relative to the singlet, giving a small electron affinity and a large singlet–triplet splitting. Fluorine substitution makes this orbital interaction much less strong because the energy of the CF bonding orbital is lower than the energy of the CH σ-bonding orbital. Thus the energies of the anion and both triplets for the monofluorovinylidene and difluorovinylidene decrease relative to the singlet.

π donation by the fluorine substituents may explain the reversal of the ordering of the triplet states from H_2CC: to HFCC: to F_2CC:. In the anion, singlet, and $^3B_2$ triplets, the π-bond is doubly occupied and electron donation from the fluorine into this bond is repulsive. In the $^3A_2$ state of difluorovinylidene, the π-bond is only singly occupied, making electron donation from the fluorine atoms less unfavorable. This effect could stabilize the $^3A_2$ state relative to the $^3B_2$ state upon fluorine substitution.

Conclusion

The 351-nm photoelectron spectra are reported for monofluorovinylidene and difluorovinylidene anions. Transitions to the neutral singlet states exhibit extensive vibrational progressions, indicating a large change in equilibrium geometry between the anion and the neutral ground state. Vibrational frequencies are reported for the singlet and triplet neutral states and for the anions. Examination of the ground-state singlet spectrum of monofluorovinylidene combined with the results of ab initio calculations shows that the straightening of the CCF bond angle in the CCF bending mode is an important part of the isomerization process. Modeling the CCF bend as a Morse oscillator yields an estimated barrier height of 2 ± 1 kcal/mol. Transition energies to excited triplet states are also reported.

Note Added in Proof. We discovered after submission of this paper that the O^- reaction with vinyl fluoride has also been studied by Rabasco, J. J.; Kass, S. R. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 91.