of the interannular proton-transfer rate constants.\(^{(2)}\)

By contrast, the time resolution of the radiolytic technique has extended the range of measurable rate constants up to at least \(10^5 \text{s}^{-1}\). 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 confirms 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 \(\text{Me}_2\text{C}^+\) with \(\alpha,\omega\)-diphenylalkanes.\(^{(1)}\)

Acknowledgment. This work was supported by Ministero per l'Universit\'a e la Ricerca Scientifica e Tecnologica (MURST) and by the Italian National Research Council (CNR) and by the Forschungsprojekt 2194/26 of the Universit\'at Bielefeld.

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

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Abstract: The 351.1-nm photoelectron spectra of \(\text{HFC}=\text{C}^:-\) and \(\text{F}_2\text{C}=\text{C}^:-\) are reported. Transitions from the anion ground state to the neutral singlet ground state and low-lying triplet state are observed. The electron affinity of difluorovinylidene is 2.255 (6) eV, and the triplet term energy is \(T_d(\tilde{A} \rightarrow \tilde{A}') = 0.924 (9) \text{eV}\). In the singlet state of \(\text{F}_2\text{C}=\text{C}^:-\), vibrational progressions are observed at 510 (25), 905 (25), and 1670 (25) cm\(^{-1}\). Vibrational fundamentals at 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 \(T_d(\tilde{A} \rightarrow \tilde{A}^\prime \text{HFCC}) = 1.320 (9) \text{eV}\) and \(T_d(\tilde{A} \rightarrow \tilde{A}^\prime \text{HFCC}) = 1.358 (9) \text{eV}\). Vibrational fundamentals of 205 (30), 960 (30), and 1680 (30) cm\(^{-1}\) in the \(X \tilde{A}^\prime\) state of \(\text{HFC}=\text{C}^:-\), at 600 (50) and 1100 (100) cm\(^{-1}\) in the \(\tilde{A}^\prime\) state, and at 485 (30) and 710 (35) cm\(^{-1}\) in the negative ion \((X \tilde{A}^\prime)\). 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 \(X + \text{HY}\) \((X = \text{F}, \text{Cl}, \text{Br}, \text{Y} = \text{Cl}, \text{Br}, \text{I})\) have been probed by photodetachment of \(\text{XHY}^-\) species by Bradford et al.\(^2\) and Metz et al.\(^3\). Moylan et al.\(^4\) measured the photodetachment threshold of several ROHY species \((R = \text{C}_2\text{H}_5, \text{CH}_3, \text{Y} = \text{F} \text{and CH}_3\text{Y})\) to determine the well depth for proton transfer between \(\text{RO}^-\) and \(\text{HY}\) using a thermal cycle. An early study of the vinylidene anion revealed vibrational structure in the photoelectron spectrum of singlet vinylidene, which readily isomerizes to acetylene.\(^5\) In a more recent study from this laboratory, 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 \(X \tilde{A}\) state of vinylidene against rearrangement was found to be 0.04–0.2 ps.

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

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Since difluorovinylidene and vinylidene are both \(C_\text{sp}^3\), they have the same symmetry labels; the symmetry labels for monofluorovinylidene \((C_\text{sp}^3)\) are slightly different. The singlet states arise from detachment of an electron from the in-plane terminal carbon \(p\) orbitals of the anions. There are two low-lying triplet states. The \(^3\)B\(_1\) \((3\tilde{A}^-)\) states arise from photodetachment from the carbon lone-pair \(p\) orbital of the anion. The \(^1\)A\(_2\) \((\tilde{A}^\prime)\) triplet arises from photodetachment of an electron from the \(C=C\) \(p\) bond of the anion or from the singlet neutral ground state via a \(b_2\) \(\rightarrow a_1\) \((\pi)\) excitation. In vinylidene the \(^3\)B\(_1\) 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


and energy for the hydrogen migration and vibrational frequencies were also calculated. The frequencies and geometry of singlet difluorovinylidene have also been reported.14,15

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)9 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 (∼30–35 kcal/mol) that the F₂C=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 F₂C=C:- has been indirect. In these experiments,14,16,17 carbene insertion reactions with the parent molecules are quite common, indicating the presence of F₂C=C:-. The 1,2 fluorine migration product FCCF has not been observed in these experiments. Difluoroacetylene has only recently been observed from irradiation of difluoroethylene,18 produces H₂C=C:- and F₂C=C:-, respectively. A similar reaction12 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 elsewhere23 and in a recent review article,24 only a brief introduction is given here. The negative ions HFC=C:- and F₂C=C:- are produced in a flowing afterglow source from vinyl fluoride and 1,1-difluoroethene, respectively, using O₂ to abstract H₂. 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 (hv = 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

\[ A(-e^+) + hv \rightarrow A(e^-) + e^-(eKE) \]

where A(-e) denote the vibrational states of the anionic and neutral species. In the present case, A(0-) is either HFC=C:- or F₂C=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

<table>
<thead>
<tr>
<th>Table I. Electron Affinities (eV)</th>
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<tr>
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<tr>
<td>H₂C=C:-</td>
</tr>
<tr>
<td>HFC=C:-</td>
</tr>
<tr>
<td>F₂C=C:-</td>
</tr>
</tbody>
</table>

*Reference 5.
The Monofluorovinylidene–Fluoroacetylene Rearrangement:

Figure 2. Photoelectron spectra of monofluorovinylidene anion (HFC=C:\textsuperscript{−}) and the difluorovinylidene anion (F\textsubscript{2}C=C:\textsuperscript{−}) 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 binding energy are indicated (\(E_b\)), and triplet-state origins are designated by an arrow. See text for a discussion and symmetry assignments of these transitions.

Results and Discussion

Photoelectron spectra of \(\tilde{X}^2\text{A}'\) HFC=C\textsuperscript{−} and \(\tilde{X}^2\text{B}_1\) F\textsubscript{2}C=C\textsuperscript{−} are displayed in Figure 2; both exhibit extensive vibrational structure in the ground-state neutral and show two or more electronic states. In the spectrum of HFC=C\textsuperscript{−}, transitions to the ground-state singlet (\(\tilde{X}^1\text{A}'\)) and two triplet states (\(\tilde{3}\text{A}'\) and \(\tilde{b}^1\text{A}'\)) are observed. In the spectrum of F\textsubscript{2}C=C\textsuperscript{−}, transitions to the \(\tilde{X}^1\text{A}_1\) state and the \(\tilde{3}\text{A}_2\) 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 \(E_b\) 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\textsuperscript{6} is included with these in Table I. The resulting trend is EA(H\textsubscript{2}C=C\textsuperscript{−}) < EA(HFC=C\textsuperscript{−}) < EA(F\textsubscript{2}C=C\textsuperscript{−}). 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.

Substituent results in notable stabilization of the negative ion. The only previous estimates of the electron affinities relied upon appearance potentials for HFC=C\textsuperscript{−} and F\textsubscript{2}C=C\textsuperscript{−}, the heats of formation of the acetylenic forms, and calculated rearrangement barriers.\textsuperscript{10} This procedure gave EA(HFC=C\textsuperscript{−}) \(\geq 2.2 \pm 0.9\) eV and EA(F\textsubscript{2}C=C\textsuperscript{−}) \(\geq 2.2 \pm 0.4\) 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 large separation 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\textsuperscript{−} (\(C\text{\_}s\) symmetry) there are six normal coordinates, which we label as the CCF bend (\(a\)), the out-of-plane bend (\(a'\)), the \(\pi\text{-}\pi^*\) stretch (\(a''\)), the C--C bend (\(c\)), the C--F stretch (\(d\)), and the C--H stretch (\(e\)). For the singlet state of F\textsubscript{2}C=C\textsuperscript{−} (\(C\text{\_}p\)) the totally symmetric modes are the C=C stretch (\(a\)), the C--F symmetric stretch (\(a''\)), and the C--H stretch (\(e\)). For the anion the singlet state of F\textsubscript{2}C=C\textsuperscript{−} (\(C\text{\_}p\)) the non-totally symmetric modes are allowed. Although five vibrational modes are symmetry allowed for HFC=C\textsuperscript{−}, only three vibrational modes are distinctively observed. This is the same number of vibrational modes observed in the spectrum of F\textsubscript{2}C=C\textsuperscript{−} number congestion in the photoelectron spectrum of HFC=C\textsuperscript{−} compared to that of F\textsubscript{2}C=C\textsuperscript{−} is not simply due to a larger number of active vibrational modes.

Equation 38. The resulting trend is EA(H\textsubscript{2}C=C\textsuperscript{−}) < EA(HFC=C\textsuperscript{−}) < EA(F\textsubscript{2}C=C\textsuperscript{−}). 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
vibrational frequencies for each of the electronic states of movibrational coordinate of the singlet vinylidene the simulation and the complexity of the molecule. Experimental quite good, considering the simplicity of the models employed for change in geometry in this transition. The C-F bond length is calculated to be substantially shorter in the neutral than in the cofluorovinylidene are summarized in Table II.

DeLeeuw et al., 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. 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 monofluorovinyldiene are summarized in Table II.

DeLeeuw et al., 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. 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 monofluorovinyldiene are summarized in Table II.

Reaction Coordinate for the Monofluorovinyldiene — 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 of H$_2$C=C: we found that the CH$_2$ rock normal 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$_2$C=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$_2$C=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 CCF bending mode. On the other hand, the lowest frequency mode in HFC=C: according to the calculations of DeLeeuw et al., 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. We have used both normal coordinates involve substantial hydrogen atom motion, only the CCF bend also leads to a straightening of the FCC bond and a decrease in the C-C bond distance.

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

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Figure 3. Photoclectron spectrum (351 nm) of the monofluorovinyldiene anion showing the ground-state singlet (upper portion). The peak corresponding to the adiabatic electron affinity is indicated $\tilde{O}^1$. 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.

Figure 4. Drawings of the CCF and CCH bending modes calculated using a 6-31+G(d,p) basis set in Gaussian 90. 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$^{-1}$).
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Figure 5. Potential energies for HFC=C: along the intrinsic reaction coordinate (IRC) calculated at the HF/6-31+G(d,p) level. The IRC is expressed in mass-weighted internal coordinates relative to the mono-fluorovinylidene local minimum. Calculated molecular geometries are shown to scale at each extremum of the potential energy curve.

Intrinsic Reaction Coordinate (amu$^{-1/2}$ bohr)

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

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<tr>
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<td>905 (25)</td>
<td>1670 (25)</td>
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<td>~890</td>
<td>~1640</td>
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</table>

$^a$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 $\pi$-bond.

Crossings between the frequency curves in Figure 6, with the same vibrational symmetry in C$_2$ 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$_2$ 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: X$^1$A'-state photoelectron spectrum including the origin and first peak in the vibrational progression assigned to the CCF bending mode ($v_6$) 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 $\omega_0$, 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 $\omega_0 = 205$ (30) cm$^{-1}$ and $\omega_{0x} = 14$ cm$^{-1}$ for the singlet Morse parameters. The resulting well depth is $D_e = 0.09$ eV (2 kcal/mol). Varying both $\omega_0$ and $\omega_{0x}$, 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.$^8$, which give a classical barrier of 2.4 kcal/mol; inclusion of zero-point energy corrections$^7$ 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) are not possible.

Singlet F$_2$C=C:. The portion of the photoelectron spectrum showing transitions terminating in the X$^1$A' 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=C$\ddagger$ stretch, and the C=C$\ddagger$ stretch. These vibrational assignments were based upon the calculated frequencies of Gallo and Schafer$^4$, 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=C$\ddagger$ asymmetric frequency is also accurate. This agreement makes it likely that Bürger et al.$^{19}$

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did observe the F,C=C: asymmetric stretch with difluorocetylene 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 510 (25) and 800 (25) cm⁻¹ were assigned to the CF₂ 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 Å (g/mol)⁻¹ for the CF₂ 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.

Figure 8. Photoelectron spectrum of difluorovinylidene (F₂C=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.

Figure 7. Photoelectron spectrum of the ground-state monofluorovinylidene displaying only the vibrational origin and the first neutral vibrational progression (ν₂). The Franck-Condon simulation, shown by the solid line, of the CCF bending mode employed a Morse potential. The best fit was obtained with ω₂ = 205 cm⁻¹ and ω₃x₃ = 14 cm⁻¹. The resulting well depth is D₀ = 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.

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 amu₁/₂ bohr.

Intrinsic Reaction Coordinate (amu₁/₂ bohr)

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Intrinsic Reaction Coordinate (amu₁/₂ bohr)

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Intrinsic Reaction Coordinate (amu₁/₂ bohr)
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 \( \beta \, 3A'' \) 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 feature. The possibility is very remote, however, since it would leave the peak indicated \( \beta \, 3A'' \) to lie underneath the peak marked C-F. This feature must arise from photoelectron detachment of HFC=C: but it cannot be a part of the \( \beta \, 3A'' \) state. In monofluorovinylidene the peak marked 0–0 is \( \sim 7 \) times more intense than the peak indicated \( \beta \, 3A'' \). This indicates that the 0–0 peak belongs to the \( \beta A' \) state and the peak immediately to the right in Figure 9 belongs to the \( \beta A'' \) state. Since the origin for the \( \beta A'' \) state is so weak, the C-C 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 C-C stretch expected for the \( \beta A'' \) transition, and the intensity ratio of the 0–0 peak to the peak indicated \( \beta \, 3A'' \), all support the assignment of peak 0–0 to the \( \beta A'' \) state. Our inability to attribute the peak at 3.038 eV to mass contamination and the similarity in intensity to the vinylidene \( \beta \, 3A'' \) state are strong evidence that this peak belongs to the \( \beta A'' \) state. This must also be the vibrational origin of this state, since little else was observed in the photoelectron spectrum of the vinylidene \( \beta \, 3A'' \) state.6 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 \( \beta A'' \) state unidentified. The measured excitation energies to each of triplet states are summarized in Table IV.

In the \( \beta \, 3A'' \) 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 (\( \sigma \)), the out-of-plane bend (\( \pi' \)), and the C-F stretch (\( \pi'' \)). 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 A (g/mol\(^{1/2}\)) for the CCF bend and 0.25 A (g/mol\(^{1/2}\)) for the C-F stretch.

In the photoelectron spectrum of F\(_2\)C=C:: shown in Figure 2, very little vibrational structure is observed in the excited \( \beta \, 3A'' \) 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 \( \beta \, 3A'' \) excited triplet state of difluorovinylidene is not observed. By comparison to H\(_2\)CC and HFC\(_2\), we would expect this transition to have a strong intensity. Its absence implies

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

<table>
<thead>
<tr>
<th>species</th>
<th>( \Delta S - T )</th>
<th>triplet EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)C=C::</td>
<td>2.065 (6) (( \beta , 3B_2 ))</td>
<td>2.555 (6)</td>
</tr>
<tr>
<td>HFC=C:</td>
<td>2.754 (20) (( \beta , 3A'_1 ))</td>
<td>3.244 (20)</td>
</tr>
<tr>
<td>H(_2)CC</td>
<td>1.320 (9) (( \beta , 3A'' ))</td>
<td>3.038 (6)</td>
</tr>
<tr>
<td>F(_2)C=C::</td>
<td>0.924 (9) (( \beta , 3A'' ))</td>
<td>3.179 (6)</td>
</tr>
</tbody>
</table>

*Reference 5.*
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, mono- fluorovinylidene, 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$_2$C=C:) > (HFC=C:) > (F$_2$C=C:). The electron affinities increase nearly a factor of 5 from H$_2$C=C: (0.490 eV) to F$_2$C=C: (2.255 eV) with fluorine substitution. This 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 other 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 $\sigma$-bonding orbital. Thus the energies of the anion and both triplets for the monofluorovinylidene and difluorovinylidene decrease relative to the singlet.

**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.

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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.

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