# Heterogeneously Substituted Radicals and Carbenes: Photoelectron Imaging of the FC(H)CN<sup>-</sup> and FCCN<sup>-</sup> Anions

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**ABSTRACT:** This work represents the next step in the studies of heterogeneous substitution effects in cyanohalo radicals and carbenes. Negative-ion photoelectron imaging was used to investigate the substituted radical and carbene derivatives of fluoroacetonitrile. We report a closed-shell singlet ground state for cyanofluorocarbene, FCCN, with a directly measured adiabatic electron affinity EA =  $2.081 \pm 0.002$  eV and a singlet—triplet gap of  $\Delta E_{\text{S-T}} = 0.42 \pm 0.04$  eV, estimated through a combination of experimental and theoretical results. The open-shell singlet <sup>1</sup>A" state was also observed experimentally. The cyanofluoromethyl radical, FC(H)CN, was similarly estimated to have an EA of  $1.53 \pm 0.08$  eV. This value was used to estimate the C–H bond dissociation energy (BDE) of fluoroacetonitrile, DH<sub>298</sub> = 90.7  $\pm 2.8$  kcal mol<sup>-1</sup>. The results are discussed in comparison with results for other fluoro-



and cyano-substituted radicals and carbenes, and in light of our recent work on the radical and carbene derivatives of chloroacetonitrile. The estimated  $\Delta E_{S-T}$  of FCCN agrees well with the general trend of similar carbenes. We also find that, similar to chloroacetonitrile, the low C–H BDE of fluoroaceotnitrile indicates a synergistic stabilization of the corresponding radical by a  $\pi$  donor (halogen) and  $\pi$  acceptor (CN).

# 1. INTRODUCTION

Radicals and carbenes are reactive intermediates that play important roles in chemical reactions. Radicals have one unpaired electron and their stability is reflected in the bond dissociation energy (BDE) of the corresponding closed-shell molecule. The structures and energetics of many organic radical are affected by inductive effects and  $\pi$  resonance interactions with the substituents.<sup>1,2</sup> The properties of carbenes are largely determined by the two nonbonding electrons distributed between the nearly degenerate  $\sigma$  and  $\pi$  orbitals, nominally localized on a carbon center. The two-electrons-in-two-orbitals motif allows for close-lying  $...\sigma^2\pi^0$  and  $...\sigma^1\pi^1$  electron configurations.<sup>3</sup> The substituent groups affect the stability of the orbitals and, therefore, the energetic ordering of the singlet and triplet states,<sup>4</sup> as well as the magnitude of the singlettriplet splitting,  $\Delta E_{S-T}$ . The splitting dictates the reactivity of the carbene, as reaction mechanisms often vary for the singlet and triplet species.<sup>5,6</sup>

Anion photoelectron imaging is a uniquely useful tool for examining these highly reactive molecules. The negative ions of radicals and carbenes can be formed in the gas phase by H<sup>+</sup> or H<sub>2</sub><sup>+</sup> abstraction reactions of a closed-shell precursor with O<sup>-</sup>, produced in situ.<sup>7,8</sup> Although the simplest neutral radicals are doublets in their ground states, their anions are closed-shell singlet species. The anions of both singlet and triplet groundstate carbenes, on the other hand, are radical anions with the same canonical ... $\sigma^2 \pi^1$  electron configuration.<sup>3</sup> In photodetachment, a photon of sufficient energy can access the singlet (... $\sigma^2 \pi^0$ ) or the triplet (... $\sigma^1 \pi^1$ ) states of the carbene by removing an electron from the respective  $\pi$  or  $\sigma$  orbitals of the anion. Detachment from the  $\sigma$  orbital can additionally access the higher-lying open-shell singlet (... $\sigma^1 \pi^1$ ) state. Due to different characters and/or symmetry properties of the  $\pi$  and  $\sigma$  orbitals, these photodetachment processes are characterized, in general, by distinct photoelectron angular distributions (PAD). The PADs are thus instrumental in spectroscopic assignments and may assist in a straightforward determination of the ground-state multiplicity of a neutral carbene.

Many substituents involved in  $\pi$  and  $\sigma$  interactions have been studied previously.<sup>9,10</sup> Halogens act as strong  $\sigma$  withdrawers and  $\pi$  donors; the cyano group is often described as a pseudohalogen for its similarly strong  $\sigma$  withdrawing properties but acts as a  $\pi$  acceptor rather than a  $\pi$  donor. Both types of substituents, in general, increase radical stability. However, with regard to the singlet-triplet splitting in the corresponding carbenes, the halogen and CN substituents are known to act in opposition, with most halogens (F, Cl, and Br) favoring singlet ground states<sup>11,12</sup> and the CN stabilizing the triplet.<sup>3,13,14</sup>

Among the many carbene and radical species that have been studied previously, most have been either singly (i.e., :CHR, · CH<sub>2</sub>R) or homogeneously (i.e., :CR<sub>2</sub>, ·CHR<sub>2</sub>, ·CR<sub>3</sub>) substituted (here, R is either a halogen<sup>12,15,16</sup> or CN<sup>14</sup>). We target heterogeneously substituted species, with one halogen and one cyano substituent. We have recently investigated one particular case of such species, derived from the chloroacetonitrile (CH<sub>2</sub>ClCN) precursor.<sup>17</sup> The corresponding carbene (ClCCN) was found to have nearly degenerate singlet and triplet states, whereas the radical chemistry displayed some

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synergistic stabilization, indicated by the relatively low C–H BDE of chloroacetonitrile. Continuing this theme, fluoroacetonitrile is used as a precursor in the present work. Fluorine has a significantly higher  $\sigma$  withdrawing power than chlorine and, because of the size of its 2p orbitals, considerably stronger  $\pi$  donation effect. The fluoro- and difluorocarbenes show significantly destabilized triplet states,<sup>11,18</sup> whereas the fluoro-substituted methanes show a trend of increasing C–H BDE, indicating less stable radicals.<sup>19</sup>

We report our findings for cyanofluoromethyl radical and cyanofluorocarbene using anion photoelectron imaging spectroscopy. We find that the BDE of fluoroacetonitrile indicts a synergistic (captodative)<sup>20</sup> effect in the corresponding radical, analogous to the case chloroacetonitrile.<sup>17</sup> The difference in the BDEs of chloro- and fluoroacetonitriles is consistent with that when chloro- and fluoromethanes are compared. We report a singlet ground state for the FCCN carbene with a significant  $\Delta E_{\text{S-T}}$ . The results for the radical and carbene species are compared to results for the single-substituted and homogeneously double-substituted methyl species.

# 2. EXPERIMENTAL AND THEORETICAL METHODS

The photoelectron imaging experiments were carried out using a custom-built time-of-flight mass-spectrometer combined with a velocity-map<sup>21</sup> imaging<sup>22</sup> assembly, described in detail elsewhere.<sup>23</sup> A carrier gas, either O<sub>2</sub> or N<sub>2</sub>O, was flowed over fluoroacetonitrile (CH<sub>2</sub>FCN) and the resulting mixture was introduced into the source chamber using a pulsed supersonic nozzle (General Valve 9) operated at a repetition rate of 20 or 50 Hz, to match that of the laser. Atomic oxygen radical anions were formed by slow secondary electron dissociative attachment to the carrier gas, and ions of interest were produced through the well-documented  $H^+$  or  $H_2^+$  abstraction reactions.<sup>7,8</sup> The resulting anions were extracted into the Wiley-McLaren time-of-flight mass-spectrometer, where they were further accelerated to 3 keV and separated by the mass-tocharge ratio. The ion beam was intersected by a pulsed, linearly polarized laser beam, timed to interact only with an ion of interest. The second, third, and forth harmonics of a Spectra Physics, Inc. Quanta Ray Nd:YAG laser (50 Hz repetition rate) was used to produce 532 (4 mJ/pulse) nm, 355 nm (2 mJ/ pulse), and 266 nm (800  $\mu$ J/pulse) radiation by doubling, tripling, or quadrupling the fundamental output. A Continuum, Inc. ND6000 dye laser pumped by a Surelite II Nd:YAG (20 Hz) was used with Rhodamin 590 to produce 612 nm light, which was frequency-doubled to produce 306 nm (6 mJ/pulse).

Photoelectrons were projected by a series of velocity-map imaging electrodes onto a position-sensitive microchannel plate detector coupled to a P43 phosphor screen. The resulting images were recorded by a charge-coupled device (CCD) camera. Typical raw images were collected over  $\sim 10^6$  experimental cycles. The complete three-dimensional distributions were reconstructed<sup>24</sup> using the inverse Abel transformation, implemented in the BASEX program.<sup>25</sup> The energy scale was calibrated using the well-known<sup>26,27</sup> photodetachment transition of O<sup>-</sup>.

Electronic structure calculations involving geometry optimization were carried out at the CCSD level using the Gaussian 09 software package.<sup>28</sup> After the geometries for the anion and neutral ground and excited states were optimized, the normalmode analysis was used to confirm that the resulting structures corresponded to true potential minima. Equation-of-motion (EOM) ionization-potential (IP) and spin-flip (SF)<sup>29–32</sup> calculations included diagonal triples  $(dT)^{33}$  corrections for CCSD energy and were performed for the above optimized geometries using the Q-Chem 4.0 software package.<sup>34</sup>

#### 3. RESULTS AND ANALYSIS

**3.1. Cyanofluorocarbene.** Photoelectron images of FCCN<sup>-</sup> were collected at 532, 355, 306, and 266 nm. The images and corresponding spectra are shown in Figure 1. The spectra are plotted versus electron binding energy (eBE), defined as eBE =  $h\nu$  – eKE, where eKE is electron kinetic energy.



**Figure 1.** Photoelectron images and reconstructed spectra of FCCN<sup>-</sup> obtained at (a) 532 nm, (b) 355 nm, (c) 306 nm, and (d) 266 nm. Double-sided arrows ( $\varepsilon$ ) indicate the laser polarization direction. The left halves of the composite images are raw data, and the right halves are the corresponding Abel-inverted results. The stick plot in (d) shows the EOM-IP/SF-CCSD(dT)/aug-cc-pVTZ energies of the vertical transitions from the anion to the closed-shell singlet (<sup>1</sup>A'), triplet (<sup>3</sup>A''), and open-shell singlet (<sup>1</sup>A'') states of the neutral.

At 532 nm (Figure 1a), the photon energy is just above the detachment threshold of the anion. The photoelectron spectrum consists of two well-resolved peaks, separated by  $\sim$ 1800 cm<sup>-1</sup>. The outermost band in the image, corresponding to the lowest-eBE spectral peak, is assigned to the vibrational origin of the photodetachment transition, allowing for a robust and precise determination of the adiabatic electron affinity of



**Figure 2.** Manifolds of the low-lying electronic states of neutral FCCN calculated using the EOM-SF-CCSD(dT)/aug-cc-pVTZ method for the equilibrium geometries of (a) the anion, (b) the singlet (<sup>1</sup>A') neutral, and (c) the triplet neutral. The geometries were optimized at the CCSD/aug-cc-pVTZ level of theory. The bond lengths are given in Angstroms. For each of the three geometries, the vertical ordering of the <sup>1</sup>A', <sup>3</sup>A'' ( $M_S = 0$ ), and <sup>1</sup>A'' states is indicated, with the energies given in electronvolts, relative to the lowest state *at that geometry*. The dominant electron configurations for each of the target states are also indicated, with the orbitals shown corresponding to the nonbonding carbene orbitals, 12a' ( $\sigma$ ) and 3a'' ( $\pi$ ). The spectrum shown along the left side of the figure is the 266 nm experimental spectrum reproduced from Figure 1d.

FCCN, EA =  $2.081 \pm 0.002$  eV. The uncertainty range is narrower than the 0–0 bandwidth; it was determined as the standard deviation of the peak position for several independent experimental runs.

At 355 nm (Figure 1b), two transitions are apparent in the image, with the inner transition displaying a hint of a vibrational progression. The outer (lower-eBE) transition displays a prominent perpendicular anisotropy with respect to the laser polarization direction, whereas the inner (higher-eBE) transition has a notable parallel anisotropy. Qualitatively similar anisotropy properties of the two transitions persist at 306 nm (Figure 1c) and 266 nm (Figure 1d), with an additional, third transition appearing in the center of the image at the latter wavelength.

Previous examples of photoelectron imaging have shown that the assignment of the singlet and triplet states of carbenes can be aided by the anisotropy of the corresponding photodetachment transitions. The canonical electron configuration of a ground-state carbene anion is  ${}^{2}A'': ...\sigma^{2}\pi^{1}$ , where  $\sigma$  and  $\pi$  are the nominal sp<sup>2</sup> and p nonbonding orbitals of the carbene center, respectively. The transition to the singlet carbene ( ${}^{1}A': ...\sigma^{2}\pi^{0}$ ) removes an electron from the out-of-plane  $\pi$  orbital. Likewise, a transition to the triplet ( ${}^{3}A'': ...\sigma^{1}\pi^{1}$ ) requires the detachment from the  $\sigma$  orbital, which lies in the plane of the molecule and has partial s character. It is expected that the singlet transition will display a predominantly perpendicular anisotropy within a moderate eKE regime, in contrast to the triplet, which is expected to be parallel or nearly isotropic.<sup>35,36</sup> The anion of cyanofluorocarbene provides an excellent illustration of these general predictions. Two transitions with distinct anisotropy properties are clearly seen in each of the 355, 306, and 266 nm photoelectron images. The outermost transition in each case is notably perpendicular, whereas the next higher-eBE transition is predominantly parallel. On the basis of this observation, we assign the outer, lower-eBE transition to  ${}^{1}A'$  state of the carbene, and the inner, higher-eBE transition to the  ${}^{3}A''$  state.

The above determination of the adiabatic EA =  $2.081 \pm 0.002$  eV (from Figure 1a) thus corresponds to the <sup>1</sup>A' singletstate carbene. Because the lower-binding-energy side of the triplet transition overlaps with the singlet, the unambiguous determination of that band's onset is not possible from the spectrum and the exact value of  $\Delta E_{\text{S-T}}$  cannot be determined.

The vertical detachment energy, VDE, is an important property for comparison with theoretical predictions. On the basis of the positions of the singlet band maxima in the 355, 306, and 266 nm spectra (Figure 1b–d), we estimate the VDE of FCCN<sup>-</sup> corresponding to the singlet state of the neutral as  $2.40 \pm 0.01$  eV. The VDE of the triplet transition is similarly determined from the 306 and 266 nm spectra as  $3.20 \pm 0.04$  eV.

The additional weak transition at the center of the 266 nm image is a high-binding-energy feature with an onset at about 4.2 eV. The open-shell singlet state,  ${}^{1}A'': ...\sigma^{1}\pi^{1}$ , similar to the one observed in other carbenes, is a likely candidate for the assignment of this band.

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The optimized geometries of the cyanofluorocarbene anion and the singlet and triplet states of the neutral, derived from CCSD/aug-cc-pVTZ calculations, are displayed in Figure 2. In line with other carbenes, the bond angles at the central carbon are similar for the FCCN<sup>-</sup> anion and singlet FCCN (105.7° vs  $107.2^{\circ}$ ), whereas the triplet state is characterized by a more open carbene angle  $(128.3^{\circ})$ . These geometric properties are consistent with the states' nominal electron configurations. The double occupancy of the in-plane lone-pair  $\sigma$  orbital in the anion and the singlet favors the similarly sharp bond angles in these species, whereas the single-occupancy of this orbital in the triplet allows for a less constrained, more linear geometry. The  $\pi$  orbital population, on the other hand, has no significant effect on the carbene angle. The predicted angle at the central carbon in triplet FCCN is consistent with the trend exhibited by other carbenes: the angle grows more acute with a decreasing stability of the triplet state;<sup>17</sup> therefore, carbenes with halogen groups tend to have smaller bond angles in their triplet states. Based on the present calculations, the main geometric difference between the FCCN<sup>-</sup> anion and the FCCN singlet is in the respective C–F bond lengths, 1.427 Å vs 1.298 Å. This property does not change notably from the singlet to the triplet carbene. The high electronegativity of fluorine is responsible for its large effective charge in the FCCN<sup>-</sup>, significantly weakening the anionic C-F bond.

The CCSD/aug-cc-pVTZ calculations were also used to predict the VDEs of the anion, corresponding to the detachment to the singlet and triplet carbene species, as well as the adiabatic EAs of the neutral states. The results are summarized in the first row of Table 1. The VDE was

# Table 1. Energetic Parameters (eV) Obtained from the Electronic Structure Calculations on Cyanofluorocarbene and Its Anion

	adiabatic EA		VDE		
method <sup>a</sup>	singlet ( <sup>1</sup> A')	triplet ( <sup>3</sup> A")	to singlet ( <sup>1</sup> A')	to triplet ( <sup>3</sup> A")	$\Delta E_{ ext{S-T}}$
CCSD	2.093	2.462	2.391	3.097	0.369
EOM-IP/SF- CCSD(dT)	2.045 <sup>b</sup>	2.470 <sup>b</sup>	2.351 <sup>c</sup>	3.168 <sup>c</sup>	0.425 <sup>d</sup>
experiment	2.081(2)	$2.50(4)^{e}$	2.40(2)	3.20(4)	$0.42(4)^{3}$

<sup>a</sup>All calculations used the aug-cc-pVTZ basis set. <sup>b</sup>Calculated by combining the relevant energy gaps, determined from the EOM-SF-CCSD(dT) calculations, with the anion VDE, determined using the EOM-IP-CCSD(dT) method. Specifically, EA(<sup>1</sup>A') = VDE – (singlet relaxation energy); EA(<sup>3</sup>A'') = EA(<sup>1</sup>A') +  $\Delta E_{S-T}$ . <sup>c</sup>Calculated using the EOM-IP-CCSD(dT) method. <sup>d</sup>Calculated using the EOM-SF-CCSD(dT) results for the singlet and triplet geometries (Figure 2b,c). <sup>e</sup>Estimated using eq 1, the experimental VDE of the triplet, and the results of the EOM-SF-CCSD(dT) calculations. <sup>f</sup>Calculated using the experimentally determined EA(<sup>1</sup>A') = 2.081 ± 0.002 eV, and the estimated value of EA(<sup>3</sup>A'') = 2.50 ± 0.04 (see footnote e above).

determined as the electronic energy difference between the target neutral state and the anion, both at the optimized geometry of the anion. The EA is defined as the difference in electronic energy of the geometry-optimized neutral and that of the anion. The results are in reasonably good agreement with the experimental values (also included in Table 1), particularly for the singlet band.

The VDEs of the anion were also determined using the EOM-IP-CCSD(dT) methodology<sup>29,33</sup> (IP, for brevity). In these calculations, the singlet (<sup>1</sup>A': ...  $\sigma^2 \pi^0$ ) and triplet (<sup>3</sup>A'':

 $...\sigma^{1}\pi^{1}$ ) states of the neutral carbene were accessed by removing electrons from the  $\pi\alpha$  or  $\sigma\beta$  spin—orbitals of the <sup>2</sup>A":  $...\sigma^{2}\pi^{1}$  anion reference. The VDEs predicted using the IP method are included in Table 1, and indicated as by the respective orange and blue sticks in Figure 1d. As seen from the figure, the agreement between the theory predictions and the experimentally observed positions of the singlet and triplet band maxima is very good.

The diradical motif of carbenes' electronic structure gives rise to several close-lying electronic states with inherently multiconfigurational wave functions. To describe these low-lying states of FCCN, we employed the EOM-SF-CCSD(dT) method<sup>29,33</sup> (SF, for brevity), based on the spin–flip methodology pioneered by Krylov.<sup>30</sup> In these calculations, the robust high-spin ( $M_s = 1$ ) triplet reference,  ${}^{3}A'': ...\sigma^{1}\pi^{1}$ , and one-electron spin–flip excitation operators were used to produce several electron configurations, which were then combined to yield low-energy solutions with the appropriate symmetry of the target states. Consistent with our past investigation of chlorocyanocarbene<sup>17</sup> and on the basis of Krylov's recommendation,<sup>37</sup> the low-spin ( $M_s = 0$ ) component of the triplet was used to determine the singlet—triplet energy gaps.

The results of the SF calculations are summarized in Figure 2, where the relative energies of the closed-shell singlet (<sup>1</sup>A'), the triplet (<sup>3</sup>A''), and the open-shell singlet (<sup>1</sup>A'') states of FCCN are indicated for three different molecular geometries, corresponding to the CCSD/aug-cc-pVTZ optimized structures of (a) the FCCN<sup>-</sup> anion, (b) the <sup>1</sup>A' neutral FCCN, and (c) the <sup>3</sup>A'' neutral FCCN. The energy values for each vertical manifold are given in electronvolts, relative to the lowest state at that geometry. The adiabatic energy differences between the lowest states at different geometries, i.e., the singlet relaxation energy from geometry (a) to geometry (b) and the adiabatic singlet–triplet splitting  $\Delta E_{S-T}$  (b–c), are also indicated.

The results for the anion geometry (Figure 2a) can be directly compared to the experimental band positions in Figure 1. The 266 nm photoelectron spectrum is reproduced along the left-side margin of Figure 2 to illustrate the correspondence of the spectral peak positions to the predicted state energies. The vertical gap between the <sup>1</sup>A' and <sup>3</sup>A" states at the anion geometry (not to be confused with the adiabatic singlet-triplet splitting,  $\Delta E_{\text{S-T}}$ ) is 0.815 eV, per SF calculations, which agrees very well with the experimental spectra, as well as the IP result of  $VDE(^{3}A'') - VDE(^{1}A') = 0.817$  eV. The relaxation energy of the singlet carbene from the anion geometry (accessed in a vertical detachment process) to the equilibrium structure is determined to be 0.306 eV (per SF). Combined with the  $VDE(^{1}A') = 2.351 \text{ eV}$  (IP), this result places the fully relaxed singlet at 2.045 eV above the anion. The adiabatic singlettriplet splitting is determined to be  $\Delta E_{S-T} = 0.425$  eV (per SF).

The EA of the triplet carbene could not be determined directly in the experiment, because the onset of the triplet band in Figure 1 overlaps the singlet. However, it can be estimated using a combination of experimental results and theoretical predictions. Because the relaxation energy of triplet FCCN from the anion geometry to the equilibrium structure equals the difference between the corresponding VDE and the triplet-state EA, the latter can be estimated by the relationship:

$$EA_{est} = VDE_{exp} - \Delta E_{rel}$$
(1)

where  $\Delta E_{\rm rel} = 0.696$  eV, as determined from the SF calculations, and VDE<sub>exp</sub> = 3.20 ± 0.04 eV is the experimental

VDE value corresponding to the triplet band. Using eq 1, we estimate the electron affinity of the triplet as  $EA_{est}(^{3}A'') = 2.50 \pm 0.04 \text{ eV}$  (Table 1). The uncertainty range of the estimated EA reflects only that of the experimentally determined VDE. Further, using the experimental EA value of the singlet and estimated EA value of the triplet, the singlet—triplet splitting of the carbene can be calculated as  $\Delta E_{\text{S-T}} = 0.42 \pm 0.04 \text{ eV}$ , in agreement with the SF result of  $\Delta E_{\text{S-T}} = 0.425 \text{ eV}$ .

Thus, FCCN has a singlet ground state, by a wide margin. In comparison, the singlet and the triplet states of ClCCN are effectively degenerate.<sup>17</sup> These results are in agreement with the trend observed in HCCl and HCF, where the F-substituent stabilizes the singlet over the triplet by 0.46 eV more than Cl. The  $\Delta E_{\text{S-T}}$  determined here for FCCN is, on the other hand, smaller than that of HCF (0.65 ± 0.02 eV),<sup>11,18</sup> indicating that, as discussed in the Introduction, the cyano group stabilizes the triplet configuration and narrows the energy gap between the states.

The SF calculations also predict that at the anion geometry the open-shell singlet  ${}^{1}A''$  state of FCCN lies 2.292 eV above the closed-shell singlet,  ${}^{1}A'$  (Figure 2a). Using the experimental value of 2.40  $\pm$  0.02 eV for the singlet-band VDE, we estimate the VDE of the  ${}^{1}A''$  state to be around 4.69 eV (red stick in Figure 1d), just above the 266 nm photon energy (4.66 eV). This prediction is consistent with the appearance of a weak band at the center of the 266 nm photoelectron image in Figure 1d.

The open-shell singlet comes much closer in energy to the triplet state at the triplet geometry (Figure 2c), suggesting that the relaxed geometry of the open-shell singlet is more similar to the triplet geometry than that of the anion or the closed-shell singlet. This is not surprising, because the <sup>1</sup>A" and <sup>3</sup>A" states arise from the same nominal electron configuration  $(...\sigma^{1}\pi^{1})$ . It can be further predicted that, similar to the triplet band, the open-shell singlet transition should have a broad Franck–Condon envelope.

**3.2.** Cyanofluoromethyl Radical. The 355 nm photoelectron image and the corresponding spectrum of  $FC(H)CN^{-}$  are presented in Figure 3. The image displays slightly negative



**Figure 3.** Photoelectron image and spectrum of  $FC(H)CN^-$  at 355 nm. The double-sided arrow ( $\varepsilon$ ) indicates the direction of laser polarization. The red curve is a scaled Gaussian function fitted to the spectrum. \*The EA value is determined from the experimental VDE in conjunction with the CCSD/aug-cc-pVTZ results, using eq 1.

photodetachment anisotropy with respect to laser polarization direction. The spectrum consists of a single broad, vibrationally unresolved band, similar to that observed for the anion of the chlorocyanomethyl radical,  $ClC(H)CN^-$ . In both cases, the broad band indicates a large geometry change between the anion and the neutral. The  $FC(H)CN^-$  band in Figure 3 was

fitted with a scaled Gaussian function, including an  $eKE^{1/2}$  prefactor to account for the low-eKE behavior of the photodetachment cross sections.<sup>38,39</sup> The VDE = 2.13 ± 0.04 eV, determined from the fit, corresponds approximately to the position of the band maximum. Though no clear band onset is discernible, we estimate EA ~ 1.5 eV corresponding to the spectral region where the signal-to-noise ratio increases sharply to ~3.

The geometries of the anion and neutral radical species were optimized at the CCSD level using the aug-cc-pVTZ basis set. The resulting structures are shown in Figure 4, with the



**Figure 4.** CCSD/aug-cc-pVTZ optimized geometries of FC(H)CN<sup>-</sup> and FC(H)CN. The anion has a trigonal pyramidal structure, and the neutral radical is planar. The bond lengths are indicated in Angstroms. Other optimized structural parameters are as follows. Anion:  $\angle$ F-C-C = 108.0°,  $\angle$ C-C-H = 109.8°,  $\angle$ C-C-N = 173.3°, dihedral(F-C-C-N) = 123.8°, dihedral(H-C-C-N) = -122.3°. Neutral (planar):  $\angle$ F-C-C = 118.5°,  $\angle$ C-C-H = 125.2°,  $\angle$ C-C-N = 178.2°, dihedral(F-C-C-N) = 180°.

quantitative structural parameters summarized in the figure and its caption. Similar to the case for ClC(H)CN<sup>-</sup>, the relaxed geometry of FC(H)CN<sup>-</sup> is trigonal pyramidal, whereas that of the neutral radical, FC(H)CN, is trigonal planar. The large geometry difference between FC(H)CN<sup>-</sup> and FC(H)CN is consistent with the broad photoelectron band in Figure 3. The same calculations predict an adiabatic EA = 1.410 eV, which is in good agreement with the above experimental estimation. Similarly, the predicted VDE = 2.015 eV is close to the experimental value of 2.13  $\pm$  0.04 eV.

Although an adiabatic EA cannot be determined directly from the experimental spectrum, an estimate is obtained using the experimental VDE value in a manner similar to the EA of the triplet carbene. Specifically, we use eq 1 with the experimental VDE value and a relaxation energy,  $\Delta E_{\rm rel} =$  VDE – EA, determined from CCSD calculations.<sup>16,17</sup> Per the results summarized in Table 2, the calculated  $\Delta E_{\rm rel}$  values, depending on the basis set used, all fall within a 0.06 eV wide range. Substituting the result obtained with the largest basis set used (aug-cc-pVTZ),  $\Delta E_{\rm rel} = 0.605$ , and VDE<sub>exp</sub> = 2.13 ± 0.04 eV into eq 1, we estimate the EA of the FC(H)CN radical as

Table 2. Energetic Parameters (eV) Obtained from the Electronic Structure Calculations on Cyanofluoromethyl Radical and Its Anion

method/basis set	EA	VDE	$\Delta E_{\rm rel}$
CCSD/6-311++G**	1.226	1.859	0.633
CCSD/aug-cc-pVDZ	1.393	2.058	0.665
CCSD/aug-cc-pVTZ	1.410	2.015	0.605
experimental	$1.53(8)^{a}$	2.13(4)	

<sup>*a*</sup>Determined from the experimentally determined VDE in conjunction with the CCSD/aug-cc-pVTZ results using eq 1.

 $1.53 \pm 0.08$  eV. The above confidence range is a combination of the 0.04 eV uncertainty in the experimental VDE value and a similar spread in the calculated  $\Delta E_{\rm rel}$  values.

**3.3.** C–H Bond Dissociation Energy of Fluoroacetonitrile. The EA of the cyanofluoromethyl radical, FC(H)CN, obtained in section 3.2, can be used for an indirect determination of the first C–H BDE of fluoroacetonitrile, DH<sub>298</sub>, by way of the general gas-phase acidity–electron affinity cycle. The cycle is represented by the equation:<sup>2,40</sup>

$$DH_{298}(R-H) = \Delta_{acid}H_{298}(RH) + EA(R) - IE(H)$$
  
+ [thermal corrections] (2)

where R = FC(H)CN,  $\Delta_{acid}H_{298}(RH) = 369.0 \pm 2.1 \text{ kcal mol}^{-1}$ is the gas-phase acidity of fluoroacetonitrile, <sup>41</sup> i.e., the enthalpy of the reaction  $CH_2FCN \rightarrow H^+ + CHFCN$  at room temperature,  $EA(R) = 1.53 \pm 0.08 \text{ eV}$  is the EA of the radical determined in section 3.2, and  $IE(H) = 313.6 \text{ kcal mol}^{-1}$  is the ionization energy of the hydrogen atom (13.60 eV).<sup>42</sup> The thermal corrections are ~0.3 kcal mol<sup>-1</sup> and can be neglected in comparison to the larger experimental uncertainties.<sup>40</sup> Using these values, the first C–H BDE of fluoroacetonitrile is determined to be  $DH_{298} = 90.7 \pm 2.8 \text{ kcal mol}^{-1}$ . For comparison, Table 3 lists the C–H BDEs of some other

Table 3. C–H Bond Dissociation Energies (DH<sub>298</sub>) and Radical Stabilization Energies (RSE) of Selected Halo- and Cyano-Substituted Methanes (kcal mol<sup>-1</sup>)

species	DH <sub>298</sub>	ref	RSE <sup>a</sup>
$CH_4$	$104.9 \pm 0.4$	2	0
fluoromethanes			
CH <sub>3</sub> F	$103.2\pm1.0$	19	$1.7 \pm 1.1$
$CH_2F_2$	$106.4 \pm 0.7$	19	$-1.5 \pm 0.8$
CHF <sub>3</sub>	$106.7 \pm 1.0$	19	$-1.8 \pm 1.1$
chloromethanes			
CH <sub>3</sub> Cl	$100.1\pm0.6$	19	$4.8 \pm 0.7$
$CH_2Cl_2$	$95.7 \pm 0.5$	19	$9.2 \pm 0.6$
CHCl <sub>3</sub>	$93.8 \pm 0.6$	19	$11.1 \pm 0.7$
cyanomethanes			
CH <sub>3</sub> CN	$94.2 \pm 2.0$	45, 46	$10.7 \pm 2.0$
$CH_2(CN)_2$	$88.7 \pm 2.1$	17, 46	$16.2 \pm 2.1$
$CH(CN)_3$	unknown		
cyanohalomethanes			
CH <sub>2</sub> ClCN	$87.0 \pm 2.7$	17	$17.9 \pm 2.7$
CH <sub>2</sub> FCN	$90.7 \pm 2.8$	this work	$14.2 \pm 2.8$
<sup><i>a</i></sup> The radical stabilization DH <sub>298</sub> (CH <sub>3</sub> -H) - DH <sub>2</sub>	on energies ar <sub>298</sub> (R–H).	e calculated as	RSE(R-H) =

halogen and cyano-substituted molecules. For the ease of comparison, the table includes the relative stabilization energies (RSE) of these compounds, calculated as the BDE of methane relative to that of the given molecule.<sup>43</sup>

Similar to chloroacetonitrile, fluoroacetonitrile has a low BDE. Of the species in Table 3, only  $CH_2(CN)_2$  and  $CH_2CICN$  have lower BDEs. The RSE of fluoroacetonitrile is 14.2 kcal mol<sup>-1</sup>, which is measurably greater than the combined RSEs of fluoromethane (1.7 kcal mol<sup>-1</sup>) and cyanomethane (10.7 kcal mol<sup>-1</sup>). This is similar to the effect of the heterogeneous CN and Cl substitution in chloroacetonitrile on the corresponding radical stability.<sup>17</sup> These findings suggest that the heterogeneously substituted cyano-halo-radicals benefit from a cooperative, synergistic interaction of the unsaturated  $\pi$ 

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resonance attributed to CN and the  $\pi$  donation due to the halogen substituents. A captodative combination of these effects yields a radical of increased stability.<sup>20</sup>

# 4. EFFECTS OF HETEROGENEOUS SUBSTITUTION

Both halogens and the cyano-group are strong  $\sigma$  withdrawers. In relation to the carbene,  $\sigma$  withdrawal from both types of substituents stabilizes the singlet state, because paring both electrons in the carbene  $\sigma$  orbital contributes more electron density to the hybridized  $\sigma$  system than the triplet configuration does.

In the  $\pi$  system, any appropriate  $\pi$  orbitals of a substituent will mix with the nonbonding  $2p(\pi)$  orbital on the carbene center. Molecular orbital diagrams for carbenes with different types of substituents are shown in Figure 5, with the orbital



**Figure 5.** Schematic molecular orbital diagrams illustrating the interaction of the  $\pi$  and  $\sigma$  orbitals on the carbene center with different types of substituents: (a)  $\pi$  donor, (b)  $\pi$  acceptor, and (c)  $\pi$  donor and  $\pi$  acceptor (heterogeneous double-substitution). The double-sided arrows on the right in each case indicate the resulting splitting between the carbene  $\sigma$  orbital and lowest available  $\pi$  vacancy. The MO populations shown correspond to a triplet carbene.

populations shown corresponding to the triplet state.<sup>3</sup> Because halogens act as  $\pi$  donors, the resulting  $\pi$  orbitals of the carbene molecule must contain the two  $\pi$  electrons of the halogen. The lower energy orbital of this mixed pair is therefore occupied in any configuration, and the nonbonding electron of the carbene may only occupy the higher-energy orbital of the pair, as illustrated in Figure 5a. This increases the gap between the  $\sigma$ and the lowest vacant  $\pi$  orbital, having the effect of raising the energy of the triplet state and increasing the  $\Delta E_{\text{S-T}}$ . In contrast, the cyano group is a  $\pi$  acceptor; it has a  $\pi$  system like a halogen but adds no additional electrons. The mixing, therefore, has the effect of creating a lower energy  $\pi$  orbital for a nonbonding carbene electron (Figure 5b), lowering the energy of the triplet state and decreasing the  $\Delta E_{S-T}$ .

When both a  $\pi$  accepting (CN) and a  $\pi$  donating (halogen) substituent are present in a heterogeneously substituted carbene, there are three distinct  $\pi$  interactions (acceptor-carbene center, donor-carbene center, and donor-acceptor) and therefore three mixed  $\pi$  orbitals (Figure 5c). In general, then, the triplet state cannot be destabilized as much as with only the  $\pi$  donating group. Thus,  $\Delta E_{\text{S-T}}$  is expected to be intermediate between the cases of either substituent alone.

Similar effects control the stability of the cyanofluoromethyl radical; however, there is only one electron configuration to consider. Instead of the variable occupancy of the carbene  $\sigma$ orbital, in a radical the corresponding  $\sigma$  orbital participates in covalent bonding and only the  $\pi$  orbital of the radical carbon center remains nonbonding. Both halogens and CN are strong  $\sigma$  withdrawers lowering the energy of the entire molecule (relative to methyl radical) through the  $\sigma$  orbital system. However, in relation to the BDE, it must be considered that the closed-shell parent molecule is also affected by strong  $\sigma$ withdrawing effects. Furthermore, because the parent molecule has an additional bond to hydrogen (with two more  $\sigma$ electrons), its energy is lowered more than that of the radical with the same substitution (F, Cl, CN). Thus, the energy difference between the parent and radical is larger, leading to a greater BDE. In general, BDE is larger for more strongly  $\sigma$ withdrawing substituent groups and greater numbers of them in the absence of other effects.44 This effect on BDE is illustrated in the schematic energy diagram in Figure 6.



**Figure 6.** Schematic energy diagram indicating the effects of  $\sigma$  withdrawal and  $\pi$  resonance stabilization on the relative stability of the parent closed-shell molecule (RH) and the corresponding radical (R<sup>•</sup> + H<sup>•</sup>). See the text for details.

The effect of  $\pi$  acceptance from the cyano group in the substituted radical is easily understood in the same context as for the carbene. As illustrated in Figure 7, the mixing of the



**Figure 7.** Schematic energy diagram illustrating the effects of interaction between the nonbonding  $2p(\pi)$  electron of the central carbon and substituents of different types in substituted methyl radicals. See the text for details.

radical's  $\pi$  orbital with a  $\pi$ -acceptor substituent lowers the radical electron's energy. Because this interaction lowers the energy of the radical (and not of the parent molecule, which has no  $\pi$  orbitals), it lowers the parent molecule's BDE. The  $\pi$ donating effect of the halogen is also similar to the effect on the carbene  $\pi$  orbital; however, in the radical's case as described above, there is no available nonbonding  $\sigma$  orbital to complicate the electronic structure. For this reason, there are always three electrons in the  $\pi$  donating group's interaction. From a simple molecular orbital picture though, this interaction still has a net 1 electron stabilization as compared to unmixed orbitals (Figure 7). This, like a  $\pi$  acceptance effect, lowers the energy of the radical and thus lowers the BDE. Adding a second substituent introduces a third orbital to the mixing, which further lowers the energy of the radical. In this context, the captodative effect between two groups can be understood as introducing this third orbital, and maximizing the number of electrons contributing to a lower energy.

#### 5. SUMMARY

Cyanofluorocarbene, FCCN, has a singlet ground state with an adiabatic EA = 2.081 ± 0.002 eV and a singlet-triplet splitting  $\Delta E_{\text{S-T}} = 0.42 \pm 0.04$  eV. A third photodetachment transition, with an onset of approximately 4.2 eV is attributed to the openshell singlet state of the carbene. These results are in excellent agreement with the theoretical predictions.

The VDE of the cyanofluoromethylide is  $2.13 \pm 0.04$  eV. Although the corresponding band origin is not directly observable, the adiabatic EA was estimated to be  $1.53 \pm 0.08$ eV. Using the estimated EA, the first C–H BDE of fluoroacetonitrile was determined through the general electron affinity/gas-phase acidity thermodynamic cycle, DH<sub>298</sub> = 90.7 ± 2.8 kcal mol<sup>-1</sup>.

The measured  $\Delta E_{\text{S-T}}$  of FCCN agrees well with the general trend of similar carbenes. The low C–H BDE of fluoroaceotnitrile, compared to most organic compounds, indicates a synergistic stabilization of the corresponding radical by a  $\pi$  donor and a  $\pi$  acceptor substituents.

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#### Notes

The authors declare no competing financial interest.

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