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Photochemistry of Fumaronitrile Radical Anion and Its Clusters

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ABSTRACT: The photodetachment and photochemistry of the radical anion of fumaronitrile (*trans*-1,2-dicyanoethylene) and its clusters are investigated using photoelectron imaging and photofragment spectroscopy. We report the first direct spectroscopic determination of the adiabatic electron affinity (EA) of fumaronitrile (fn) in the gas phase, EA = 1.21 ± 0.02 eV. This is significantly smaller than one-half the EA of tetracyanoethylene (TCNE). The singlet—triplet splitting in fumaronitrile is determined to be $\Delta E_{S-T} \leq 2.6$ eV, consistent with the known properties. An autodetachment transition is observed at 392 and 355 nm and assigned to the ²B_u anionic resonance in the vicinity of 3.3 eV. The results are in good agreement with the predictions of the CCSD(T) and EOM-XX-CCSD(dT) (XX = IP, EE) calculations. The H₂O and Ar solvation energies of fn⁻ are found to be similar to the corresponding values for the anion of TCNE. In contrast, a very large (0.94 eV) photodetachment band shift, relative to fn⁻, is observed for



 $(fn)_2^-$. In addition, while the photofragmentation of fn⁻, fn⁻·Ar, and fn⁻(H₂O)_{1,2} yielded only the CN⁻ fragment ions, the dominant anionic photofragment of $(fn)_2^-$ is the fn⁻ monomer anion. The band shift, exceeding the combined effect of two water molecules, and the fragmentation pattern, inconsistent with an intact fn⁻ chromophore, rule out an electrostatically solvated fn⁻·fn structure of $(fn)_2^-$ and favor a covalently bound dimer anion. A C_2 symmetry $(fn)_2^-$ structure, involving a covalent bond between the two fn moieties, is proposed.

1. INTRODUCTION

Fumaronitrile (*trans*-1,2-dicyanoethylene) is obtained from ethylene by substitution of two cyano groups (CN) in the *trans*-position. It is, therefore, an intermediate case between ethylene and fully substituted tetracyanoethylene (TCNE).¹⁻⁴ The cyano group has a significant effect on the electronic properties of the molecule, due to its electron-withdrawing and π -conjugating properties. Each cyano group acts as an electron acceptor, analogous to the halogens. However, in contrast to true halogens, CN has unoccupied π orbitals that can conjugate with the vinyl π system, facilitating strongly bound anionic states.

The electronic properties of cyano-substituted ethylenes, and in particular the doubly substituted case of fumaronitrile, have been studied both experimentally and theoretically. The known experimental value of adiabatic electron affinity (EA) of fumaronitrile (fn) is 28.8 ± 2 kcal/mol (1.25 ± 0.09 eV); it was determined indirectly from electron-transfer equilibrium measurements.⁵ Investigations using the density functional theory (DFT) with five different gradient-corrected functionals give a range of EA values from 1.35 to 2.13 eV, depending on the method used.⁶

The triplet state of fumaronitrile was observed to lie 59 ± 2 kcal/mol (2.56 \pm 0.09 eV) above the ground-state singlet, using the Herkstroeter–Hammond laser flash photolysis method.⁷ The triplet energy surface has a minimum at a bisected geometry, with a depth ~9 kcal/mol with respect to H–C–CN rotation, as determined from the M06-2X/6-311+G(2d,p) density-functional theory (DFT) calculations.⁸ The same calculations predicted that the radical anion surface has a

minimum at a planar geometry and the barrier to geometric isomerization of 31.2 kcal/mol.

In the present work, we generate the fumaronitrile radical anion (fn^-) in the gas phase and examine the electronic properties of the ground (singlet) state and the first excited (triplet) state of neutral fumaronitrile via photoelectron imaging. We report the first direct spectroscopic determination of the electron affinity and the singlet-triplet splitting of fumaronitrile, significantly improving on the uncertainty of the previous indirect measurements. Using a combination of photoelectron imaging and photofragment mass-spectrometry, we gain additional insight into the photochemistry of the fumaronitrile anion and its clusters. Specifically, we examine the clusters of fn^- solvated by water or argon, as well as the dimer anion of fumaronitrile, $(fn)_2^{-}$.

2. EXPERIMENTAL AND THEORETICAL METHODS

The experiments were performed using a tandem linear timeof-flight/reflectron mass-spectrometer described in detail previously.⁹ A sample holder with crystalline fumaronitrile was mildly heated to 40 °C, in order to increase the vapor pressure (0.635 mmHg at 25 °C). The fumaronitrile vapor was seeded in an Ar carrier gas (backing pressure of ~20 psi) and introduced into a high-vacuum chamber through a pulsed nozzle (General Valve, Series 9) operated at a repetition rate of 50, 70, or 20 Hz, depending on the laser system used. The

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supersonic expansion was crossed with a 1 keV electron beam from an electron gun. Anions were formed via secondaryelectron attachment to neutral molecules and clusters.¹⁰ Water clusters were formed from residual water vapor trapped in the gas delivery lines.

The anions were extracted from the source chamber into a linear Wiley-McLaren time-of-flight spectrometer, where they were separated by the mass-to-charge ratio and detected with a microchannel plate (MCP) detector mounted at the far end of the flight tube. In the detection region of the instrument, the ion beam was intersected with a linearly polarized pulsed laser beam, synchronized in time with the ions of interest. Three different laser systems were used in this work. A Nd:YAG (Yttrium Aluminum garnet) laser (Quanta Ray, Lab 50, 8 ns pulse duration) was used to generate the second (532 nm, 10 mJ/pulse), third (355 nm, 4 mJ/pulse), and fourth (266 nm, 2 mJ/pulse) harmonics of the fundamental output. The 780 and 392 nm radiation was generated as the fundamental (0.8 mJ/ pulse, 100 fs pulses) and second-harmonic output of an amplified Ti:sapphire laser system (Spectra Physics, Inc.). The 612 nm radiation was the fundamental output of a Continuum, Inc. ND6000 Dye Laser system, pumped with second harmonic (532 nm, 20 Hz) of Surelight II-20 Nd:YAG laser, operating on the Rhodamine 640 dye (20 mJ/pulse, \sim 10 ns duration pulses). The 306 nm light (5 mJ/pulse) was obtained by frequency doubling the above output of the dye laser.

Two types of experiments were performed: photoelectron imaging and photofragment-ion mass-spectrometry. Photoelectron images were recorded using a perpendicular (with respect to the ion beam) velocity-map¹¹ photoelectron imaging^{12,13} assembly.⁹ The photodetached electrons were accelerated by a series of electrodes and projected onto a 40 mm diameter position-sensitive MCP detector, coupled to a P43 phosphor screen (Burle, Inc.). The resulting images were recorded using a charge-coupled device (CCD) camera and accumulated for $\sim 10^5 - 10^6$ experimental cycles. Two different cameras were used at different stages of this work (due to the longevity of the project): Dalsa DS-1A-01M30 CamLink with a 1 megapixel resolution (Camera I) and thermoelectrically cooled Photometrics CoolSnap MYO with 2.8 megapixels (Camera II). Where relevant, the camera used for specific images is indicated in the figures; however, the results do not depend on the camera employed.

Taking advantage of the cylindrical symmetry of the images with respect to the laser polarization direction, photoelectron probability distributions in the three-dimensional velocity space were reconstructed via the inverse Abel transform,¹³ as implemented in the BASEX program.¹⁴ The speed (energy) scale was calibrated using the well-known photodetachment transitions of $O^{-15,16}$ The photoelectron angular distributions were not analyzed in this work.

The photofragment-ion mass-spectra were recorded using a single-stage linear-field reflectron mass-spectrometer.⁹ The reflectron potential was scanned while monitoring the ion signal with an off-axis MCP detector to determine the fragment masses.¹⁷ For each ion fragment, 512 time-traces were averaged and the final photofragmentation spectra were obtained by combining them together.

Electronic-structure calculations involving geometry optimizations of fn and fn⁻ at the coupled-cluster level of theory with single and double excitations (CCSD) were performed using the Gaussian 09 suites of programs.¹⁸ The low-lying electronic states of both the neutral and anion of fumaronitrile were explored using the equation-of-motion (EOM) ionization potential (IP) and electronic excitation (EE) methodologies,^{19–21} combined with the coupled-cluster theory, including diagonal triples corrections (dT).²² The EOM-XX-CCSD(dT) calculations (XX = IP or EE) were carried out using the Q-Chem 4.0 software package.²³ Q-Chem was also used for similar calculations on $(fn)_2^{-}$. Due to the forbidding size of the dimer anion, geometry optimizations were carried out using the Minnesota-06 (M06) DFT method^{24,25} (rather than CCSD), using a variety of basis sets, up to aug-cc-pVTZ. The reported electronic-state energies, EAs, and VDEs exclude the vibrational zero-point energy corrections.

3. EXPERIMENTAL RESULTS

The photoelectron images of the bare fn⁻ anion, obtained at different wavelengths, are presented in Figure 1. The corresponding photoelectron spectra are plotted with respect to electron binding energy, $eBE = h\nu - eKE$.

At wavelengths longer than 532 nm, only the ground state of neutral fumaronitrile (X ${}^{1}A_{g}$) is accessible. A partially resolved vibrational progression is prominent, with an average frequency of 1610 \pm 160 cm⁻¹. It is assigned to the C=C stretch, in agreement with the previously measured and calculated vibrational spectra.^{26,27} From the position and the width of the first peak in the 612 nm spectrum, the adiabatic electron affinity of fumaronitrile is determined: EA(${}^{1}A_{g}$) = 1.21 \pm 0.02 eV. This is the first direct spectroscopic determination of this important property. It is in agreement with the previous indirect determination (1.25 \pm 0.09 eV),⁵ but it reflects a significant improvement in the uncertainty. The electron affinity of fumaronitrile is therefore significantly less than half that of TCNE (3.16 \pm 0.02 eV).⁴

At 392 and 355 nm, corresponding to the photon energies of 3.16 and 3.49 eV, respectively, the images have high intensity in the center, giving rise to structureless low-eKE features in the photoelectron spectra (labeled C in Figure 1). One might assume that these features represent the first excited state of neutral fumaronitrile. However, because there is no sign of similarly intense features at eBE $\sim 3-3.5$ eV at higher photon energies (i.e., at 306 and 266 nm), this assignment does not hold. With the support of subsequent analysis (Section 4.1), we assign feature C to autodetachment from electronically excited fumaronitrile anion. The ¹A_g transition, while visible, is significantly weaker than the autodetachment feature, with the loss of vibrational resolution reflecting lower instrumental resolution for higher kinetic energy electrons. It is for these reasons that the spectra obtained at lower photon energies were used for the EA assignment.

The first excited state of neutral fumaronitrile is accessible at the 306 and 266 nm. It corresponds to the broad transition peaking around 4 eV (labeled ³A due to reduced symmetry, as explained below). The broad and congested nature of the band reflects a significant change in equilibrium geometry upon the photodetachment to the triplet state, which is consistent with its previously calculated nonplanar structure.⁸ For this reason, we can estimate only the upper limit for the adiabatic binding energy of the ³A state, EA(³A) \leq 3.8 eV. This upper bound is determined based on the first peak in the 306 nm spectrum (see the inset in Figure 1). Combined with the EA(¹A_g) = 1.21 \pm 0.02 eV (determined above), this result yields an upper bound of the singlet—triplet splitting in fumaronitrile, $\Delta E_{S-T} \leq$ 2.6 eV, consistent with the previously reported value of 2.56 \pm 0.09 eV.⁷ The vertical detachment energy corresponding to the



Figure 1. Photoelectron images and corresponding photoelectron spectra of fn⁻ collected at 780 (Camera I), 612, 532, 392, 355, 306, and 266 nm (Camera II). The laser polarization direction is vertical in the plane of all images. The green and blue vertical bars superimposed with the 306 nm spectrum correspond to the VDEs from the ground-state anion to the singlet (${}^{1}A_{g}$) and triplet (${}^{3}A$) states of the neutral determined from the single-point EOM-IP-CCSD(dT)/aug-cc-pVTZ calculations using the CCSD/aug-cc-pVTZ optimized geometry of the anion.

 $fn^- \rightarrow fn(^{3}A)$ transition, VDE = 4.05 ± 0.05 eV, was determined from a scaled Gaussian fit²⁸ to the highest peak in the ³A band at 266 nm (Figure 1).

The 532 nm photoelectron images and spectra of the cluster anions fn⁻·Ar, fn⁻·H₂O, fn⁻(H₂O)₂, and (fn)₂⁻ are presented in Figure 2. The cluster anion spectra can be compared to the 532 nm spectrum of unsolvated fn⁻ in Figure 1. The fn⁻·Ar spectrum is better resolved than the bare fn⁻ spectrum, because



Figure 2. Photoelectron images and spectra of fn⁻·Ar, fn⁻·H₂O, fn⁻(H₂O)₂, and (fn)₂⁻ collected at 532 nm (Camera I). The laser polarization direction is vertical in the plane of all images.

of the colder temperature of Ar-tagged anions.²⁹ The vibrational progression in the fn⁻·Ar, fn⁻·H₂O, and fn⁻· (H₂O)₂ spectra in Figure 2 corresponds to the same electronic band as in the fn⁻ 532 nm spectrum in Figure 1 (¹A_g). The vibrational spacing is approximately unaffected by the solvation (~1600 cm⁻¹).

With the exception of fn^-Ar , the photoelectron spectra of the cluster anions (Figure 2) are shifted toward higher electron binding energy, relative to the corresponding fn^- bands (Figure 1). All observed band shifts are summarized in Table 1. For

Table 1. Observed Band Shifts in the Photoelectron Spectra of Fumaronitrile (fn) Cluster Anions^a

cluster	band shift (eV)
fn ⁻ ·Ar vs fn ⁻	<0.02
fn ⁻ ·H ₂ O vs fn ⁻	0.32(3)
$fn^-(H_2O)_2$ vs $fn^- \cdot H_2O$	0.32(3)
$(fn)_2$ vs fn	0.94(5)

"For electrostatically solvated clusters, such as fn⁻.Ar and fn⁻(H_2O)_{1,2}, the band shifts reflect (approximately) the corresponding solvent binding energies to the reference ion.

electrostatically solvated ions, the shift reflects (approximately) the corresponding ion solvation energy. The results indicate that the first and second hydration energy of fn^- are both 0.32 eV. This value is significantly smaller than that observed for many smaller anions, but similar to the 0.35 eV first hydration energy of TCNE^{-,4} Similar to TCNE⁻, we attribute the low hydration energy of fumaronitrile anion to its delocalized-charge structure. The water molecule is likely to bind to one of the electronegative CN groups in fn^- , interacting effectively with only part of the charge. This interpretation finds further

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support in that the second hydration energy (the binding of the second H_2O molecule to fn⁻) has the same value as the first, 0.32 eV. It is consistent with the second H_2O binding to the second CN group, interacting with a partial charge of similar magnitude.

For the same reasons, the binding energy of argon to fn^- is also expected to be smaller than the typical small-anion value (~0.05 eV).³⁰ In fact, the fn^- band shift associated with Ar solvation is so small that it cannot be discerned in the present data, and only an upper limit of 0.02 eV can be assigned for the first Ar solvation energy.

In contrast to all the other clusters studied, the $(fn)_2^-$ photodetachment band in Figure 2 exhibits a very large (0.94 eV) shift with respect to the fn⁻ spectrum. The shift suggests a significant covalent character of the interaction between the two fumaronitrile moieties. Hence, the dimer anion of fumaronitrile should be viewed as $(fn)_2^-$, rather than fn⁻·fn.

In addition, photofragment-ion mass-spectrometry was performed on the fumaronitrile anion and its clusters at 355 and 266 nm. The CN⁻ fragment was found to dominate the fragmentation of fn⁻, fn⁻·Ar, and fn⁻(H₂O)_{1,2} at both wavelengths, but a qualitatively different pattern was observed for the dimer anion. For (fn)₂⁻, the CN⁻ channel was almost completely suppressed at both wavelengths studied, and the only intense photofragment was fn⁻ (i.e., the monomer anion). This fragmentation pattern also points to the unique (compared to the other clusters studied) covalent bonding character between the two fumaronitrile moieties in (fn)₂⁻. In the past, analogous dimer \rightarrow monomer dissociation channels were observed, for example, for the covalent dimer anions of CO₂³¹⁻³³ OCS,³⁴ CS₂³⁵⁻⁴⁰ and O₂^{.17,41-45}

4. MODELING AND DISCUSSION

4.1. Fumaronitrile. To characterize the electronic structure and help assign the observed photodetachment transitions, we performed ab initio calculations for the fn^- anion and the lowest singlet and triplet states of neutral fumaronitrile. The geometries were optimized at the CCSD level with the aug-cc-pVTZ basis set, followed by an exploration of the vertical excitation transitions using the EOM family of methods, combined with the coupled-cluster theory.⁴⁶

The equilibrium structures of the ${}^{2}B_{g}$ ground state of fn⁻ as well as the closed-shell singlet (${}^{1}A_{g}$) and triplet (${}^{3}A$) states of the neutral are shown in Figure 3. The anion and triplet geometries are qualitatively similar to the analogous structures determined previously from the M06-2X/6-311+G(2d,p) DFT calculations.⁸ The anion and singlet geometries are both planar and similar to each other, with the most significant difference in the C=C (ethylene) bond length. This is consistent with the B_g symmetry character of the fn⁻ HOMO, which has an antibonding π^{*} character with respect to the ethylene bond. The optimized triplet-state geometry is nonplanar (C_{2} symmetry), with a 92.4° out-of-plane twist about the ethylene bond.

On the basis of the optimized structures, we expect a relatively sharp photodetachment transition to the singlet and a broad Franck–Condon envelope for the triplet. This is in agreement with the data in Figure 1. The singlet transition is relatively narrow, with a resolved vibrational progression attributed to the C=C stretching mode. In contrast, the triplet transition is broad and weak, consistent with the large geometry change. The EA of the triplet cannot be determined



Figure 3. CCSD/aug-cc-pVTZ optimized geometries of the ground ${}^{2}B_{g}$ state of fn⁻, and singlet ${}^{1}A_{g}$ and triplet ${}^{3}A$ states of neutral fumaronitrile. All bond lengths are in Angstroms, and angles are in degrees. The electron configurations are indicated schematically by the populations of the HOMO $(2a_{u})$ and LUMO $(2b_{g})$ of fumaronitrile.

unambiguously from the data, due to the small Franck– Condon overlap for the 0-0 transition.

For comparison with the experiment, the adiabatic EAs of the ${}^{1}A_{g}$ and ${}^{3}A$ states of fn, as well as the corresponding anion VDEs, were computed using the coupled-cluster theory with the aug-cc-pVTZ basis set. In addition, single-point CCSD(T) calculations were carried out for the above CCSD-optimized geometries. The VDEs were also determined directly from a single-point EOM-IP-CCSD calculation including the diagonal triples corrections for energy (dT), using the above anion geometry. The results are summarized in Table 2.

The EOM-IP-CCSD(dT) calculations, as well as the EOM-EE-CCSD(dT) described below, involved one-electron excitations from the doublet anion reference, corresponding to the ${}^{2}B_{g}$: ... $(1b_{g})^{2}(8b_{u})^{2}(9a_{g})^{2}(2a_{u})^{2}(2b_{g})^{1}$ ground state. The $2a_{u}$ and $2b_{g}$ orbitals are the canonical HOMO and LUMO of the neutral fumaronitrile molecule, respectively. Their nominal populations in different electronic states are indicated schematically alongside the equilibrium structures in Figure 3. The complete dominant configurations of the anion and neutral states of fumaronitrile are summarized in Table 3.

The calculated VDEs, corresponding to the detachment to the ${}^{1}A_{g}$ and ${}^{3}A$ states, are in good agreement with the peak energies in the experimental spectra. For the ease of

Table 2. Adiabatic Electron Affinities (EA) and Vertical Detachment Energies (VDE) Corresponding to the Detachment from the ${}^{2}B_{g}$ Ground State of the Fumaronitrile Anion to the X ${}^{1}A_{g}$ and ${}^{3}A$ States of the Neutral^{*a*}

	$fn^{-}(^{2}B_{g}) \rightarrow fn(^{1}A_{g})$		$fn^{-}(^{2}B_{g}) \rightarrow fn(^{3}A)$	
method ^b	EA	VDE	EA	VDE
$CCSD^{c}$	1.082	1.308	3.425	3.948
$CCSD(T)^d$	1.102	1.251	3.596	4.092
$EOM-IP-CCSD(dT)^d$		1.295		4.027
experiment	1.21(2)	1.21(2)	≤3.8	4.05(5)

^{*a*}All values are in electron volts. ^{*b*}All calculations employed the aug-ccpVTZ basis set. ^{*c*}Full geometry optimizations were performed at the CCSD level of theory. ^{*d*}Single-point calculations using the molecular geometries optimized at the CCSD level.

comparison, the EOM-IP-CCSD(dT) results (VDE = 1.295 and 4.027 eV for the singlet and triplet bands, respectively), are indicated in Figure 1 by the green and blue vertical bars superimposed with the 306 nm spectrum.

To further investigate the nature of the low-eKE band C observed at 392 and 355 nm, we explored the electronically excited states of fn-. The excited-state calculations using the EOM-EE-CCSD(dT)/aug-cc-pVTZ method were carried out at the anion ground-state equilibrium geometry. The results are included in Table 3. In support of the autodetachment hypothesis, the calculations predict two anionic states, embedded in the detachment continuum, with vertical excitation energies within the 3-3.5 eV photon energy range. They are the ${}^{2}A_{g}$ and the ${}^{2}B_{u}$ states, found 3.031 and 3.327 eV above the ground state of fn-, respectively. While the optical excitation of the ²A_g state from the ²B_g ground state is dipoleforbidden, the ${}^{2}B_{g} \xrightarrow{\circ} {}^{2}B_{u}$ transition is allowed. The predicted vertical excitation energy of this transition, 3.327 eV, agrees very well with the photon energy range where feature C is observed, whereas the presumably short lifetime of the temporary anion state may explain the spectral width of the band. Hence, we assign band C to autodetachment via the ${}^{2}B_{\mu}$ anionic resonance.

Similarly, the ${}^{2}A_{u}$ excited state, predicted to lie vertically 4.272 eV above the anion ground state, may be responsible for some of the signal at or near the center of the 306 nm image in Figure 1, assigned to the ${}^{3}A$ neutral state. It is revealing that the ${}^{3}A$ band intensity drops significantly relative to ${}^{1}A_{g}$ as the laser

is tuned from 306 to 266 nm. On the basis of its structure and the 266 nm maximum being shifted away from zero eKE, the weak band labeled ³A in the 266 nm spectrum is attributed to the ²B_g \rightarrow ³A photodetachment transition. This transition is characterized by a poor Franck–Condon overlap between the planar anion and nonplanar neutral equilibrium structures.

4.2. Covalent Dimer Anion of Fumaronitrile. The photoelectron spectra of fn^-Ar , and $fn^-(H_2O)_{1,2}$ in Figure 2 reflect the progressively stronger electrostatic solvation of the fn^- anion in these clusters. The photofragment-ion mass spectra of these clusters, dominated by the CN⁻ fragment, are consistent with this interpretation. The fn^- core anion plays the role of a dissociating chromophore, whereas the Ar or H_2O solvent acts as a spectrator.

For $(fn)_2^{-}$, however, two pieces of experimental evidence suggest covalent bonding between the two fn moieties. The first is the large (0.94 eV) photodetachment band shift for $(fn)_2^{-}$, relative to fn⁻, which is larger than the 0.64 eV shift induced by two H₂O molecules (Table 1). The second is the $(fn)_2^{-}$ photofragmentation pattern, dominated by the fn⁻ anion fragments. The $(fn)_2^{-} \rightarrow fn^- + fn$ photofragmentation pathway is difficult to reconcile with an fn⁻ chromophore within the parent cluster. Photoabsorption by fn⁻ would lead to a fragmentation pattern similar to that observed for fn⁻, fn⁻Ar, and fn⁻(H₂O)_{1,2} (i.e., dominated by CN⁻, not fn⁻). In-cluster caging⁴⁷⁻⁵² of the photofragments and vibrational predissociation of the cluster are both alternate possibilities, but with just one solvent molecule in the hypothetical fn⁻.fn scenario, they are unlikely to be dominant mechanisms.

The formation of covalently bound dimers upon electron attachment to a pair of neutral molecules is a common phenomenon.^{31–37} At the electronic-structure level, it can result from at least three distinct bonding motifs. The first involves the bonding between two monomers that are closed-shell species in their respective neutral states. A dimerizing bond in this case can result from a bonding combination of vacant monomer orbitals, populated by an electron in the anionic state of the dimer. An example of such dimerization is the $(CO_2)_2^{-1/2}$ dimer anion with a high-symmetry $^{-1/2}O_2C-CO_2^{-1/2}$ equilibrium structure.⁵³

The second motif involves anionic pairing of neutral radicals or diradicals, with one famous example being $O_4^{-.17,41-45}$ Unlike CO₂, O₂ is a triplet diradical in its ground state and the bonding in O₄⁻ results from a charge-sharing combination of

Table 3. Dominant	Electron	Configurations	and Vertica	al Excitation	Energies	of the	Low-Lying	Anion and	d Neutral	States of
Fumaronitrile ^{<i>a</i>}										

state and configuration	excitation ^c	energy (eV)	accessible? ^d
anion states/resonances (fn ⁻)			
${}^{2}B_{g}:(1b_{g})^{2}(8b_{u})^{2}(9a_{g})^{2}(2a_{u})^{2}(2b_{g})^{1}$	null (reference)	0	n/a
${}^{2}A_{g}:(1b_{g})^{2}(8b_{u})^{2}(9a_{g})^{2}(2a_{u})^{2}(10a_{g})^{1}$	$2b_g \rightarrow 10a_g$	3.031	no
${}^{2}B_{u}:(1b_{g})^{2}(8b_{u})^{2}(9a_{g})^{2}(2a_{u})^{2}(9b_{u})^{1}$	$2b_g \rightarrow 9b_u$	3.327	yes
${}^{2}A_{u}:(1b_{g})^{2}(8b_{u})^{2}(9a_{g})^{2}(2a_{u})^{2}(3a_{u})^{1}$	$2b_g \rightarrow 3a_u$	4.272	yes
${}^{2}B_{g}:(1b_{g})^{2}(8b_{u})^{2}(9a_{g})^{2}(2a_{u})^{2}(3b_{g})^{1}$	$2b_g \rightarrow 3b_g$	4.993	no
neutral states (fn)			
${}^{1}A_{g}$: $(1b_{g})^{2}(8b_{u})^{2}(9a_{g})^{2}(2a_{u})^{2}(2b_{g})^{0}$	$2b_g ightarrow \infty$	1.295	yes
${}^{3}B_{u}:(1b_{g})^{2}(8b_{u})^{2}(9a_{g})^{2}(2a_{u})^{1}(2b_{g})^{1}$	$2a_{\mu} \rightarrow \infty$	4.027	yes

^{*a*}At the equilibrium geometry of the anion (fn *b*), determined from the EOM-XX-CCSD(dT)/aug-cc-pVTZ (XX = EE, IP) calculations. ^{*b*}The CCSD/aug-cc-pVTZ optimized anion geometry shown in Figure 3. ^{*c*}Dominant excitation from the ²B_g ground state of the anion. ²B_g:... (8b_u)²(9a_g)²(2a_u)²(2b_g)¹ is used as a reference for the EOM-EE and EOM-IP calculations. ∞ indicates a continuum (free-electron) state. ^{*d*}Indicates whether the state is accessible from the ²B_g ground state of the anion via the specified one-electron electric-dipole excitation.

the partially filled π^* orbitals of the monomers. The third bonding motif involves anionic dimerization of closed-shell molecules, whereas the neutral core electron configuration of the dimer results from singlet coupling of the monomers promoted to their respective triplet states. Examples of such dimers include certain states of $(CS_2)_2^-$ and $(OCS)_2^{-.34-40}$ Below, we show that the dimer anion of fumaronitrile too falls under this category.

We carried out exploratory calculations on $(fn)_2^-$ using the M06 method^{24,25} with a variety of basis sets. The covalent dimer—anion potential minimum was found by optimizing the starting π -stacking geometry (fn⁻ and fn placed one on top of the other in parallel planes). The resulting C_2 symmetry structure, optimized at the M06/aug-cc-pVTZ level of theory, is shown in Figure 4. It has a covalent (1.54 Å in length) bond



Figure 4. Covalently bound $(fn)_2^-$ dimer anion, ²B: ...(21*a*)² (19*b*)²(20*b*)¹ electronic state. The geometry was optimized at the M06/aug-cc-pVTZ level of theory.

between the two equivalent fumaronitrile moieties and corresponds to the ${}^{2}B$ electronic state. Additional doublebonded structures were also found, all involving high-strain four-membered carbon rings. These structures were less stable and did not correspond to true potential minima, with the imaginary vibrational frequencies indicating instability to isomerization toward the single-bonded geometry shown in Figure 4.

The distorted geometries of the individual fn groups in the proposed $(fn)_2^-$ structure suggest that its building blocks must be the triplet-fn monomers. The analysis of the electronic wave functions confirms this prediction. The nominal electron configuration of $(fn)_2^{-}$ is ${}^{2}B:...(21a)^2(19b)^2(20b)^1$, so its closed-shell neutral core is ${}^{1}A:...(21a)^{2}(19b)^{2}$. In comparison, the electronic state of the neutral van der Waals dimer (for the purpose of this comparison, constrained to C_2 symmetry) is ¹A:... $(22a)^2(18b)^2$. Thus, the neutral-core configuration of $(fn)_2^-$, is doubly excited, $(22a)^2 \rightarrow (19b)^2$, with respect to two weakly interacting singlet-fn monomers. It results from the singlet coupling of two triplet fn moieties and the structure and bonding of $(fn)_2^-$ are best described using the correlation: $fn(^{3}A) + fn(^{3}A) + e^{-} \rightarrow (fn)_{2}^{*} + e^{-} \rightarrow (fn)_{2}^{-}$. Although this diabatic chain illuminates the salient details of the dimer-anion structure, it is not intended as the $(fn)_2^-$ formation mechanism. In the experiment, $(fn)_2^-$ is likely formed via electron

attachment to $(fn)_n$ van der Waals clusters, followed by evaporative cooling and internal conversion to the above $(fn)_2^-$ state.

In a broader context, $(fn)_2^{-}$ is similar to the $(OCS)_2^{-}$ and $(CS_2)_2^{-}$ dimer anions, which are also based on the tripletmonomer building blocks,^{34,36} and contrasts $(CO_2)_2^{-}$, which is based on singlet neutral monomers.⁵³ These structural motifs reflect the different singlet-triplet excitation energies, ΔE_{S-T} , in the corresponding monomers. In fn, $\Delta E_{S-T} \leq 2.6 \text{ eV}$ (as reported here and elsewhere⁷); in OCS and CS₂, $\Delta E_{S-T} \sim 3.4$ eV and ~3.2 eV, respectively, whereas in CO₂, $\Delta E_{S-T} \sim 5.3$ eV.^{34,36} The ΔE_{S-T} values in fn, OCS, and CS₂ are sufficiently small so that the triplet excitation energy of two neutral monomers is more than recovered due to the covalent bonding and the large electron affinity of the dimer. In the case of $(CO_2)_2^{-}$, the price of promoting two CO₂ moieties to the triplet state is too high, and the most stable $(CO_2)_2^{-}$ structure⁵³ results from the addition of an electron to the LUMO of the van der Waals dimer configuration.

The photodetachment of $(fn)_2^-$ accesses the above doubly excited $(fn)_2^*$ neutral species, which correlates to $fn(^3A)$ + $fn(^{3}A)$. Because each of the triplet monomers is diradical in character,⁸ NC(H) \dot{C} - $\dot{C}ZC(H)CN$, the (fn)₂* state involves the interaction of four radical centers: C2, C3, C6, and C7 in Figure 4; hence, it is nominally a quad-radical. However, with two of the radical centers involved in the dimerizing C2-C6 bond, $(fn)_2^*$ is reduced to a diradical. The remaining C3 and C7 radical centers are involved in through-bond and throughspace interactions, giving rise to a manifold of closed-shell singlet, triplet, and open-shell singlet states.⁵⁴ The 2.59 Å wide C3-C7 spatial gap is smaller than the 3.06 Å inter-radical distance in the recent experiment on ring-open oxazole.55 Hence, the $(fn)_2^-$ anion may potentially provide an even more striking example of spectroscopy of a nearly broken bond in the corresponding neutral.⁵⁵ This realization motivates more detailed future studies of $(fn)_2^{-}$.

Some key spectroscopic properties of $(fn)_2^-$ are summarized in Table 4. The M06/aug-cc-pVTZ calculations predict an adiabatic EA of 1.88 eV, which compares well with the onset of the $(fn)_2^-$ spectrum in Figure 2 at approximately 2.0 eV.

Table 4. Energetics of Relevant Processes (in eV) Reflecting the Thermodynamic Stability of the Covalent Dimer Anion of Fumaronitrile

	theory	experiment
adiabatic electron affinities: ^a		
$fn^- \rightarrow fn + e^-$	1.37	$1.21(2)^{c}$
$(fn)_2 \xrightarrow{-} fn + fn + e^-$	1.88	< 2.0 ^d
vertical detachment energies $(fn)_2^- \rightarrow (fn)_2^*$, corresponding to the following neutral states: ^b		
$^{1}\text{A:}(21a)^{2}(19b)^{2}$	2.02	$2.15(5)^{e}$
${}^{3}\text{B}$: $(20a)^{2}(19b)^{2}(21a)^{\dagger}(20b)^{\dagger}$	2.16	$2.15(5)^{e}$
1 B:(20 <i>a</i>) ² (19 <i>b</i>) ² (21 <i>a</i>) [†] (20 <i>b</i>) ^{\downarrow}	3.09	n/a

^{*a*}Theoretical EA values are from M06/aug-cc-pVTZ calculations. ^{*b*}Theoretical values are from EOM-IP-CCSD/3-21G single-point calculations carried out for the M06/aug-cc-pVTZ optimized structure shown in Figure 4, using the anion ²B: ...(21*a*)²(19*b*)²(20*b*)¹ reference. ^{*c*}From Figure 1 and Table 2. ^{*d*}The onset of the (fn)₂⁻ band in Figure 2 at eBE = 2.0 eV corresponds to the upper bound of (fn)₂ EA. The detachment is expected to be dissociative, (fn)₂⁻ \rightarrow fn + fn + *e*⁻, because the intermediate (fn)₂* structure is adiabatically unstable relative to the fn + fn limit. ^{*c*}From Figure 2.

Assuming that the adiabatic ground state of $(fn)_2$ corresponds to two fn monomers (or a van der Waals dimer), a large equilibrium geometry change is expected upon the photodetachment. Thus, the observed band onset is but an upper bound for the dimer electron affinity, EA ≤ 2.0 eV, in agreement with the DFT result.

The VDE of the covalent $(fn)_2^{-}$ structure was determined directly from single-point EOM-IP-CCSD calculations on the M06/aug-cc-pVTZ optimized dimer-anion geometry, employing the ²B anion reference. Due to the large size of the system, only a very small basis set (3-21G) could be used in these preliminary calculations. With this caveat, the calculations predict close-lying singlet (¹A) and triplet (³B) states, with vertical excitation energies of 2.02 and 2.16 eV, respectively, in addition to the open-shell singlet state (¹B) at 3.09 eV. The electron configurations of these states, as well as the predicted VDE values, are summarized in Table 4.

The above closed-shell singlet state (¹A) corresponds to the "doubly-excited" (fn)₂* species, whereas the van der Waals dimer state is expected to lie (vertically) higher in energy at the $(fn)_2^-$ anion geometry. The VDE = 2.15 ± 0.05 eV maximum of the $(fn)_2^-$ band in Figure 2 agrees well with the computed VDE values for the ¹A and ³B diradical states. In light of the present results, it is not possible to make a definitive assignment of the observed transition to one of these states or their combination. Future measurements at various wavelengths and the analysis of the photoelectron angular distributions may shed light on this transition.

5. SUMMARY

We have reported the first spectroscopic determination of the adiabatic electron affinity of trans-1,2-dicyanoethylene (fumaronitrile) in the gas phase, EA = 1.21 ± 0.02 eV. This result represents an improvement in precision compared to the previous indirect determination.⁵ The singlet-triplet splitting in fumaronitrile was determined to be $\Delta E_{\rm S-T} \leq 2.6$ eV, in agreement with the previously reported value of 2.56 ± 0.09 eV.⁷ An additional autodetachment transition was observed at 392 and 355 nm (3.16 and 3.49 eV photon energies) and assigned to the excitation of the ²B_u anionic resonance in the vicinity of 3.3 eV. The results are in agreement with the predictions of the CCSD(T) and EOM-XX-CCSD(dT) (XX = IP, EE) calculations performed for fn⁻ and the singlet and triplet neutral species.

Photoelectron imaging of fumaronitrile cluster anions revealed that solvation energies of fn^- by H_2O and Ar are significantly smaller than the corresponding values for many other (smaller) anions, but similar to the corresponding solvation energies of TCNE^{-,4} Similar to TCNE⁻, the present results are attributed to the delocalized-charge structure of fn^- . The H_2O or Ar solvents bond to only one of the CN groups and interact with effectively only part of the anion charge.

In contrast, a very large (0.94 eV) photodetachment band shift, relative to fn⁻, is observed for $(fn)_2^-$. In addition, although the anionic photofragmentation of fn⁻ and its H₂O and Ar clusters yielded only the CN⁻ fragment ion, the corresponding channel is diminished in $(fn)_2^-$, replaced by the dominant fn⁻ photofragment. The large band shift, exceeding the combined effect of two water molecules, and the fragmentation pattern, inconsistent with an intact fn⁻ chromophore in the dimer anion, rule out an electrostatically solvated fn⁻ fn structure and argue in favor of a covalently bond dimer anion. A C_2 symmetry $(fn)_2^-$ structure, involving a covalent bond between the two fn moieties, has been proposed. The photodetachment of this $(fn)_2^-$ structure accesses a manifold of diradical states, which will be the target of a more detailed experimental and theoretical exploration in the near future.

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Notes

The authors declare no competing financial interest.

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